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Ecofriendly method to get rid of eosin dye contamination using Nanoparticles of silver - silver chloride prepared in a biological way.

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Abstract

Environmental protection by photocatalytic removal of organic pollutants, like leftover colored dyes, was one strategy that showed a lot of promise. To boost the photocatalytic efficiency, however, efficient photocatalysts were required. It was previously believed that Ag/AgCl was a highly effective catalyst for photocatalytic degradation. AgCl was made from tap water, and silver nanoparticles were made with prickly pear extract. X-Ray diffraction (XRD) revealed that the sizes of AgNPs and AgClNPs, which were close-up FE-SEM nanomeasurments, were 43–112 nm and 14–65 nm, respectively. Ag/AgCl nanoparticles were found to exhibit strong visible light absorption in the UV–visible study, with the two peaks appearing at 415 nm and 203 nm, respectively. The outcomes demonstrated the nanoparticles' photocatalytic efficacy.Therefore, Ag/AgCl was suitable for the active photodegradation of eosin dye removal when exposed to sunlight.

Key words: silver nanoparticles, silver chloride nanoparticles, prickly pear, green synthesis, eosin stain, photocatalysis .

Introduction

A class of materials known as silver nanoparticles (AgNPs) has sizes ranging from 1 to 100 nm. AgNPs' distinct and alluring physical, chemical, and biological characteristics have recently sparked a greater interest in the study of these diverse behaviors [1-7]. AgNPs are also well known for having a distinct toxicity, surface plasmon resonance, and electrical resistance properties. According to these, a great deal of research has been conducted to look at their properties and potential applications for a range of things, such as digital gadgets, anticancer medications, wound dressings, and water treatment [8-13]. Despite warnings that AgNPs are hazardous, can stop the growth of bacteria, endanger zebrafish and humans, and destroy cell-based in vitro systems, they are extensively utilized in a wide range of commercial goods, such as

contraceptive pills and feminine hygiene products [14-17]. To date, a number of inorganic NPs have been effectively produced using a range of techniques, including metals, metal oxides, metal sulfides, and noble metal chlorides. Among these, selective use of AgCl-NPs as a photocatalyst has been made [18]. Detecting a substance [19]. Material for adsorptive desulfurization [20]. As well as antifungal, antioxidant, antibacterial, and anticancer substances [21, 22].

Green synthesis of nanoparticles

The majority of methods for producing nanoparticles through chemical synthesis are exceedingly costly and require the use of risky, toxic chemicals that are potentially harmful to humans. This demonstrates the growing need for biological techniques and green synthesis in the development of environmentally friendly processes, Sometimes using different plants and their extracts to produce nanoparticles can be more advantageous than using other biological synthesis methods that need laborious steps to maintain microbial cultures [23, 24]. The most widely used method for creating environmentally friendly, green nanoparticles is the synthesis of plant extracts, which also has the advantage of being easily obtainable. broadly distributed, much safer to work with, and a source of multiple metabolites [25]. The production of silver nanoparticles using plants is depicted in **Figure 1** [26].

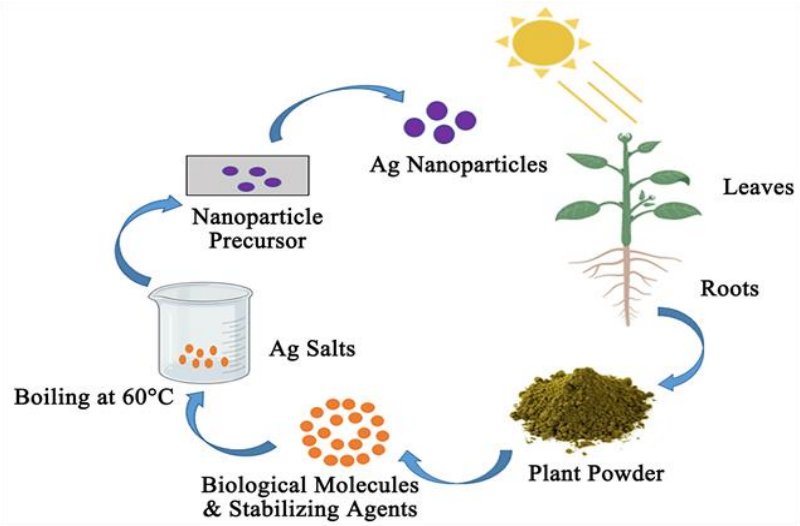

Figure1. the production of nanoparticles using plant extract

Ag-AgClNPs synthesis

Typically, physical and chemical methods which are costly economically and involve hazardous chemicals are used to synthesize silver- silver chloride nanoparticles [27]. Furthermore, toxic chemical residues from chemical synthesis may be absorbed by silver-silver chloride nanoparticles, which could have negative effects on their ability to be used in biomedical applications. As a result, a different technique for synthesizing silver and silver chloride nanoparticles is biogenic synthesis as shown in **Figure 2** , which uses plant extract. Commonly,

the plant extract is made up of various phytochemical compounds that function as capping agents to help stabilize silver nanoparticles and contribute to the reduction of Ag^{+} to Ag^{0}. Compared to the physicochemical method, the biological synthetic approach for producing silver nanoparticles is more advantageous because it is straightforward, economical, environmentally friendly, and simple to scale up for mass production [28]. Furthermore, because the silver-silver chloride nanoparticle produced by biogenically synthesizing it is biocompatible, it can be safely used for a variety of therapeutic applications. Nevertheless, the synthesis of silver-silver chloride nanoparticles from agricultural wastes has been the subject of relatively few studies.

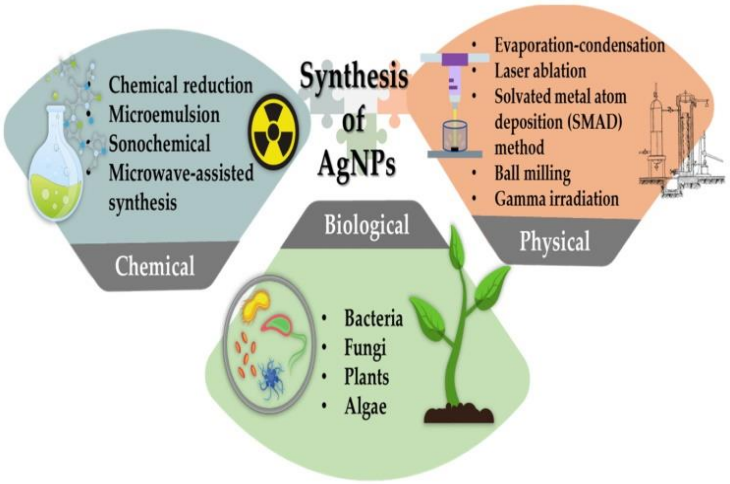

Figure 2. syntheses of AgNPs

The opuntia ficus indica (prickly pear)

Opuntia species is a genus that belongs to the Cactaceae family. The genus Opuntiaspp. remains one of the largest in the family Cactaceae, with over 1500 known species [29]. Due to their commercial value, some Opuntia species, such as Opuntia ficus-indica, have attracted the attention of most researchers, whereas other species have received less documentation. Originating in Mexico, Opuntia spp have since spread to other regions of the world [30, 31]. The Opuntia ficus indica species have long been recognized in traditional medicine for their medicinal and therapeutic value [32, 33]. It has proven to be an adequate supply of antioxidants and nutrients. Its health benefits include hepatoprotective properties, antiproliferative, anticancer, antiproliferative, and neuroprotective effects [30, 31, 33, 34]. Certain Opuntia species have been utilized in the treatment of oxidative stress, diabetes, obesity, and cancer. **Figure 3** shown the prickly pear fruit

Figure3. prickly pear fruit

Application of Ag-AgClNPs in removing stains by photocatalytic application

Biogenic Ag NPs were created in order to assess their efficacy in photocatalytically removing two common industrial dyes, given the significance of a highly efficient system for photocatalytic applications. such as reactive yellow 186 (RY186) and RB19. RB19 and RY186 are examples of industrial dyes that are more difficult to degrade than lab dyes like methylene blue and congo red and hematoxyline , eosine stains because of their large molecular masses and slow diffusion rates. In order to ascertain the significance of activation energy at various temperatures, the effectiveness of photocatalytic degradation against industrial dyes was investigated. Ag NPs were used as a photocatalyst in a direct sunlight environment. Beyond their outstanding efficacy in deteriorating dyes, The generated Ag NPs photocatalysts are attractive because they are easy to recover and have a high potential for reuse, which are necessary to achieve effective photocatalysis. Consequently, Ag NPs' photocatalytic properties strongly supported their great potential for disinfecting contaminated water by removing harmful pollutants [35].

2.Materials and methods

2.1.Materials

Prickly pear fruit were collected from plant in the month of october in ar-ramadi city , Anbar province , Iraq , the eosine stain was collected from histological laboratory , ar-ramadi teaching hospital , Deionized water (H_2O) was obtained from Chem-Lab, AgNO3was purchased from South Glens Falls, New York.

2.2.Methods

2.2.1.prepration of Prickly pear extract

The prickly pears had been thoroughly cleaned and washed to remove all contaminants. After separating the pulp from the peel, filter paper, blinder, and centrifuging were used to extract the fruit juice. When the juice dries at 60°C, it solidifies. Weight 0. 1g was dissolved in 100 milliliters of deionized water to create a 1000 parts per milliliter concentration that was used in the AgNP synthesis experiment.

2.2.2.Biosynthesis of silver nanoparticles

Prickly pear extract was added to an aqueous solution containing 200 ppm of AgNO3, and 5 milliliters of PP were mixed with 10 milliliters of AgNO3. The mixture was then continuously stirred for two hours at 60 ˚C to create the silver nanoparticle. The transition from colorless or white to brown signified the formation of silver nanoparticles. the color shift depicted in **Figure 4**. After allowing the resultant solution to cool to room temperature, it was isolated using centrifugation at 11,000 rpm.

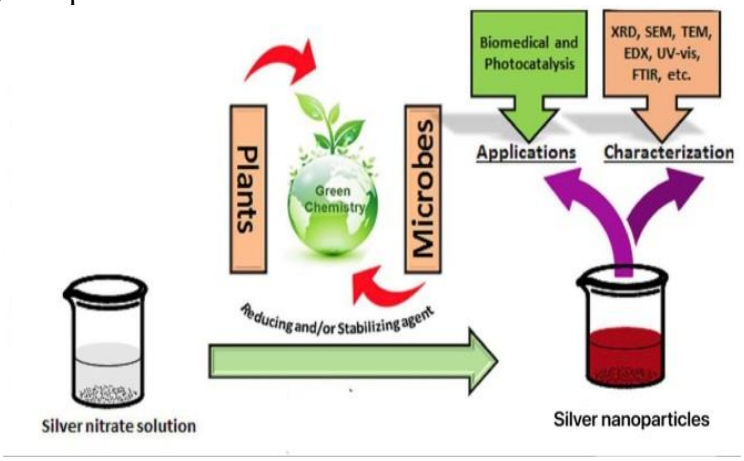

Figure 4. the formation of silver nanoparticles

2.2.3. the silver chloride synthesized

The mixture of 10 milliliters of tap water and 5 milliliters of AgNO3 (400 PPm) produced a white precipitate of AgCl. Ten milliliters of AgCl and five milliliters of DF extract were combined to create an aqueous solution of 1000 parts per million. The mixture was then continuously stirred for three hours at 60 ˚C. The color transitioned from white to grey, signifying the AgClNP formation. After allowing the resultant solution to cool to room temperature, it was isolated using centrifugation at 11,000 rpm.

2.2.3.prepration of eosin stain

Dissolved 1 g of eosin powder stain in 1 liter of deionized water , formation a bright pink solution that we can use it.

2.3. photolysis of eosin dye

Decomposition of Eosin is study alone on sun light radiation as compare of its analysis with AgNPs concentration 198 ppm, AgClNPs concentration 150 ppm , at times 30, 60, 90, 120, 150, 180, 210, 240 min and 10 ml, 10 ppm eosin.

Study the toxicity of degradable substances.

2.4. Hemolysis Assay

The hemolysis test was carried out using the Feuser et al. method [36]. The University of the Extreme South Catarinense's medical ethics committee, located in Criciuma, Brazil, approved the research. Three healthy donors provided the erythrocytes, or red blood cells, used in the study. Blood tubes were placed inside a 3.2 weight percent sodium citrate volume.Centrifugation at 1500 ×g for 10 minutes was used to separate the erythrocytes from the serum. after combining eight milliliters of regular saline solution with four milliliters of whole blood, The erythrocytes

were then washed three times using the saline solution. utilized in Eppendorf tubes. Two milliliters of saline solution were used to dilute the erythrocytes following the final wash. After that, A dilution of 40 µL was added to a brand-new tube that held 960 µL of saline. For five minutes, the tubes were centrifuged at 10,000×g. The precipitate was then transferred to a microtiter plate with 96 wells. A (SpectraMax M3) instrument was used to measure the absorbance at 540 nm. as controls, both positive and negative.970 microliters of distilled and saline water were used to incubate 30 microliters of the erythrocyte suspension [37].

2.2.4.characterisation of Ag-AgClNPs

The following techniques were used to describe Ag-AgClNPs: Using an auto-matched diffraction meter (Shimadzu 6000 XRD). To ascertain the nanoparticles' crystalline size and structure, X-ray diffraction (XRD) was employed, To examine the Ag-AgClNPs solution and determine which functional groups were in the sample, Fourier transform infrared (FTIR) spectroscopy (Shimadzu 8400) was used. The optical properties of the generated Ag-AgClNPs were investigated using an ultraviolet–visible (UV–Vis) spectrophotometer (Shimadzu 1800, Japan). Moreover The Feuser et al. technique was applied when performing the hemolysis assay. As for the concentration, it was measured using an atomic absorption spectrometer (Phoenix 986).

3. Results and discussion

3.1. photolysis of eosin dye

The concentration of eosin dye before photolysis was 10 ppm, The effect of AgNPs and AgClNPs increases the photodegradation of eosin dye as shown in **Table 1** and **Table 2**.

Table 1. the effect of AgNPs on decomposition of eosin dye

Exposure time (min)	Conc of eosin (ppm)	Conc of eosin+AgNps (ppm)
0	10	----
30	8.306	6.985
60	6.009	5.970
90	1.762	1.975
120	1.653	1.475
150	1.321	1.272
180	1.074	1
210	1.034	0.970
240	1.029	0.935

Table 2. the effect of AgClNPs on decomposition of eosin dye

Exposure time (min)	Conc of eosin (ppm)	Conc of eosin+AgClNPs (ppm)
0	10	----
30	8.306	6.762
60	6.009	1.881
90	1.762	1.455

120	1.653	1.128
150	1.321	0.970
180	1.074	0.806
210	1.034	0.747
240	1.029	0.673

3.2. Identification of prepared Ag-AgClNPs

3.2.1. FE-SEM

- **FE-SEM of AgNPs**

To ascertain the form and surface morphology, FESEM was used. As seen in **Figure 5**, Ag have spherical forms with diameters ranging from 10 nm to 30 nm.

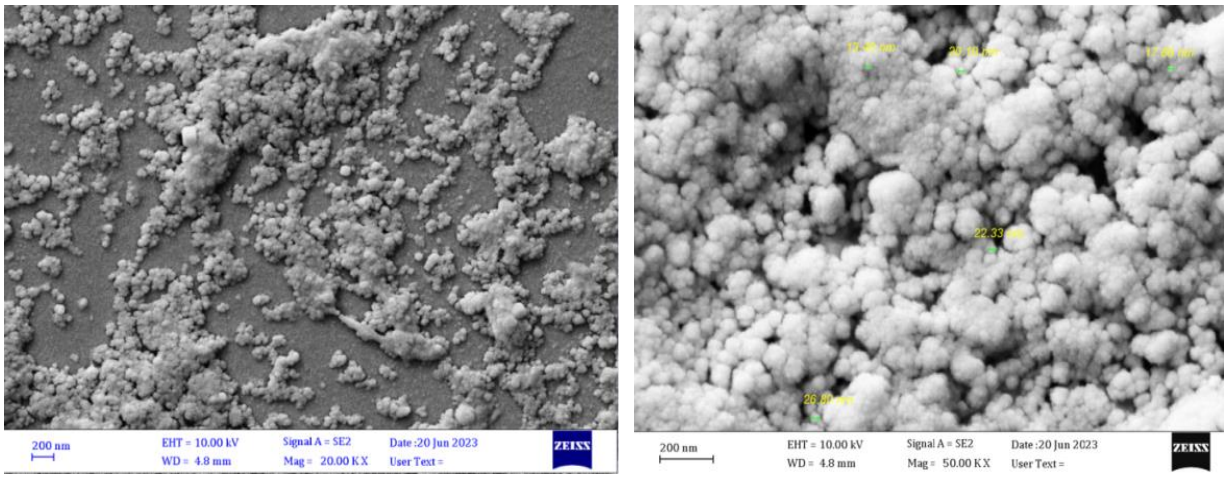

Figure5. SEM of AgNPs

- **FE-SEM of AgClNPs**

AgCl had diameter ranging from 20 nm to 45 nm and cluster of spherical shapes as demonstrated in the FE-SEM image presented in **Figure 6.**

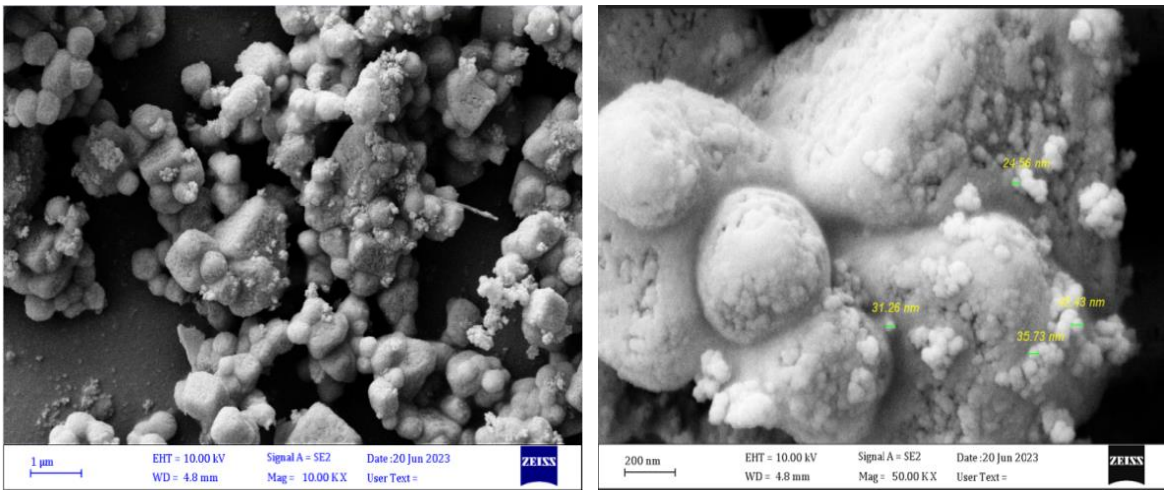

Figure 6. SEM of AgClNPs

3.2.2. FTIR

Eosin stain and AgNPs and eosin stain with AgClNPs were identified as distinct peaks in the FT-IR spectra obtained with the Shimadzu 8400. **Figures 7 and 8** illustrate this.

The band between 3431 and 3463 cm-1 is representative of H-bonded alcohols and phenols, as well as O-H stretching. The peak between 2962 and 2964 cm-1 indicates an O-H stretch in carboxylic acids [38]. The bands at 3425 cm^{-1} and 2362 cm^{-1} in **Figure 8** of the silver chloride nanoparticles indicate the stretching vibration of NH of the primary and secondary amines within the protein molecule [39, 40]. The peak of the carbonyl (C=O) stretching bond was located at 1722–1708 cm^{-1}.[41] N-H bent primary amines are assigned at 1627 cm^{-1}. The peak at 1388 cm^{-1} represents the C-N stretching of the aromatic amine group, and the bands at 1114-1161 and 1053-1045 cm^{-1} represent the C-N stretching of the alcohols, carboxylic acids, ethers, and esters [38].

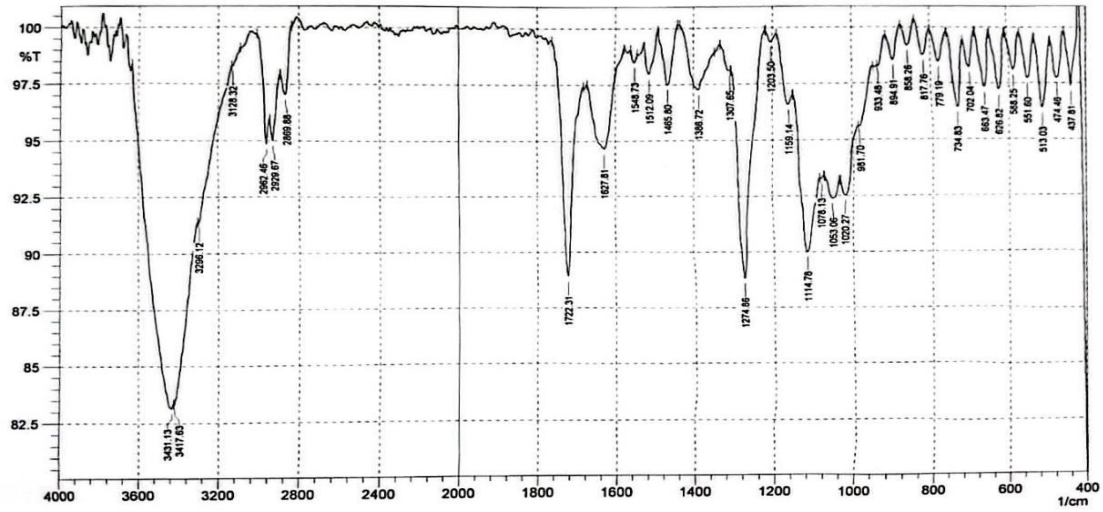

Figure7. FTIR of AgNPs

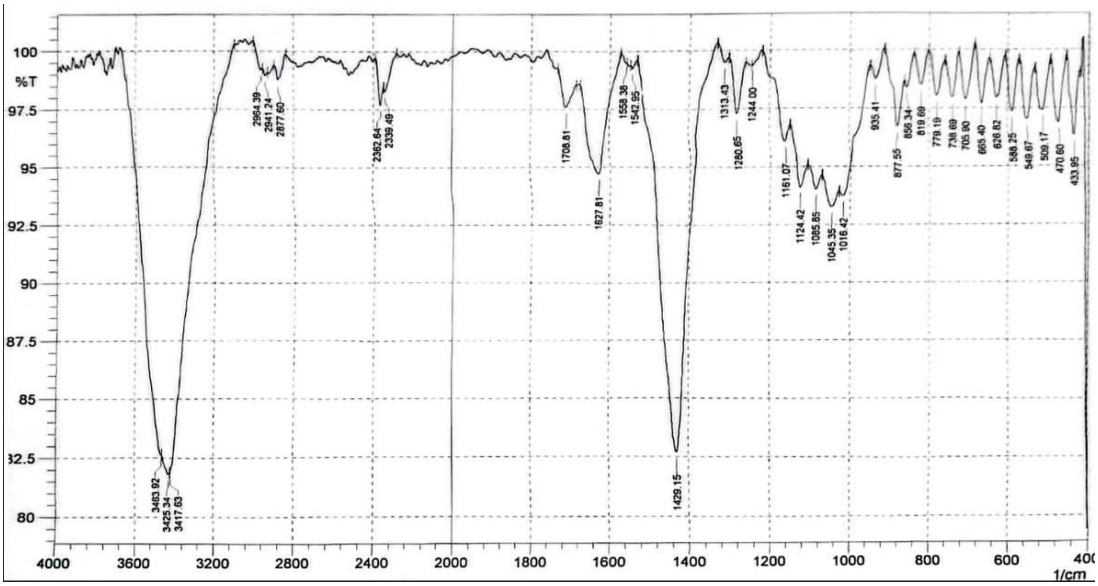

Figure 8. FTIR of AgClNPs

3.2.3. X-Ray diffraction (XRD)

- **XRD of AgNPs**

The synthetic AgNPs' crystal structural phase is estimated using X-ray diffraction. AgNPs' XRD graph is displayed in **Figure 9.** The standard diffraction data for face-centered cubic Ag in JCPDS file No. 04-0783 exactly matches all of the diffraction peaks of the AgNPs [42].
Sharp peaks of 2θ at 27.85, 32.28, 46.26, 67.43, and 76.61, which correspond to the (121), (111), (200), (220), and (331) planes, indicate the formation of pure silver nanoparticles, And the other three peaks of 2θ at 31.79, 54.85 and 57.53 indicates for AgNo3. The product's average crystal size was 49.2 nm as determined by the X-ray diffraction profile.

- **XRD of AgClNPs**

As depicted in **Figure 10.** The (111) and (220) reflection planes for cubic Ag were identified as the source of the distinctive XRD peaks at ♠2θ 36.2° and 69.7° (JCPDS No. 65-2871). Planes (200), (220), (311), (222), (400), (321), and (420) of the cubic phase of AgCl crystal were identified as the source of the distinct and prominent seven peaks at 31.8°, 47.5°, 56.6°, 67.9°, 68.8°, 72.5°, and 76.9° (JCPDS No. 31-1238) [43]. Additional peaks at 2θ 34.4° and 62.8° could be ascribed to impurities, these planes, ♦302 and ♥414, correspond to AgClO2 and Ag2O3. The product's X-ray diffraction profile showed that its average crystal size was 56.82 nm.

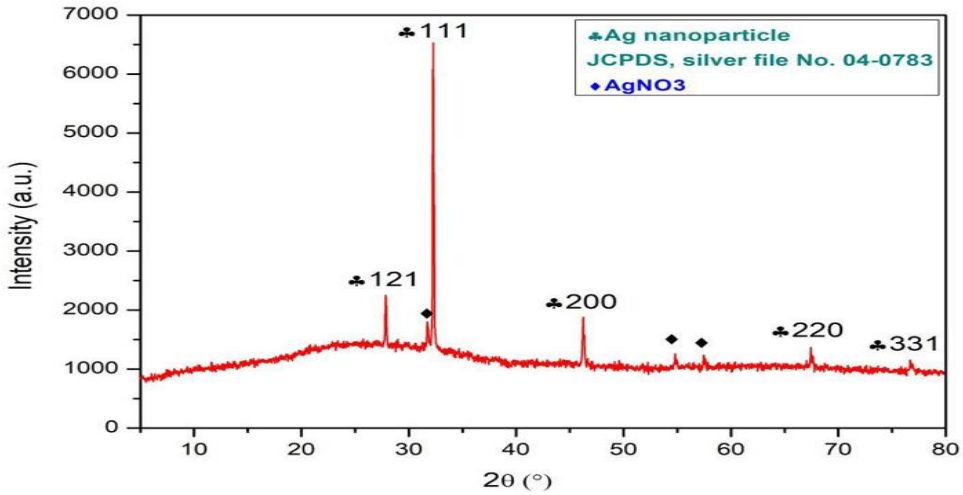

Figure 9. XRD of AgNPs

A useful method for determining crystalline size, lattice strain, and dislocation densities is X-ray diffraction. The following equation provides the Debye-Scherrer's formula, which was used to calculate the average crystalline size of the prepared samples [44].

$$D = \frac{0.9\lambda}{\beta cos\theta} \text{ nm}$$

The Braggs peak's full width at half maximum (FWHM) is given in radians, the X-ray wavelength is k (k = 0.154056 nm for (CuKa), the crystalline size is indicated by D, and the reflection's diffraction angle is h.

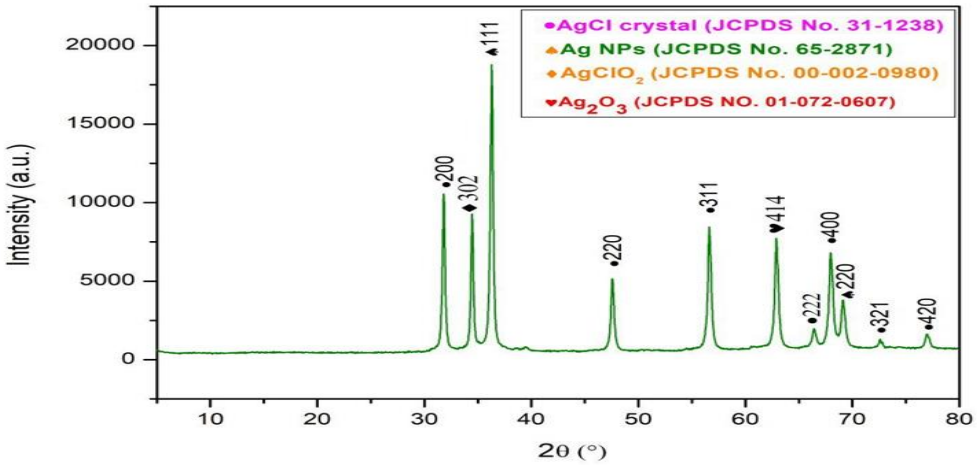

Figure 10. XRD of AgClNPs

3.3.4. UV-Visible spectroscopy

The peak in **Figure 11** at 415 nm indicates the process of producing silver nanoparticles, and the peak in **Figure 12** at 203 nm indicates the creation of silver chloride nanoparticles subject to surface selection. Strong band intensities and peaks below the visible spectrum are characteristics of plasmon resonance (SPR).

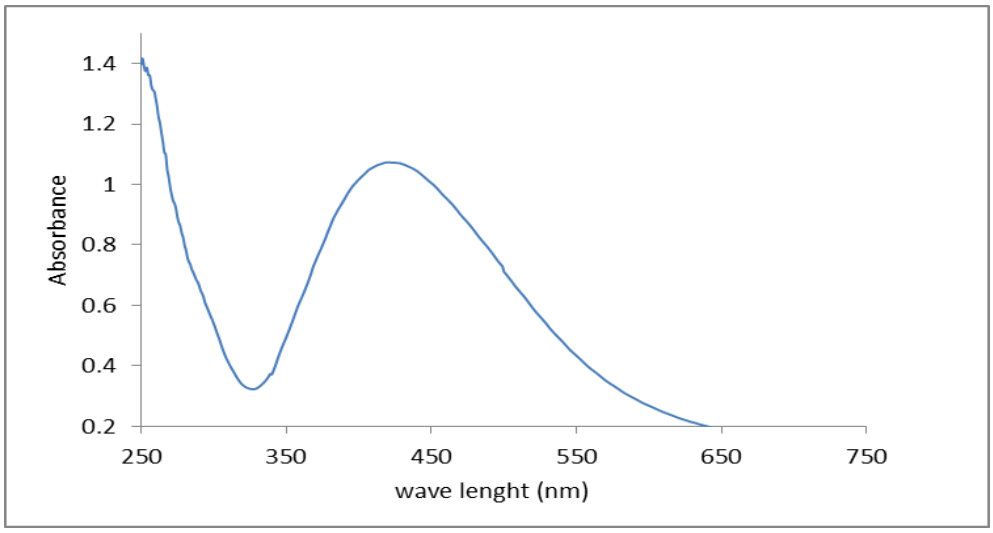

Figure 11. UV-Visible of AgNPs

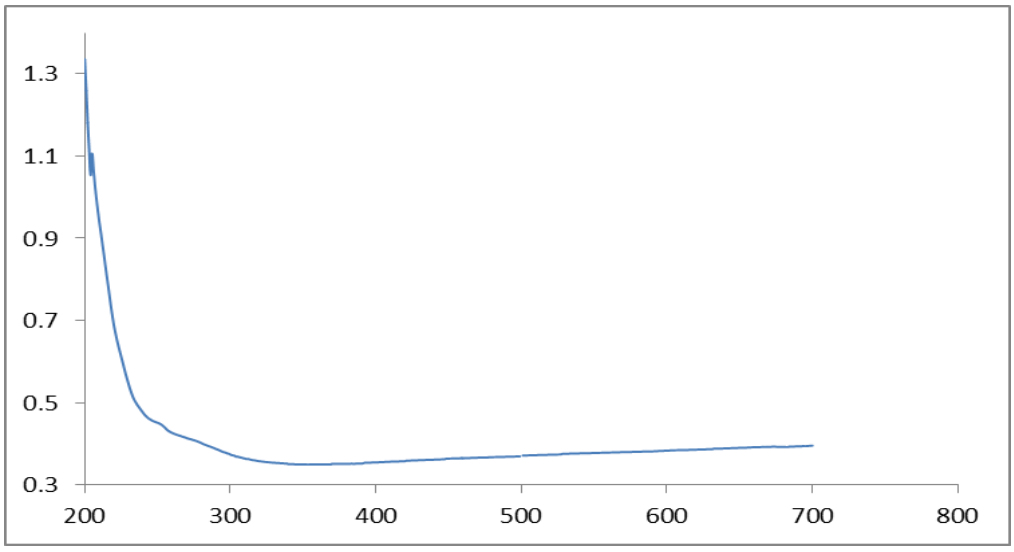

Figure 12. UV-Visible of AgClNPs

3.1.5. Atomic absorption spectroscopy (AAS)

Atomic absorption spectroscoby was conducted to determine the concetration of AgNPs and AgClNPs as shown in **table 3**.

Table 3. concentration of AgNPS and AgClNPs

No.	Name of nanoparticles	Con. (ppm)
1	Silver nanoparticles	198
2	Silver chloride nanoparticles	150

4. Hemolysis assay

The hem compatibility was evaluated using a hemolysis assay. Sunlight radiation was used to treat The human erythrocytes with all degraded material. The standard test method for evaluating the hemolytic properties of nanoparticles (E2524-08) indicates that the percentage of hemolysis is less than 5%. indicates that the human erythrocyte was not harmed by AgNPs and AgClNPs. It is safe to use these nanoparticles.

5. Conclusion

Summarily, it could be seen from the presentation above that Ag-AgClNPs could be biochemically prepared with help of prickly pear fruit extract. The UV-Visible study showed that Ag-AgClNPs have strong visible light absorption and exhibit excellent visible-light-driven photocatalytic performance . This property was utilized in the degradation of eosin dye after exposure to sun light ,So AgCl have more activity than Ag. This biochemical method of synthesizing nanomaterials opens a new gate for the strategies and application of nanoparticles that made academic staff in supporting this type of research technically and academically.

Data availability

There were no data utilized for the study that was the subject of the article.

Acknwoledgement

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Declaration of competing interset

No known competing financial interest or personal relationship could have influenced any of the work reported in this paper, the authors declare.

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