

## **Schiff base as a Nanosorbent for Eliminating Lead from Contaminated Water**

**Ahmed M. Zaidan<sup>1</sup>, Zainab TY Alabdullah<sup>2</sup> and Uhood J. Al-Hamdani<sup>2</sup>**

<sup>1</sup>**Ahmed M. Zaidan** , Department of Chemistry, College of Marine Science centre, University of Basrah, 61001, Iraq

<sup>2</sup>**Zainab TY Alabdullah , Uhood J. Al-Hamdani** , Department of Chemistry, College of Education for Pure Sciences, University of Basrah, , 61001, Iraq

*\*Corresponding Author:*(e-mail: zt\_yasin@ yahoo.com)

### **Abstract**

Schiff base was first created, and it was subsequently employed as a reducing and capping agent to create silver nanoparticles. Schiff base serves as a capping to stop silver oxide from overgrowing. Schiff base provides silver nanoparticles a new form, producing them in a distinctive manner. Spectral information from the <sup>1</sup>H nuclear magnetic resonance, mass spectra, were used to analyze the structure of schiff base. UV-Vis Spectroscopy was used to characterize the structure of silver nanoparticles in order to track how the surface plasmon band that emerges at (433.5) nm affects the formation of silver nanoparticles. In order to analyze the morphology of silver nanoparticles, scanning electron microscopy (SEM) was performed. In the image, silver nanoparticles with sizes between 50 and 100 nm have spherical shapes. Energy dispersive x-ray spectroscopy EDX was also employed the spectra shows silver at 49.4% in the specimen. Dynamic light scattering (DLS) prove that prepared silver nanoparticles in nano size. The prepared sample schiff base coated nanoparticles was applied for adsorption lead from polluted water and the percentage of adsorption was 74.34.

**Keywords: Adsorption, Schiff base, Silver nanoparticles,**

## **1.Introduction**

A fused benzene and thiazole ring makes up the chemical molecule known as benzothiazole. Due to its adaptability, it has attracted considerable interest in a number of sectors, including medicinal chemistry, materials science, and agrochemical research. Numerous biologically active chemicals are produced using benzothiazole as a fundamental building component.[1].

The application of benzothiazole in the synthesis of Schiff bases is important. Schiff bases are organic compounds that contain a carbon-nitrogen double bond ( $\text{-C=N-}$ ) and are formed by the condensation reaction between a primary amine and an aldehyde or ketone. Benzothiazole, with its unique structure and reactivity, serves as a valuable starting material for the synthesis of diverse Schiff bases. The reaction between benzothiazole and an aldehyde or ketone typically proceeds through the nucleophilic addition of the primary amine group of benzothiazole to the carbonyl group of the aldehyde or ketone, followed by the elimination of water. This results in the formation of the Schiff base, which contains a carbon-nitrogen double bond. The reaction can be catalysed by various acidic or basic catalysts, and the conditions can be optimized to achieve high yields and selectivity.[2].

Schiff bases derived from benzothiazole exhibit interesting chemical and biological properties, making them attractive for various applications. They have been investigated as potential ligands for coordination chemistry, where they can form complexes with transition metals. These metal complexes have shown diverse catalytic, luminescent, and biological activities. In addition, Schiff bases derived from benzothiazole have been explored for their antimicrobial, anticancer, and antioxidant properties. The synthesis of Schiff bases using benzothiazole as a starting material provides access to a wide

range of compounds with versatile applications. The structural modifications of both the benzothiazole and the aldehyde or ketone components allow for the fine-tuning of the properties and activities of the resulting Schiff bases.[3].

The utilization of Schiff bases in the synthesis of nanoparticles has emerged as a promising field of research. Schiff bases, offer a versatile approach to control the size, shape, and surface properties of nanoparticles. Schiff bases can function as stabilizing agents, preventing nanoparticle agglomeration and enabling precise control over their growth and morphology. By coordinating with metal ions, Schiff bases stabilize the nanoparticles and influence their nucleation and crystal growth. This technique has been successfully applied to synthesize metal nanoparticles, including silver, gold, and palladium nanoparticles, with tailored properties for various applications.

Additionally, during the creation of nanoparticles, Schiff bases can function as reducing agents. Schiff bases can efficiently lower metal ions and encourage the formation of nanoparticles because they include functional groups like imine or amine groups. This environmentally friendly technique has been used to create a variety of metal nanoparticles, including iron oxide, copper oxide, and platinum nanoparticles. Typically, metal precursors and the Schiff base are mixed together under particular reaction conditions to create nanoparticles. To acquire exact control over the size, shape, and characteristics of the resultant nanoparticles, these conditions can be optimised [4].

The resulting nanoparticles stabilized or reduced by Schiff bases exhibit unique properties and have a wide range of applications. They can be used as catalysts, sensors, drug delivery systems, and imaging a result of their improved reactivity and customizable surface chemistry [5].

In conclusion, the production of nanoparticles utilising Schiff bases offers a versatile and regulated method for adjusting the characteristics of

nanomaterials [6-8]. The exact production of metal nanoparticles with desirable properties is made possible by the use of schiff bases, which work well as stabilising or reducing agents. This creates opportunities for the creation of classy nanomaterials for a range of uses [9-12].

The utilisation of the nanoparticles as effective, affordable, and environmentally friendly adsorbents for the removal of several harmful substrates from wastewater, such as heavy metals, azo dyes, and other contaminants, may be successful [13].

Toxic substances must be removed from wastewater in order to safeguard human health and the environment. Conventional techniques like reduction, precipitation, adsorption, oxidation, and ion exchange are frequently utilised for this purpose. However, due to its great efficiency and economic benefits, the adsorption process is the best approach among them [14-17]. This study finds that nanoparticles have numerous distinctive morphological and structural characteristics that make them suitable for usage as efficient adsorbents to solve a variety environmental problem. Therefore, it was applied for adsorption of lead ion from polluted water.

## **2. Experimental**

### **2.1 General**

Infrared spectrum was measured as KBr pellets on a Buck-M500 spectrophotometer.  $^1\text{H}$ NMR spectrum was measured using a Bruker-400MHz instrument using  $\text{CDCl}_3$  as solvent and TMS as internal standard. Mass spectra were recorded on an Agilent technologies 5957VC spectrometer.

### **2.2 Synthesis of compounds**

### 2.2.1 Synthesis of Schiff base

One molar equivalent of the appropriately substituted aniline was added to a solution of the 2,4-dihydroxy benzaldehyde in ethanol (1:1) to which a few drops of acetic acid were added according to the earlier reported method. The mixture was heated under reflux for 2 h, and the solid obtained upon cooling was filtered and twice recrystallised from ethanol to give pure compounds [6,7].

### 2.2.3 Synthesis of esters (E-3OCH<sub>3</sub>)

1 mmol of Trimethoxy benzoic acid dissolved in DCM was added to a mixture continuous of Schiff compound dissolved in DCM with 1 mmol of DCC (dicyclohexylcarbodiimide) the added to the resulting mixture 1 mmol of DAMP and left the mixture for 24 hours with continuous stirring at room temperature and at the end of the reaction the mixture was filtered and the solvent evaporated then orange crystals were formed and the dicyclohexylurea(DCU) formed was neglected as a by-product in the filter paper [8 , 9].

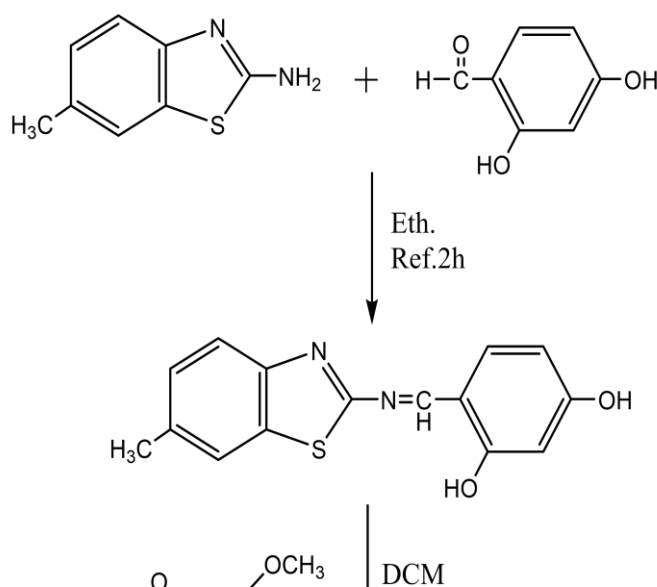


Fig.1. Synthesis routes of the E-3OCH<sub>3</sub>compound.

### 2.3 Characterization of 3-hydroxy-4-(((6-methylbenzo[d]thiazol-2-yl)imino)methyl)phenyl 3,4,5-trimethoxybenzoate.

Chemical Formula: C<sub>25</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>S, Yellow solid; yield 32% , m.p240 °C ;<sup>1</sup>H-NMR : , 2.46 ppm(S, 3H, CH<sub>3</sub>), 3.90 ppm(S, 9H, 3OCH<sub>3</sub>), 7.33- 7.83 ppm(m, 13H,Ar-H), 8.35 ppm(S, H, CH = N), 12.17 ppm(s, H, OH) .(Fig. 2 ) ;MS (m/z) 478.2 [M<sup>+</sup>](Fig. 3) , .

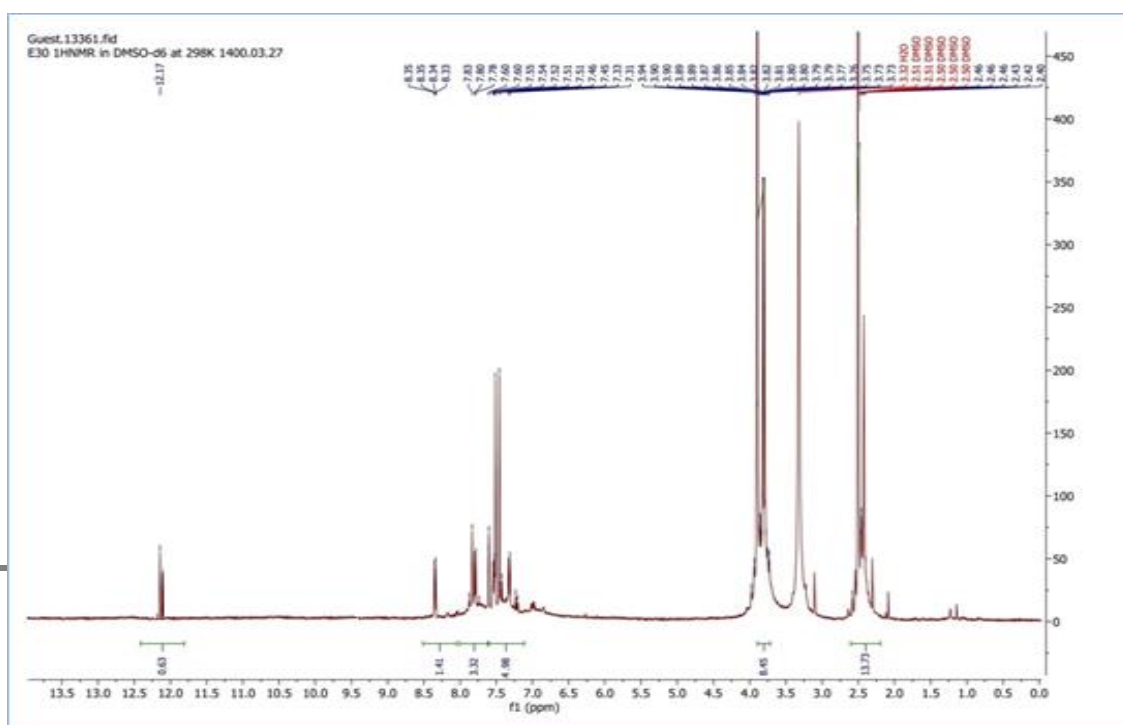
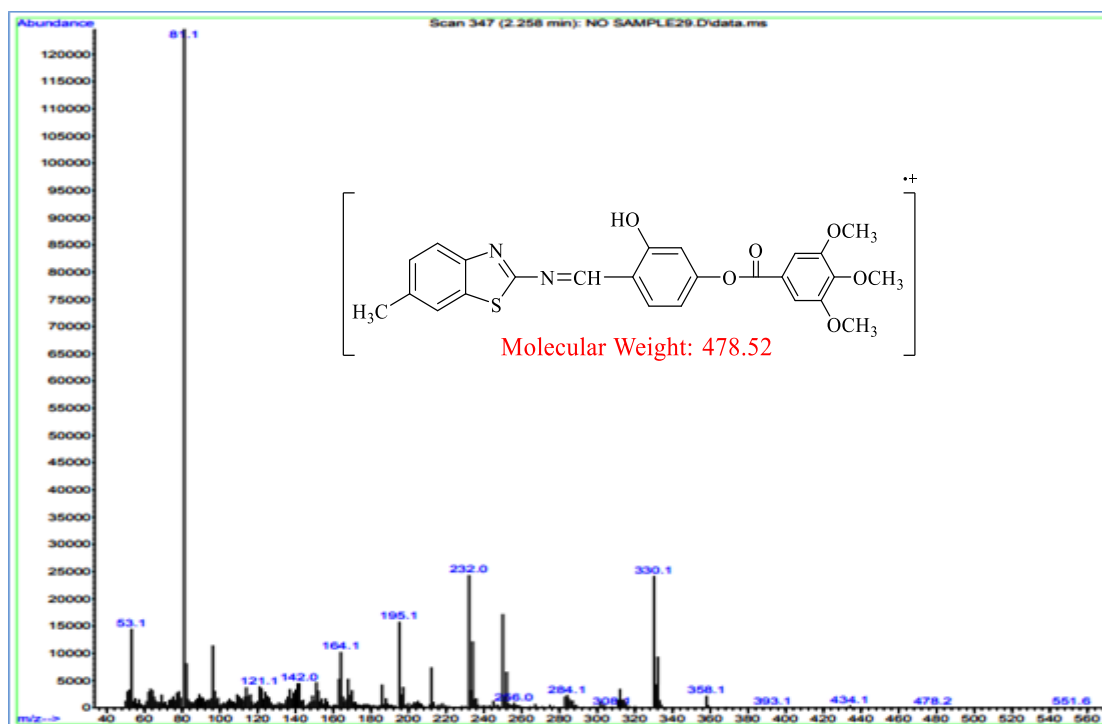
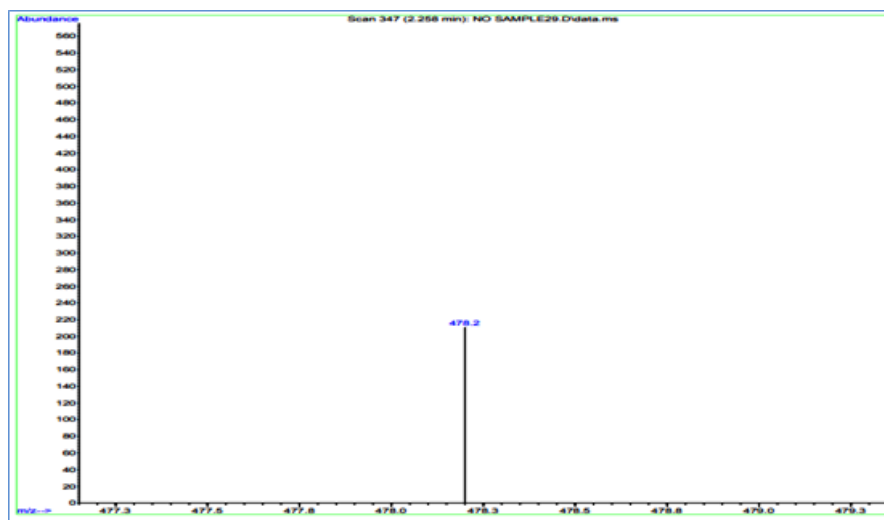


Fig. 2.  $^1\text{H}$ -NMR spectrum for E-3OCH<sub>3</sub>compound.Fig.3. Mass spectrum for E-3OCH<sub>3</sub>compound .Fig. 4. Expansion for molecular ion in Mass spectrum of E-3OCH<sub>3</sub>compound

## Experimental

### Synthesis of silver nanoparticles

Schiff base consist of hydroxyl groups that have a strong capability to bind with silver ions. Hence, once the interaction occurred, silver ions is reduced to  $\text{Ag}^0$  and therefore induces the creation of silver nanoparticles. It was found that Schiff base is excellent reducing agent for the synthesis of silver nanoparticles. Although the green method is presented in the recent researches in case of preparation of metallic nanoparticles the schiff base prove the ability to reduce and stabilize nanoparticles eliminates the necessity of using several reagents that acts specifically as reducing and stabilizing agent. Moreover, the schiff base can be used as masking agent of nanoparticles which is give the stability of nanoparticles in the solution and give the nanoparticles the ability for covering presence of active groups (such as amine) on the schiff base surface, making it suitable for electrostatic adsorption and interaction with nanoparticle surfaces and also to adsorb the metal from the polluted water.

## **Results and Discussion**

### **UV-Vis spectroscopy of silver nanoparticles**

The reduction reaction of  $\text{Ag}^+$  ions to create  $\text{Ag}^0$  was observed by recording the UV-Vis spectra of silver nanoparticles (1.0 mL) after diluting them with deionized water to (3.0 mL). In silver nanoparticles, a localised surface plasmon band is excited, and this causes absorbance peaks to form between 400 and 800 nm.

The highest absorbance at (433.5) nm, as seen in Fig. 5, is caused by a surface plasmon band (SPB) generated by the creation of silver nanoparticles. The phenomena for metal that announces the production of nanomaterials is the plasmon spectra, which are expressed on the resonance of metal in the correct wave length. Hence the two peaks were appearing from schiff base(217, 279 nm) fig5(A) and one plasmon peak was appears when schiff base covering nanoparticles refers to silver nanoparticles. fig 5(B).

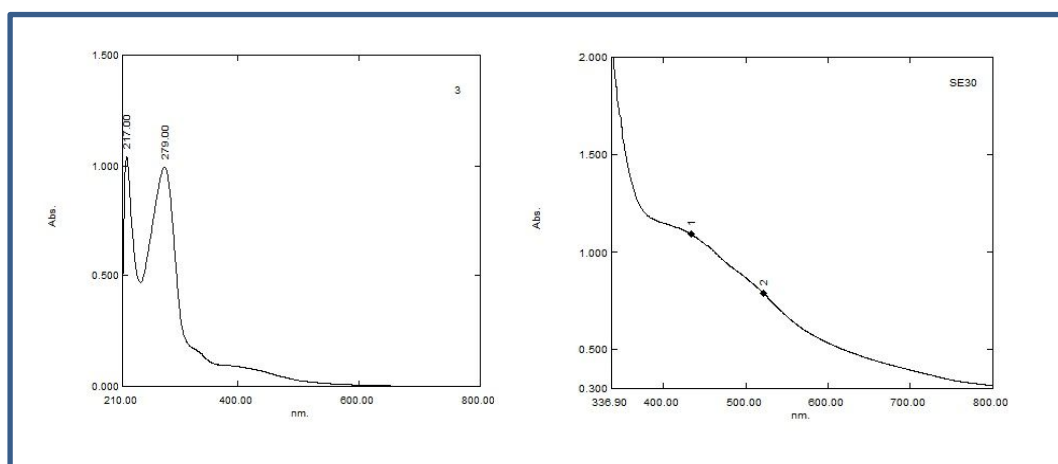


Fig.5. The plasmon spectra of (A) Schiff base (B) silver nanoparticles

### SEM -EDX Spectra

Using a SEM picture, the dimensions of silver nanoparticles were determined. Schiff base is an essential capping agent in the manufacture of silver nanoparticles because it can reduce and stabilise dispersive nanoparticles. In Figure 8, the silver nanoparticles are distinct from one another. Furthermore, the frequency of

occurrence of these nanoparticles in the fluid. It was discovered that silver nanoparticles were spherical and ranged in size from 50 to 100 nm.

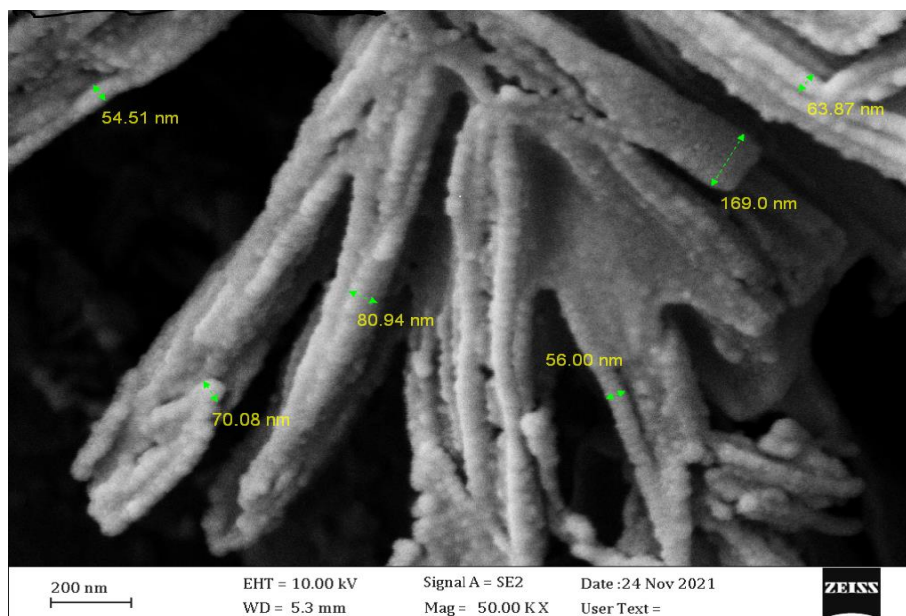


Fig. 6. SEM image of silver nanoparticles in the presence of schiff base.

One-capacity silver ions should diminish under carefully controlled thermodynamic conditions, and the main nanoproduct should have spherical geometry since the lowest volume spherical particles have a higher thermodynamic stability. Silver nanoparticles have been investigated using the energy dispersive x-ray method. Figure 7 illustrates the formation of silver nanoparticles by showing the proportions of silver (49.4%) and oxygen (50.6%).

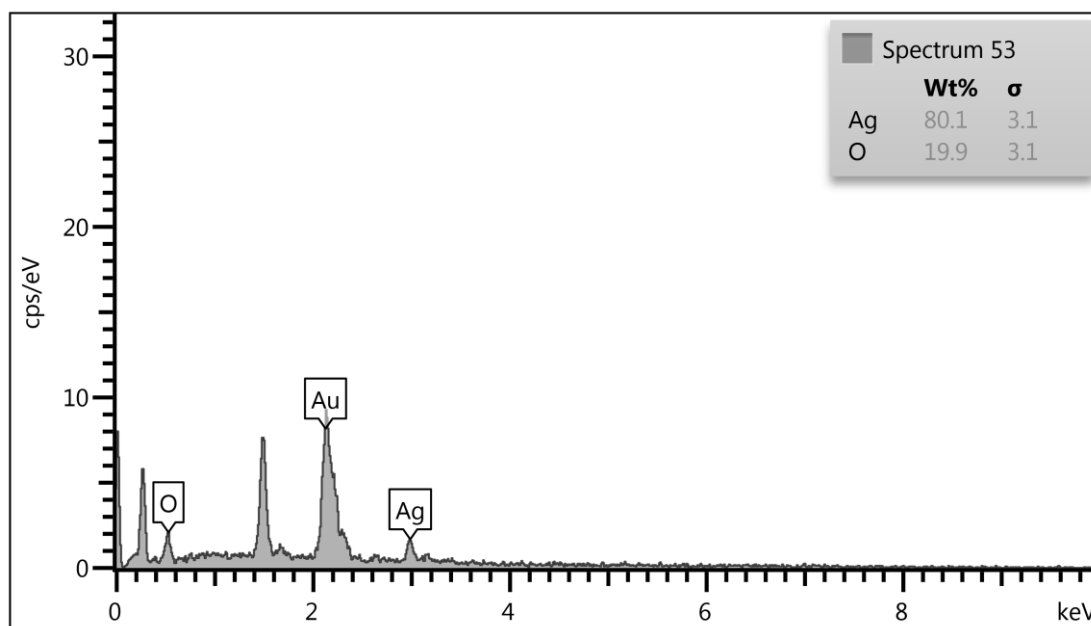


Fig.7. Energy dispersive analysis spectra of silver nanoparticles

### Dynamic light scattering (DLS)

Zata sizer used to analyse the size distribution of nanoparticles. The size distribution of silver nanoparticles is represented in Figures 8. the size distribution of silver nanoparticles identical to 100 nm-sized particles.

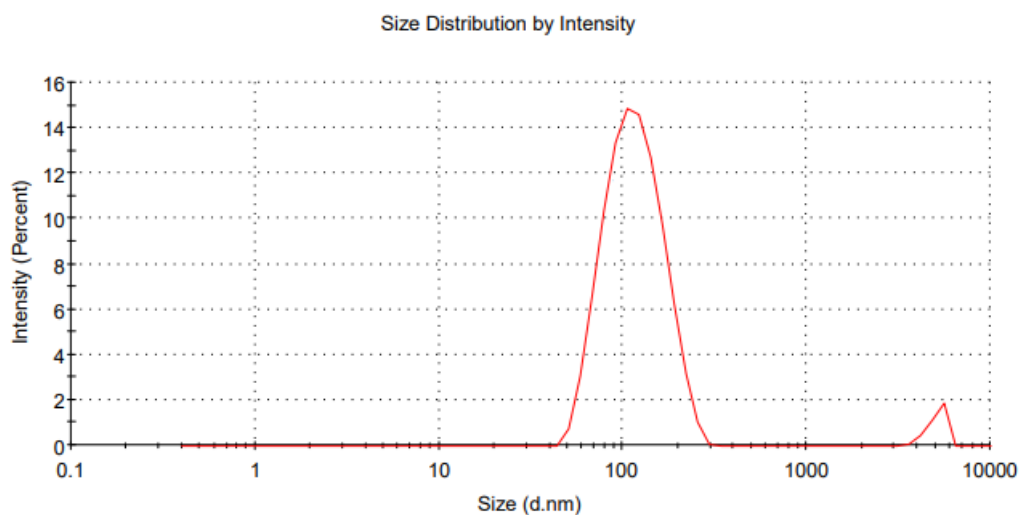


Fig.8 The size distribution of silver nanoparticles.

## Applied nanoparticles in purification of water

Based on their unique properties, nanomaterials have been widely investigated for the removal of heavy metals and dyes from wastewater due to their high surface area and tiny particle size, which results in a high number of adsorption active centres.

The prepared silver nanoparticles capping by schiff base were utilised as an adsorbent to remove lead, one of the most common heavy metals, from polluted water. Lead concentrations were measured using atomic absorption spectra before and after the absorption on silvernanoparticles surface. Table 1 shows the results of utilising silver nanoparticles capping by schiff bases for the releasing of lead ion from polluted water.

the adsorption % of lead ions on (silver nanoparticles coated by schiff base) using atomic absorption spectroscopy (AAS) at optimum conditions such (25°C), (30 min) contact time and (10 mg/L) conc. of lead).

First of all the calibration standard curve of lead was prepared as shown in fig.9.

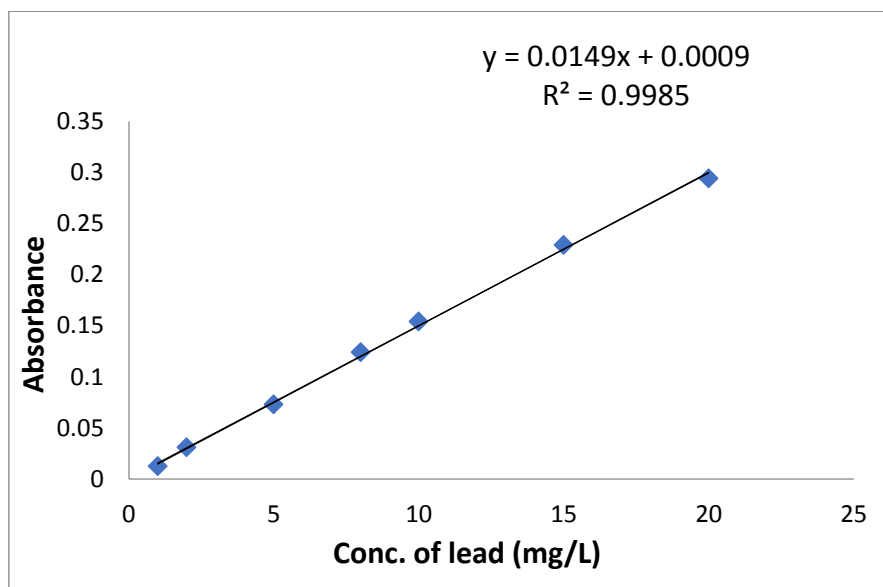


Fig. 9. Standard curve of lead using atomic absorption spectroscopy

The percentage of adsorption of lead was measured using equation 1.

$$\% \text{ Ads} = (A_0 - A_t / A_0) * 100\% \dots \dots \dots (1)$$

the prepared silver nanoparticles were applied for removal of lead from water pollutant. The optimum conditions were studied as following:

### The influence of contact time

The time effect on lead ion removal process on the silver nanoparticles surface was studied in different time periods ranging from (10-80) min at a fixed volume of silver nanoparticles 15ml and a constant concentration and volume of lead 10ppm. It was found as seen in fig.10 that 30 min the best contact time for adsorption. The adsorption percentage of lead ions increases with increasing time rapidly during the adsorption process because the active sites on silver nanoparticles were available at these times.

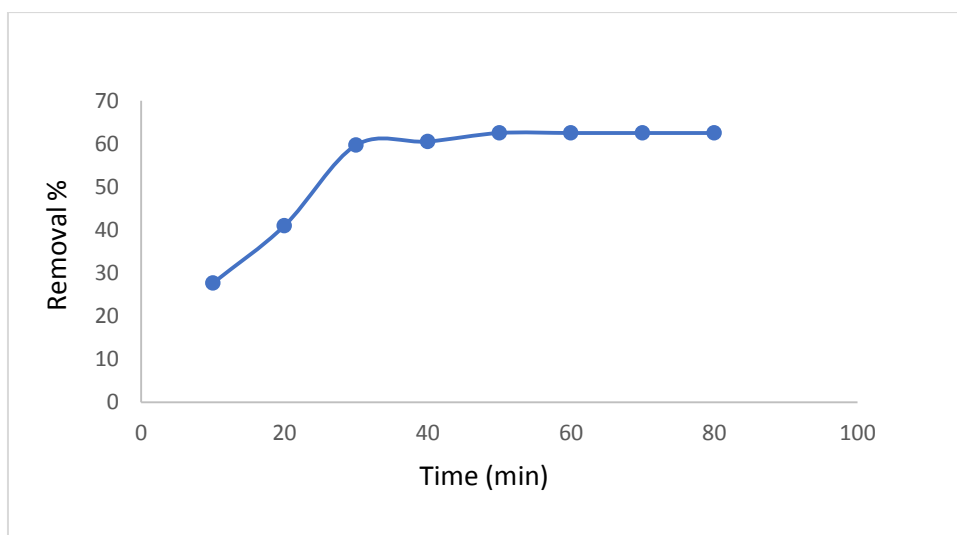
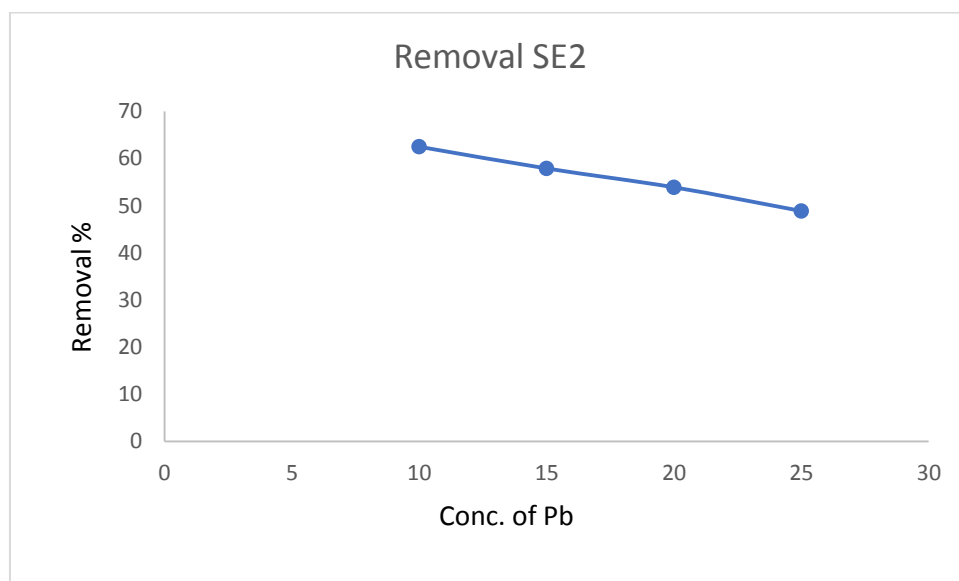


Figure10 . The influence of contact time on lead removal by silver nanoparticles.

## The influence of initial metal concentration

It is clear from the results in fig.11 that the percentage of removal increases by decreasing the initial concentration of the lead ions under study. The increasing in the percentage of adsorption is due to the fact that in the case of high concentrations, there is a relatively large number of elemental ions and thus they occupy the largest possible number of active sites on the adsorbing surface[18][19].



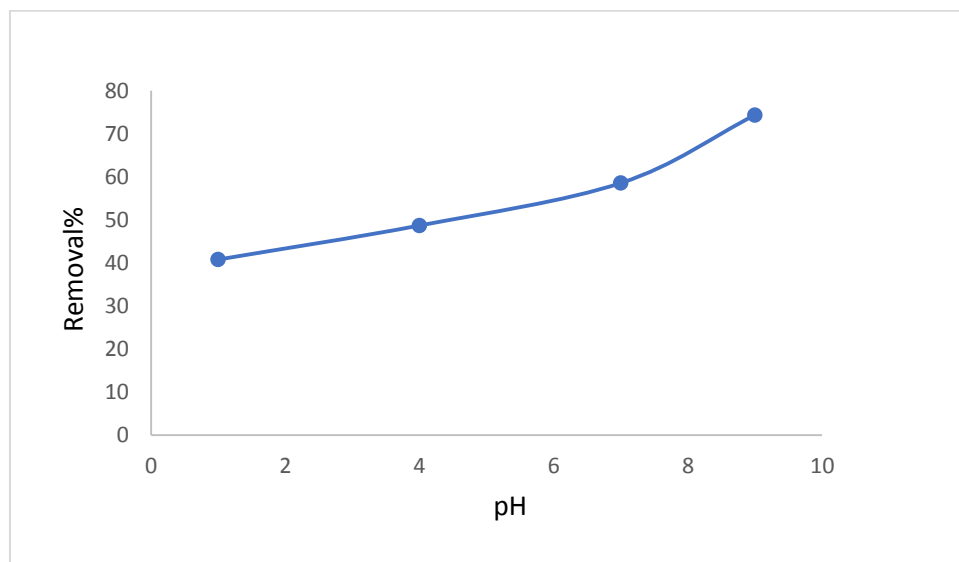
**Figure. 11 The influence of concentration of metal on the lead removal by silver nanoparticles capping by schiff base.**

## The influence of pH on adsorption of lead

An aqueous solution's pH is important in adsorption processes, because pH affects the type of charge of the adsorbent surface, and thus the adsorption ratio of  $\text{Pb}^{2+}$  from it.

The adsorption of heavy metal ions from aqueous solutions affected by several factors, the most important one the acidity function which affecting due to its influence on the solubility of the metal ion. The adsorption of lead ion on the surface of silver nanoparticles in different acidic functions ranging from 1 - 9 has been studied. The percentage of the lead(II)ions adsorption increased rapidly with the increase in the pH from 1 to 9; The reason for the increase in the percentage of

lead(II) ions adsorption is due to the increase in the concentration of the  $\text{OH}^-$  ions on the silver nanoparticles, surface, with an increased pH from 2 to 12, thus charging the surface with a negative charge, which increased the potential of the lead ion adsorption on the silver nanoparticle surface.



**Figure 11. The influence of pH on the lead removal by gold nanoparticles**

The percentage of adsorption 74.34% was calculated for lead before and after adsorbing on silver nanoparticles capping by schiff. However, many of conditions should be study especially the structure of schiff base which might be affect the adsorption. More charge on the nanoparticles with their capping might be more adsorption site for metal. due to the fact that nanoparticles can be manufactured in a different shape by changing schiff base therefore such studies should be taken.

## Conclusion

This quick and easy procedure for making silver nanoparticles coated by schiff bases can be modified to yield more reliable outcomes. There is no longer a

requirement for numerous reagents that operate specifically as a reducing or masking agent because schiff base can reduce metal and stabilize of nanoparticles. As a result, schiff base's ability to operate as a reducing agent was unaffected by the researchers' varied methods. This straightforward technique can also be enhanced to deliver consistent outcomes. Additionally, SEM pictures show a distinct separation between silver nanoparticles created with the schiff base. Additionally, because of the surface charge that enables adsorbed materials, it can be utilised in a range of sectors. A variety of separation and purification methods could be developed to improve the activity of nanoparticles capped by schiff base while lowering their toxicity, as they are new to water treatment applications. The utilisation of nanoparticles as ethically and economically appropriate adsorbents for water filtration was acknowledged in this paper. This work underlines how nanoparticles are ideal candidates for future use as adsorbents due to their distinctive morphological and structural properties.

### **Conflicts of interest**

The authors declare that there are no conflicts of interest regarding this article.

### **References**

- [1] Saxena, S., et al. (2012). Schiff bases and their metal complexes as a new class of antimicrobial agents. *Int. J. Pharm. Sci. Rev. Res.*, 15(1), 61-66.  
<https://www.degruyter.com/document/doi/10.1515/revis-2015-0007/html?lang=de>

- [2] El-Agrody, A. M., et al. (2017). Synthesis, characterization, and antimicrobial activity of some Schiff bases derived from benzothiazole. Arab. J. Chem., 10(3), S1639-S1646. <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4190236/>
- [3] Nagaraja, B. M., et al. (2019). Benzothiazole and its versatile biological activities. Eur. J. Med. Chem., 176, 145-167. <https://pubmed.ncbi.nlm.nih.gov/25293580/>
- [4] Arunachalam, R., et al. (2019). Schiff base-metal nanomaterials: synthesis, properties, and applications. Materials Today Chemistry, 11, 93-109. <https://www.intechopen.com/chapters/84570>
- [5] Wang, D., et al. (2016). Schiff base chemistry in the synthesis of nanomaterials: recent advances. Chemistry - An Asian Journal, 11(17), 2324-2337. <https://pubmed.ncbi.nlm.nih.gov/11784145/>
- [6] Cao, R., et al. (2019). Schiff base-based nanomaterials for sensing applications. Journal of Materials Chemistry C, 7(32), 9810-9824. <https://pubs.rsc.org/en/content/articlelanding/2019/tb/c9tb00666d>
- [7] Gribble, G. W. (2000). Naturally Occurring Organohalogen Compounds. Acc. Chem. Res., 33(7), 416-425. <https://pubs.acs.org/doi/abs/10.1021/ar9701777>
- [8] Sartori, G., et al. (2014). Benzothiazoles: synthesis, structural diversity and pharmacological applications. ChemMedChem, 9(3), 453-470. <https://pubmed.ncbi.nlm.nih.gov/18086151/>
- [9] Huseen, Taha A and Abdul Hussien A., Cytotoxicity and Antibacterial Activities of Coated and NonCoated Magnetic Nanoparticle, J Nanostruct 2021; 11(4), 698-710 [https://jns.kashanu.ac.ir/article\\_111552.html](https://jns.kashanu.ac.ir/article_111552.html)
- [10] Sulaf Hussein Ali, Saba S. M. Al-Obaidy, Faris Hamood Mohammed, Enhancing the Antibacterial and Anticancer Activity of Ciprofloxacin by Encapsulating into Shellac-Chitosan Nano Particles

- (CNPs), J Nanostruct 2022; 12(3): 546-556.  
[https://jns.kashanu.ac.ir/article\\_112040\\_ae3e7ece8dc9b6676c785f2fe4fc17c5.pdf](https://jns.kashanu.ac.ir/article_112040_ae3e7ece8dc9b6676c785f2fe4fc17c5.pdf)
- [11] Krutyakov, Y.A., Kudrinskiy, A.A., Olenin, A.Yu., Lisichkin, G.V., 2008. Synthesis and properties of silver nanoparticles: advances and prospects. Russ. Chem. Rev. 77 (3), 233–25  
[https://www.researchgate.net/publication/258266369\\_ChemInform\\_Abstract\\_Synthesis\\_and\\_Properties\\_of\\_Silver\\_Nanoparticles\\_Advances\\_and\\_Prospects](https://www.researchgate.net/publication/258266369_ChemInform_Abstract_Synthesis_and_Properties_of_Silver_Nanoparticles_Advances_and_Prospects)
- [12] Ali N., Al-Abdullah Z, B Alabdulaziz and , Abood M ,Green Synthesis of Cobalt Nanoparticles and their Application in Removal of Lead from Polluted Water, Basrah Journal of Science, 2021; 39 (2) 292-305. <http://basjsci.net/index.php/bsj/article/view/118>
- [13] Miao, X.-S., Bishay, F., Chen, M., Metcalfe, C.D.: Occurrence of antimicrobials in the final effluents of wastewater treatment plants in Canada. Environ. Sci. Technol. 38(13), 3533–3541 (2004)
- [14] Sadegh, H., Shahryari-Ghoshekandi, R., Tyagi, I., Agarwal, S., Gupta, V.K.: Kinetic and thermodynamic studies for alizarin removal from liquid phase using poly-2-hydroxyethyl methacrylate (PHEMA). J. Mol. Liq. 207, 21–27 (2015)
- [15] Rao, M.M., Ramesh, A., Rao, G.P.C., Sessaiah, K.: Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls. J. Hazard. Mater. 129(1), 123–129 (2006)
- [16] Bis'kup, B., Subotic', B.: Removal of heavy metal ions from solutions using zeolites. III. Influence of sodium ion concentration in the liquid phase on the kinetics of exchange processes between cadmium ions from solution and sodium ions from zeolite A. Sep. Sci. Technol. 39(4), 925–940 (2005)

- [17] Gupta, V., Moradi, O., Tyagi, I., Agarwal, S., Sadegh, H., Shahryari-Ghoshekandi, R., Makhlof, A., Goodarzi, M., Garshasbi, A.: Study on the removal of heavy metal ions from industry waste by carbon nanotubes: effect of the surface modification: a review. *Crit. Rev. Environ. Sci. Technol.* 46(2), 93–118 (2016)
- [18] Al-Senani G and Al-Kadhi N, “The synthesis and effect of silver nanoparticles on the adsorption of Cu<sup>2+</sup> from aqueous solutions,” *Appl. Sci.* 2020; 10(14). doi: 10.3390/app10144840.
- [19]
- [20] Methaq I. Abood and Zainab T. Y. Al-Abdullah, The possibility of using TiO<sub>2</sub> Nanotube Arrays as an adsorbent for removing lead ions from aqueous solutions, *Mesopot. J. Mar. Sci.*, 2023, 38(1):21-32