Review Article

Türk Fen ve Sağlık Dergisi
Turkish Journal of Science and Health

Volume 2
Number 1
Year 2021
Pages 64-75

ISSN: 2717-7173
https://dergipark.org.tr/tr/pub/tfsd

Received: 27.11.2020 *Accepted:* 24.12.2020

UV- Görünür bölge spektrofotometresi kullanarak bazı ağır metal iyonlarının tespiti için geliştirilen yüzey plazmon rezonans özelliğine sahip nanoparçacık esaslı kolorimetrik sensörler

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ÖZET:

Amaç: Özellikle, Hg^{2+}, Pb^{2+}, Cd^{2+} ve Cr^{3+} gibi ağır metal iyonları canlılar tarafından eser miktarda alındığında bile toksik etki yaratmaktadır ve bu durum canlıların sağlığını önemli derecede etkilemektedir. Dolayısıyla ağır metal iyonlarının tayini büyük önem taşımaktadır. Bu derlemenin amacı Hg^{2+}, Pb^{2+}, Cd^{2+} ve Cr^{3+} ağır metal iyonlarının UV-Görünür bölge spektrofotometresiyle kalitatif ve kantitatif analizine olanak sağlayan ve lokalize yüzey plazmon rezonans (LSPR) özelliği gösteren altın nanoparçacık (AuNP) ve gümüş nanoparçacık (AgNP) esaslı geliştirilmiş kolorimetrik sensörlerle ilgili çalışmalar hakkında bilgi vermektir.

Gereç ve Yöntem: AuNP ya da AgNP esaslı kolorimetrik nanosensörlerin çalışma yöntemi analizi istenen ağır metal iyon varlığında ilgili nanoparçacık agregasyon ya da disagregasyona uğrayarak görünür bölgede renk değişimine neden olmasına ve bu renk değişiminin UV-Görünür bölge spektrofotometre ile ölçülmesine dayanmaktadır.

Bulgular: Derlemede kısaca bahsedilen çalışmalar incelendiğinde AuNP ya da AgNP esaslı nanosensörler ile kolorimetrik olarak UV-Görünür bölge spektroskopisiyle ağır metal iyonlarının nanomolar seviyelerinde analizi yapılabildiği gözlenmiştir.

Sonuç: LSPR özelliği gösteren AuNP ya da AgNP esaslı kolorimetrik yöntemler UV-Görünür bölge spektrofotometre yardımıyla ağır metallerin yüksek seçicilik ve hassasiyetle analizine imkan vermektedir. Ağır metal iyonlarının analizi için kullanılan UV-Görünür bölge spektrofotometreler hızlı, hassas, seçici, ucuz cihazlar olmasının yanısıra taşınabilir olmasından dolayı saha analizine imkan vermektedir ve nanomolar seviyelerinde kolorimetrik yöntemlerin geliştirilmesine olanak sağlamaktadır.

Anahtar Kelimeler: *Ağır metaller, altın nanoparçacık (AuNP), gümüş nanoparçacık (AgNP), UV-Görünür Spektrofotometresi, kolorimetrik sensör.*

Nanoparticle-based with surface plasmon resonance capability colorimetric sensors developed for the detection of some heavy metal ions using UV-Visible Spectrophotometer

ABSTRACT:

Purpose: Especially heavy metal ions such as Hg^{2+}, Pb^{2+}, Cd^{2+} and Cr^{3+} create toxic effects even when taken in trace amounts by living things and this situation affects the health of living things significantly. Therefore, the determination of heavy metal ions is of great importance. The aim of this review is to give information about the studies on gold nanoparticle (AuNP) and silver nanoparticle (AgNP) based developed colorimetric sensors that allow qualitative and quantitative analysis of Hg^{2+}, Pb^{2+}, Cd^{2+} and Cr^{3+} heavy metal ions with UV-Visible spectrophotometer and have localized surface plasmon resonance (LSPR) feature.

Material and Methods: The working method analysis of AuNP or AgNP based colorimetric nanosensors is based on the aggregation or disaggregation of the relevant nanoparticle in the presence of the desired heavy metal ion, causing a color change in the visible region and monitoring this color change with UV-Visible spectrophotometer.

Results: When the studies briefly mentioned in the review are examined, it has been observed that the heavy metal ions can be analyzed at nanomolar levels by UV-Visible Spectroscopy with AuNP or AgNP based nanosensors.

Conclusion: LSPR based AuNP or AgNP based colorimetric methods allow analysis of heavy metals with high selectivity and sensitivity with the help of UV-Visible spectrophotometer. UV-Visible spectrophotometers used for the analysis of heavy metal ions are fast, sensitive, selective, inexpensive, as well as being portable, they allow field analysis and allow the development of colorimetric methods at nanomolar levels.

Keywords: *Heavy metals, gold nanoparticle (AuNP), silver nanoparticle (AgNP), UV-Visible spectrophotometer, colorimetric sensor.*

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INTRODUCTION

Heavy metals are known the group of metals and metalloids with five times higher density when the compared to the density of water due to the an atomic density of more than 4 g/cm^3 (Garbarino et al., 1995). Heavy metals are classified as essential (Cu^{2+}, Fe^{2+}, Ni^{2+} and Zn^{2+}) and nonessential metals (Cd^{2+}, Hg^{2+}, Pb^{2+} and Cr^{3+}) (LeFauve et al., 2017; Ramirez et al., 2008). The human body needs essential heavy metals in trace amounts for growth and body health. Essential heavy metals have toxic effects when taken more than the trace amount needed by the human body (Valko et al., 2005). On the other hand, nonessential heavy metals have very toxic effects on humans, plants and animals, even at trace levels. When the nonessential heavy metals are transported to the human body cells and tissues they may change the functions of nucleic acids, proteins. In addition, these heavy metals cause the health disorders such as brain disorders (loss of memory, parkinson’s disease), loss of appetite on humans, damaging the livers, lungs and the other essential organs (Jaishankar et al., 2014). The main source of heavy metal pollution is industrial wastes, and the second pollutant source is fertilizers and pesticides used in agriculture, and heavy metals in these pollutant sources are transported to surface and underground waters due to leakage and diffusion (Jaishankar et al., 2014). Heavy metals are classified as inorganic pollutants by USEPA (Wuana et al., 2010). They are not removed from the natural water resources and soils naturally such as organic pollutants. As a result, over the years, their concentration increases due to the accumulation of heavy metals in environmental systems, threatening the environment and living things significantly. In addition, even the ecological pyramid has chance to be affected by these bioaccumulations and the food chain (Papageorgiou et al., 2006).

Considering all these, it is important to find simple, cheap, rapid, reliable, reproducible, portable and sensitive methods for the analysis of especially nonessential heavy metals (Cd^{2+}, Hg^{2+}, Pb^{2+} and Cr^{3+}) in environmental systems. For this purpose, there are various kind of conventional analytical techniques such as atomic absorption spectrometry (AAS) (Kadhim et al., 2020), atomic fluorescence spectrometry (AFS) (Wan et al., 2006), inductively coupled plasma (ICP) (Davis et al., 2007) and inductively coupled plasma–mass spectrometer (ICP-MS) (Kotalova et al., 2020), inductively coupled plasma-optical emission spectrometry (ICP-OES) (Kobylinska et al., 2020), electroanalytical methods (Özbek et al., 2020; Isildak et al., 2020; Isildak and Özbek, 2020; Isildak et al., 2019) for the analysis of heavy metals. There are studies in the literature in which these methods are used comparatively in heavy metal analysis (Isildak et al., 2019; Özbek et al., 2020; Özbek et al., 2020).

Some of these methods have advantages such as high sensitivity and high selectivity, but they have also disadvantages that limit their usage such as time-consuming processes (proper method selection, complicated sample pre-treatment), requirement of expensive chemicals and skilled specialist, unportable properties (Liu et al., 2017; Ullah et al., 2018) (Table 1).

Nanoparticles and nano-structured materials have gained great importance in technological advances in recent years due to their adjustable physicochemical properties such as melting point, electrical and thermal conductivity, catalytic activity, light absorption and scattering according to their equivalent bulk states (Jeevanandam et al., 2018). Especially, gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) can be synthesized in the desired nanoscale and various modified or bare nanoparticle-based colorimetric methods have been studied for the determination of heavy metal ions. Since (AuNPs) and (AgNPs) have localized surface plasmon properties (LSPR), there are many studies on analysis of heavy metals with UV-Visible spectrophotometer by making use of color change based on aggregation or disaggregation (Huang et al., 2019; Mehta et al., 2016). For example, the color turns from red to purple for AuNPs and yellow to brown for AgNPs in the visible region when the aggregation occurs due to the LSPR property. Nanoparticle-based sensors provide analysis of heavy metal ions with high selectivity and sensitivity by using UV-Visible spectrophotometer. In addition, UV-Visible spectrophotometer enables the development of colorimetric sensors for qualitative and quantitative determination of target species

(Yardımcı et al., 2019; Balasurya et al., 2020).

Table 1. Comparison of UV-Visible Spectroscopy with the other conventional instruments.

Parameters	Conventional instruments	UV-Visible spectroscopy
Selectivity	✓	✓
Sensitivity	✓	✓
Cheapness	✗	✓
Basic sample preparation	✗	✓
Fast analysis	✗	✓
No need for skilled person	✗	✓
Ease of use	✗	✓
Portability	✗	✓

Colorimetric methods are inexpensive, easy to use, fast, color changes are viewed by the naked eye and allow field analysis due to the required portable spectrophotometer.

In this review, it is aimed to give information about the expermental studies in which the modified/bare gold or silver nanoparticle-based colorimetric methods that allow field analysis are carried out in a simpler way by using UV-Visible Spectrophotometer instead of conventional, expensive and large devices for detection of Hg^{2+}, Pb^{2+}, Cd^{2+} and Cr^{3+} and/or Cr^{6+} metal ions. Analytical statistical datas, analytical performances and application methods were discussed for each experimental study on colorimetric analysis of some heavy metals via LSPR.

Detection of Hg^{2+} ions

Hg^{2+} ions are a huge pollutant problem both environment and human health (Driscol et al., 2013). The health problems such as cognitive and motion disorders are caused by methylmercury that formed from the mercury ions via bacteria. Methylmercury is more toxic than mercury ions and also accumulate in aquatic living things (Morel et al., 1998). In addition, the brain, lungs of human beings and kidneys can be damaged and also immune, nervous and digestive systems can be affected because of Hg^{2+} ions (Chen et al., 2014). Therefore, due to the importance of the determination of mercury in environments, studies on nanoparticle supported colorimetric sensors have gained great acceleration by the researches.

Kataria et al. (2019) studied colorimetric sensor based on antiaggregation of AuNPs in the presence of 3,5-dimethyl-1-thiocarboxamidepyrazole (Pzl) **(1)** and mercury ions for the qualitative and quantitative detection of Hg^{2+} in the lake water and tap water samples without using masking agents. This method is highly selective and sensitive for the determination of Hg^{2+}. Limit of detection (LOD) for Hg^{2+} is 7.7 nM and good linear relationship (0.01-1.5 µM, R^2 = 0.9997) has been reported between the absorbance ratio (A_{680}/A_{520}) and Hg^{2+} concentration with using UV-Visible spectrophotometer (Figure 1). Aktara et al. (2019) modified the AuNPs with the 5-methyl-1,3,4-thiadiazole-2-thiol (MTT) **(2)** for the colorimetric determination of Hg^{2+} in water samples. The working principle of the sensor is related to aggregation of MTT-AuNPs in the presence of Hg^{2+} by the monitoring of UV-Visible spectroscopy. The color of AuNPs turn from red to purple in the presence of mercury. This developed method is not affected by pH values and LOD values are 14 nM for Hg^{2+} (R^2 = 0.9997) and the working concentration range of Hg^{2+} is between 0-11 µM.

Huang et al. (2019) developed functionalized AuNPs with the dithioerythritol (DETL) **(3)** for the analysis of Hg^{2+} in real water samples. In this study Hg^{2+} ions cause the disaggregation of DETL-AuNPs and color change from blue to red visible with the naked eye. The nanosensor method is selective for Hg^{2+}. It is reported that absorption ratio (A_{650}/A_{525}) linearly grows with the increase of Hg^{2+} concentration range from 0.1 to 0.5 µM (R^2 = 0.9845) and from 0.5 µM to 5 µM (R^2 = 0.9986) and also LOD is as low as 24 nM.

Aminu et al. (2020) synthesized AgNPs in orange peel medium and developed a colorimetric sensor for selective detection of Hg^{2+} in drinking water. In the presence of Hg^{2+} the brown color of AgNPs solution turns to colorless and the specific LSPR band peak disappears. The working concentration range of Hg^{2+} is between 1–100 µM with a LOD of 1.25×10^{-6} M ($R^2 = 0.97$). Bhattacharjee et al. (2014) synthesized cysteamine **(4)** capped AgNPs for colorimetric sensing of Hg^{2+} ions in water samples via specific LSPR bands. This study is found to be very sensitive and selective for colorimetric analysis of Hg^{2+} ions in water with a LOD of 0.273 nM and the working concentration range of Hg^{2+} is between 0-13.6 nM (Figure 2).

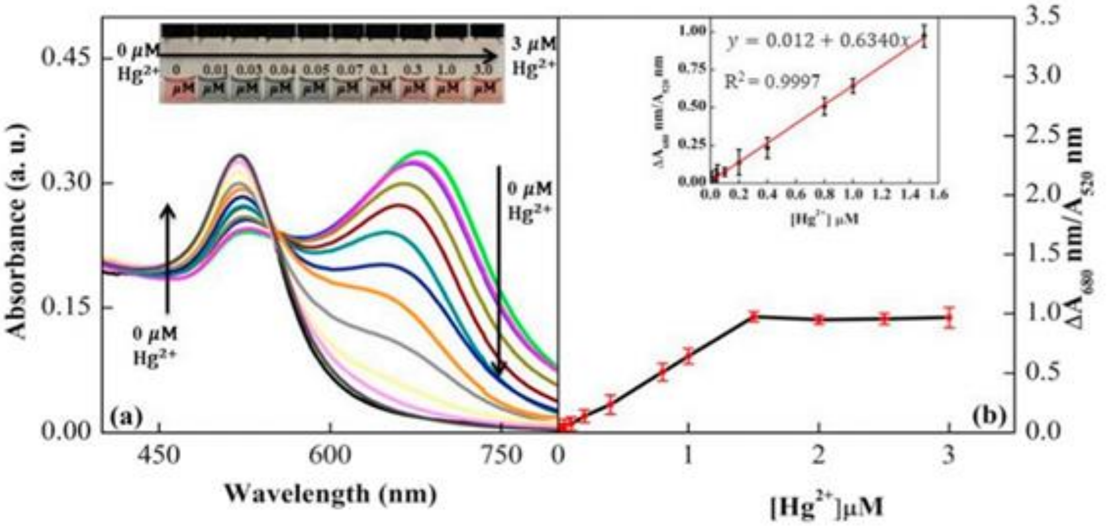

Figure 1. Absorbance spectra of AuNPs in the mixture of 1.5 µM Pzl with different concentrations of Hg^{2+} (Kataria et al., 2019).

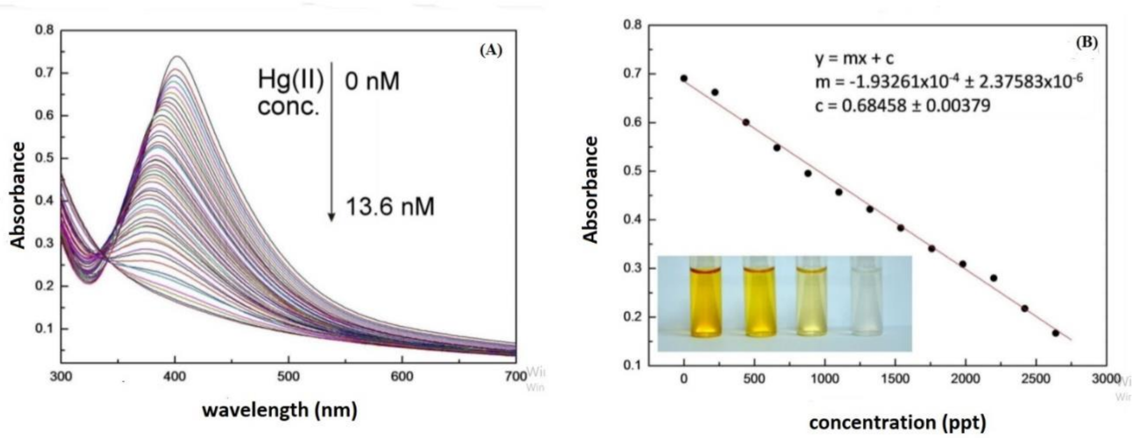

Figure 2. (A) Absorbance spectra of AgNPs with different concentrations of Hg^{2+} (0-13.6 nM) (B) Linear relationship between absorbance and concentration of Hg^{2+} and inset photos of different concentration of Hg^{2+} in the presence of AgNPs (Bhattacharjee et al., 2014).

Detection of Pb^{2+} ions

Pb^{2+} is one of the major pollutant and also explained as a carcinogen by The U.S. Environmental Protection Agency (EPA). Therefore, determination of Pb^{2+} ion is an important issue (Teh et al., 2014). Lead in high amounts causes organs and organs system disorders, while intake in low quantities causes neurobehavioural and psychological disorders (Tong et al., 2000).

Ratnarathorn et al. (2015) have been developed colorimetric detection of Pb^{2+} using maleic acid **(5)** modified AuNPs. The absorbance related to concentration of Pb^{2+} gave a linear result in the range of 0-10 µg L^{-1} in the milk samples and LOD was found 0.5 µg L^{-1} ($R^2 = 0.990$).

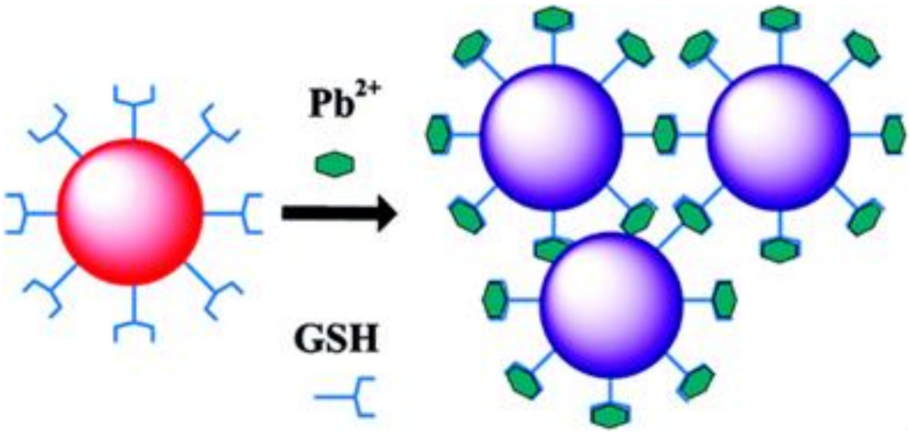

Figure 3. The working principle of developed colorimetric sensor for Pb^{2+} ions (Chai et al., 2010).

Glutathione **(6)** functionalized gold nanoparticles (GSH-AuNPs) were synthesized by Chai et al. (2010) for the colorimetric detection of Pb^{2+} in the lake samples. The basic principle of this study is based on aggregation of GSH-AuNPs in the presence of Pb^{2+} (Figure 3). There is a fine linear relationship between the $A_{700/520}$ with different working concentrations range of Pb^{2+} (0.1-10 µM). LOD is 100 nM (R^2 = 0.9851) and this developed method is very selective and sensitive to Pb^{2+} ions (Figure 4). Megarajan et al. (2020) synthesized the stabilized AuNPs using N-decanoyltromethamine (NDTM) **(7)** agent for highly selective, rapid colorimetric sensing of Pb^{2+} in water samples. A linear relationship was found between concentration of Pb^{2+} and absorbance values in the 0–30µM working range (R^2 = 0.9942). The LOD value was also found at 10 µM by naked eye and 0.35 µM by UV-Visible spectrophotometer. Shrivas et al. (2019) reported a colorimetric and highly selective sensing method using poly vinyl alcohol (PVA) **(8)** functionalized AgNPs and paper based analytical device for the determination of Pb^{2+} in surface waters, industrial waste water samples. The absorbance values versus different Pb^{2+} concentrations gave a linear response in the range of 20–1000 µg L^{-1} (R^2 = 0.99) with the LOD of 8 µg L^{-1} (Figure 5). In this study results of developed plasmonic colorimetric probe for the determination of Pb^{2+} in water samples were compared with results of ICP-AES.

Roto et al. (2020) studied colorimetric qualitative and quantitative analysis of Pb^{2+} ions using PVA-stabilized AgNPs in the presence of dithizone **(9)** due to the improve selectivity and sensitivity for Pb^{2+} ions. Developed sensor method gives linear response in the 0.5–10 µg L^{-1} concentration range of Pb^{2+} ions (R^2 = 0.9899) and LOD is 0.64 µg L^{-1}.

Detection of Cd^{2+} ions

Cadmium and cadmium derivatives are known carcinogens and also cause kidney damage, cardiovascular problems and cancer mortality (Aydın et al., 2020). Several studies have been summarized to detect Cd^{2+} ions.

Du et al. (2018) developed L-cysteine **(10)** modified gold/silver nanoparticles based sensor that is highly selective and sensitive to Cd^{2+} ions in water samples. Cd^{2+} ions interact with the L-cysteine due to the aggregation of Au/AgNPs in the presence of Cd^{2+} ions. This phenomenon causes a color change from orange-yellow to green, which enable to analysis of Cd^{2+} by the UV-Visible spectroscopy. The absorbance ratio A_{600}/A_{435} gives linear response in the 0.4–38.6 µM concentration range of Cd^{2+} ions (R^2 = 0.9985) and LOD of Cd^{2+} is 44 nM.

For a sensitive, selective and simple method, AHMT (4-amino-3-hydrazino5-mercapto-1,2,4-triazole) **(11)** functionalized AuNP based colorimetric sensor was developed for the determination of Cd^{2+} by Wang et al. (2013). The working principle of this nanoprobe is aggregation of AHMT modified AuNPs in the presence of Cd^{2+} ions (Figure 6). Developed sensor method gives linear response in the 60–480 nM concentration range of Cd^{2+} ions (R^2 = 0.9963) and LOD of Cd^{2+} is 30 nM.

Jabariyan et al. (2019) developed biosynthesized

AgNPs with grape juice due to colorimetric determination of Cd^{2+} ions in aqueous solution. The colorimetric analysis of Cd^{2+} responses a linear range from 0 to 150 µM ($R^2 = 0.9993$) and LOD of 4.95 µM for Cd^{2+} ions in aqueous solution.

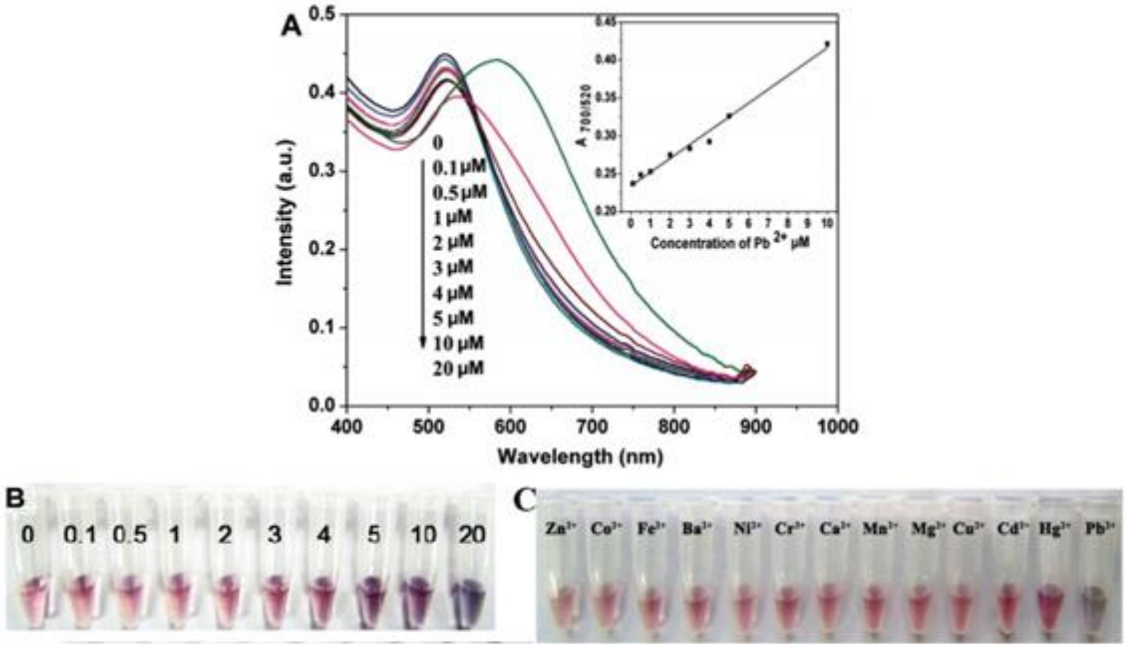

Figure 4. (A) UV-Visible spectra of lake water samples and (B) the corresponding photos of different concentrations of Pb^{2+} in lake water range between 0 to 20 µM from left to right and also absorbance ratio ($A_{700}/_{520}$) versus the concentrations of Pb^{2+} in the range of 0.1-10 µM shown by the inset. (C) The photo images of GSH-GNPs in the presence of 50 µM other metal ions compared with 20 µM Pb^{2+} (Chai et al., 2010).

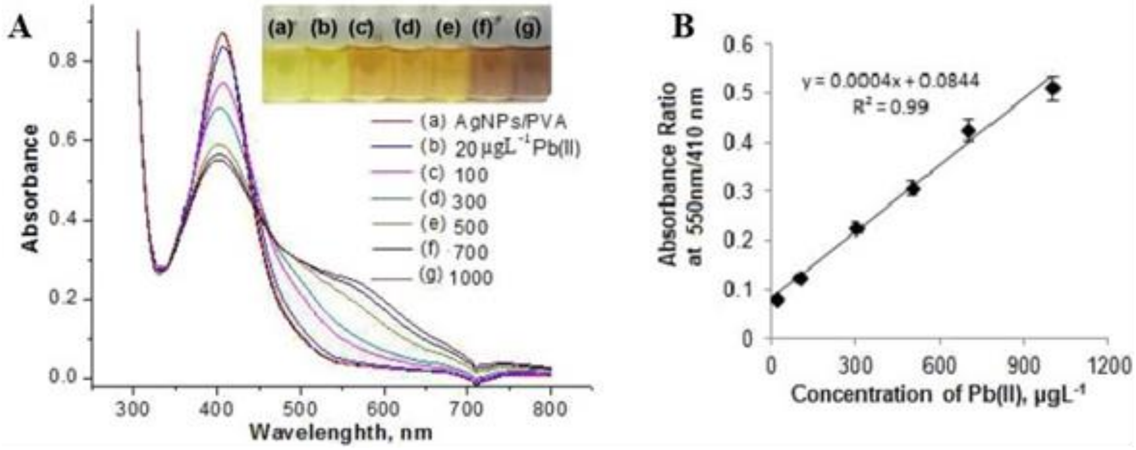

Figure 5. (A) UV-Visible spectra of different concentration range of Pb^{2+} between 0-1000 µg L^{-1} in the presence of the PVA/AgNPs solution and their photo images. (B) Absorbance ratio ($A_{550}/_{410}$) versus the concentrations of Pb^{2+} in the range of 20-1000 µg L^{-1} (Shrivas et al., 2019).

In this study 5-sulfoanthranilic acid dithiocarbamate **(12)** (SAA/DTC) modified AgNPs synthesized by Mehta et al. (2016) to detect Pb^{2+} and Mn^{2+} ions with high selectivity in aqueous solution. A color change occured from yellow to orange in the presence of Cd^{2+} ions due to the the aggregation of SAA/DTC/AgNPs. Analysis of Cd^{2+} ions method is related to LSPR peak by UV-Visible spectrophotometer provides wide linear detection ranges from 10 to 100 µM ($R^2 = 0.9973$) with the LOD of 5.8 µM for Cd^{2+} ions.

Detection of Cr^{3+} and/or Cr^{6+} ions

Excess amount of Cr(III) produces mutations and malignant cells due to the interaction with DNA. This interaction is related to intracellular reduction of Cr(VI) to Cr(III) (O'Brien et al., 2003). In addition, Cr(VI) has highly carcinogenic and mutagenic effects to human and also cause important health problem such as different types of cancers, hereditary genetic diseases and allergic disorders (Wise et al., 2012). In the presence of this crucial information, the determination of chromium ions seems to be very important and some studies for the colorimetric analysis of Cr^{3+} and/or Cr^{6+} ions are as follows:

11-mercaptoundecylphosphonic acid (MPA) **(13)** modified AuNPs were synthesized for the rapid and colorimetric determination of Cr^{3+} ions in water samples. In the presence of Cr^{3+} ions causes aggregation of MPA modified AuNPs and also the color changes from pink to blue (Figure 7). This developed method showed high selectivity for the Cr^{3+} ions compared to the other metal ions. pH range chosen from 4 to 9 for the optimum conditions. A linear range from 0 to 20 ppm ($R^2 = 0.9802$) and LOD of 9.01×10^{-6} M for Cr^{3+} ions in aqueous solution (Garcia et al., 2018).

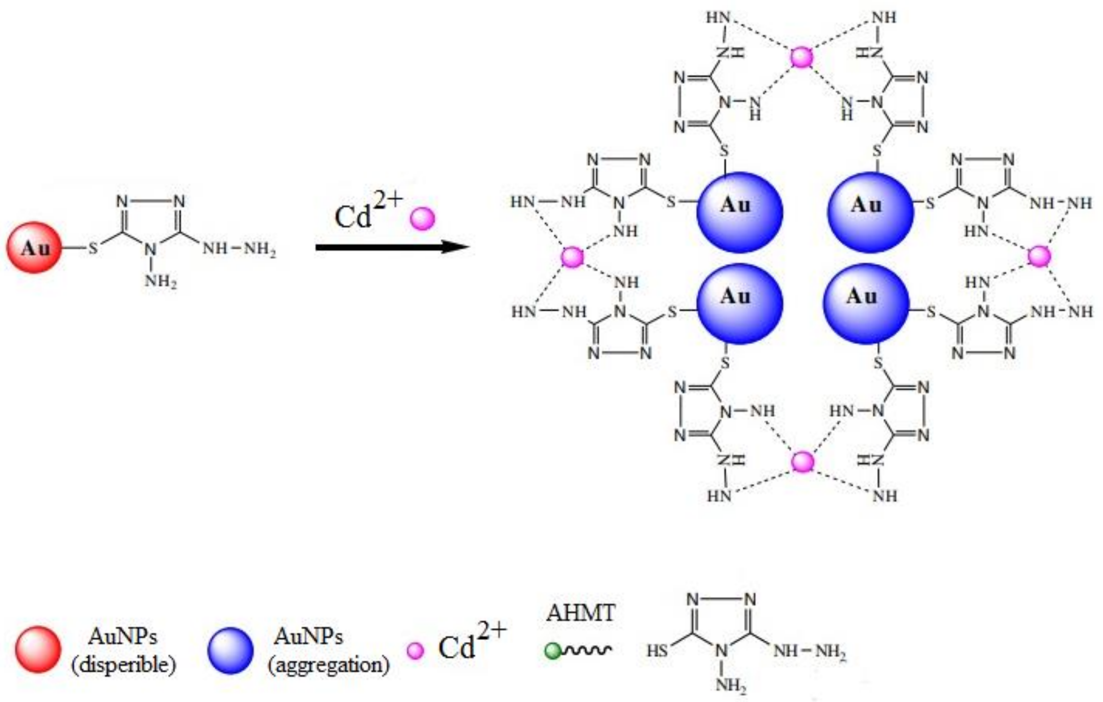

Figure 6. Aggregation of AHMT modified AuNPs in the presence of Cd^{2+} ions in water samples (Wang et al., 2013).

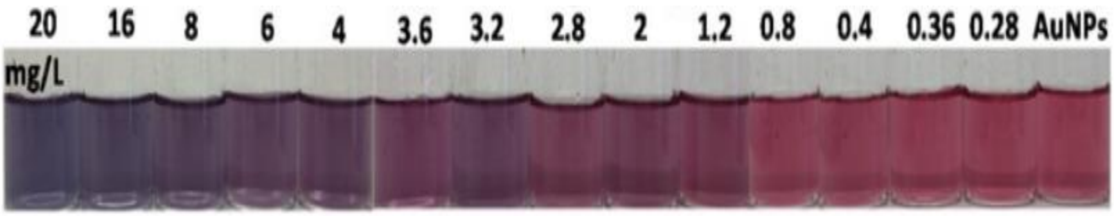

Figure 7. The photograph of different concentration of Cr^{3+} ions in the presence of MPA modified AuNPs (Garcia et al., 2018).

A sensitive colorimetric method has been developed for the determination of both Cr^{3+} and Cr^{6+} in real water samples based on aggregation of tween 20-stabilized **(14)** AuNPs and also strong chelating between Cr^{3+} and citrate, and the reduction of Cr^{6+} to Cr^{3+} due to the ascorbic acid. Cr^{3+} and Cr $^{6+}$ ions were able to be monitoring by UV–Visible spectroscopy as well as naked eyes with this developed sensor method. Good linear relationships was found for Cr^{3+} and Cr^{6+} over the range of 0.05–5.0 µM (R^2 = 0.978) and 0.02–2.5 µM (R^2 = 0.974). LOD of Cr^{3+} and Cr^{6+} were 0.016 µM and 0.009 µM in standard aqueous solution, respectively (Wang et al., 2015).

Mousapour et al. (2020) have been introduced 2-thiobarbituric acid (TBA) **(15)** modified AgNPs as a sensitive and selective colorimetric sensor for the analysis of Cr^{3+} and Cr^{6+} ions in waste water (Figure 8). The absorbance ratio (A_{520}/A_{418}) versus different concentrations of Cr^{3+} and Cr^{6+} ions in gave a linear results in the range of 0.012 to 3.25 mg L^{-1} (R^2 = 0.9944) and 0.20 to 1.40 mg L^{-1} (R^2 = 0.9913), respectively. The LOD values were found Cr^{3+} and Cr^{6+} ions 8.4 µg L^{-1} and 200 µg L^{-1}, respectively.

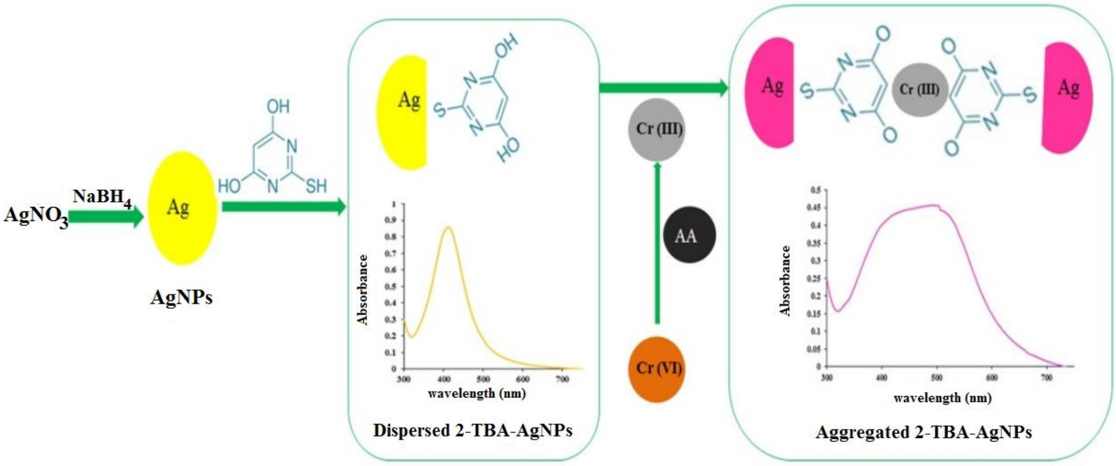

Figure 8. Working principle of colorimetric determination of Cr^{3+} and Cr^{6+} ions based on 2-thiobarbituric acid (TBA) modified AgNPs (Mousapour et al., 2020).

Table 2. A summary of different kinds of nanoparticle based-colorimetric sensors for determination of some heavy metal ions.

Ions	Types of nanoparticles	Linear range(µM)	R^2	Dedection limit (µM)	Real Samples	Ref.
Hg^{2+}	Pzl/AuNPs	0.01-1.5	0.9997	7.7x10^{-3}	Lake and tap water	(Kataria et al, 2019)
	MTT/AuNPs	0-11	0.9986	1.4x10^{-2}	Water samples	(Aktara et al., 2019)
	DETL/AuNPs	0.1-0.5	0.9845	2.4x10^{-2}	Water samples	(Huang et al., 2019)
	AgNPs	1-100	0.97	1.25	Drinking water	(Aminu et al., 2020)
	cysteamine/AgNPs	0-0.036	Not reported	2.73 x10^{-2}	Water samples	(Bhattacharjee et al., 2014)
Pb^{2+}	MA/AuNPs	0-0.048	0.990	2.41x10^{-3}	Milk samples	(Ratnarathorn et al., 2015)
	GSH/AuNPs	0.1-10	0.9851	1x10^{-1}	Lake samples	(Chai et al., 2010)
	NDTM/AuNPs	0-30	0.9942	3.5x10^{-1}	Water samples	(Megarajan et al.,2020)
	PVA/AgNPs	0.096-4.83	0.99	3.86x10^{-2}	Surface and industrial waters	(Shrivas et al., 2019)
	DTZ/PVA/AgNPs	0.0024-0.048	0.9899	3.09x10^{-3}	Ground and tap water	(Roto et al., 2019)
Cd^{2+}	L-Cys/Au/AgNPs	0.4-38.6	0.9985	4.4x10^{-2}	Water samples	(Du et al., 2018)
	AHMT/AuNPs	0.06-0.48	0.9963	3x10^{-2}	Water samples	(Wang et al., 2013)
	AgNPs	0-150	0.9993	4.95	Aqueous solutions	(Jabarian et al., 2019)
	SAA/DTC/AgNPs	10-100	0.9973	5.8	Aqueous solutions	(Mehta et al., 2016)
Cr^{3+} and Cr^{6+}	MPA/AgNPs	0-384.7 (Cr^{3+})	0.9802	9.01	Aqueous solutions	(Garcia et al., 2018)
	Tween20/AuNPs	0.050-5.0 (Cr^{3+})	0.978	0.016	Real water samples	(Wang et al., 2015)
		0.02-2.5 (Cr^{6+})	0.974	0.009		
	TBA/AgNPs	0.230-62.5 (Cr^{3+})	0.9944	1.62x 10^{-1}	Waste water samples	(Mousapour et al., 2020)
		3.85-26.93 (Cr^{6+})	0.9913	1.73x10^{-4}		
	TA/AgNPs	0.096-1.92 (Cr^{3+})	0.996	3.8x10^{-2}	Waste water samples	(Shrivas et al., 2016)
		0.192-1.92 (Cr^{6+})	0.995	5.8x10^{-2}		

Note: Units of some values have been changed for easy comparison of numerical results.

Shrivas et al. (2016) used tartaric acid (TA) **(16)** functionalized AgNPs as a simple colorimetric sensor which is visible to the naked eye for Cr^{3+} and Cr^{6+} ions determination. The formed coordination complexes between chromium ions and the tartaric acid triggered the LSPR band changes due to the aggregation of TA/AgNPs to enable to colorimetric determination of chromium ions. The absorbance values versus different Cr^{3+} and Cr^{6+} concentrations gave a linear response in the range of 5–100 µg L^{-1} (R^2 = 0.996) and 10–100 µg L^{-1} (R^2 = 0.995) with the found LOD values were 2 µg L^{-1} and 3 µg L^{-1}, respectively. Analytical statistics of nanoparticle based colorimetric sensors are given in Table 2.

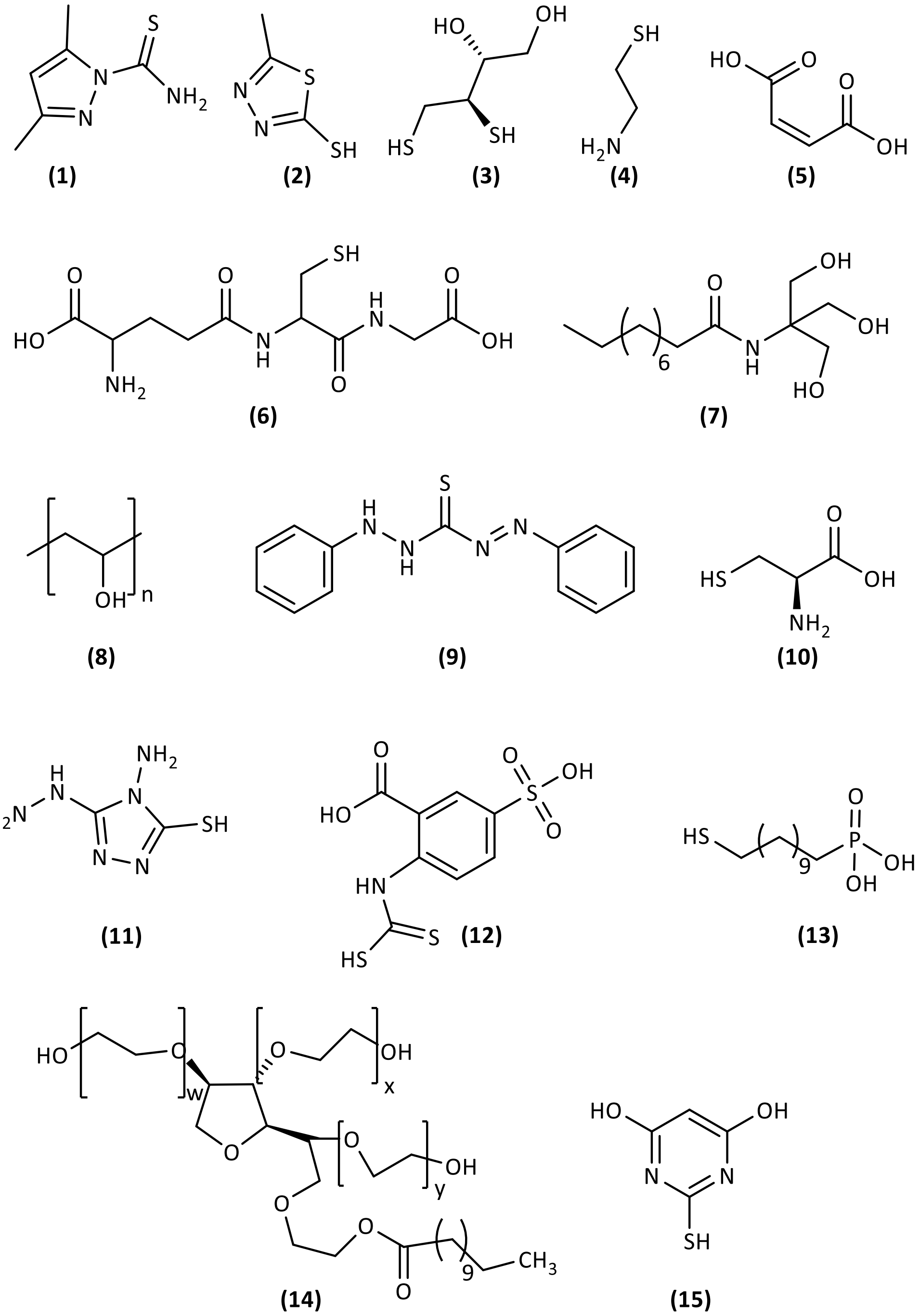

Figure 9. Molecules used to modify and/or stabilize AuNPs and AgNPs in the studies mentioned in this review.

RESULTS AND DISCUSSION

In this review, developed nanoparticle-based colorimetric sensors for the detection of some nonessential heavy metals that accumulate in nature and threaten the health of living things in recent years are mentioned. The colorimetric method is a solution-based method related to color changes in the visible region, so AuNPs and AgNPs change color in the presence of target heavy metal due to their LSPR properties. AuNPs and AgNPs can be easily stabilized and modified (Figure 9) to create a high-precision and sensitive sensor specific to the target heavy metal in solution. Some properties such as selectivity, repeatability, sensitivity, simultaneous analysis, portability are the advantages of nanoparticle based-colorimetric methods monitored by UV-Visible spectrophotometer. In summary, as can be seen in Table 1, sensors developed for target heavy ions in nanoparticle-based colorimetric studies provide high selectivity and sensitivity as well as characterization at micromolar levels.

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