

Comparative Study of the Ethanolic and Aqueous *Avicennia marina* Mangrove Extracts on the Biosynthesis of AgCl@TiO₂ Nanocomposite

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ABSTRACT: The biosynthesis of nanomaterials is an important aspect of nanotechnology due to its cost-effective and eco-friendly procedure. The present study was carried out to fabricate AgCl@TiO₂ nanocomposite using the aqueous and ethanolic leaf extracts of *Avicennia marina* mangrove plant as a reducing and stabilizing agent (RSA). The effect of aqueous and ethanolic leaf extracts with different concentrations on the biosynthesis of AgCl@TiO₂ NanoParticles (NPs) was systematically studied by X-Ray Diffraction (XRD), field emission scanning electron microscopy (FE-SEM), Energy Dispersive Spectroscopy (EDS), UV-visible diffuse reflectance spectroscopy (UV-visible DRS), and Fourier Transform InfraRed (FT-IR) spectrometer. The results illustrated the successful synthesis of AgCl@TiO₂ nanocomposite without any impurity phase using the aqueous extract. AgCl NPs were uniformly distributed on the surface of TiO₂. The absorption intensity of AgCl@TiO₂ with a band gap energy of 2.95 was improved both in the UV and VL region and displayed stronger absorption compared with pure TiO₂. FT-IR analysis confirmed that the biosynthesized AgCl@TiO₂ by using aqueous leaf extract was not just an easy physical mixture of Ag and TiO₂ species but it was a molecular-level combining of Ti–O and Ag–O domains in the nanocomposite.

KEYWORDS: Biosynthesis, AgCl@TiO₂; Nanocomposite; *Avicennia marina*; Aqueous extract.

INTRODUCTION

The chemical methods for the production of NanoParticles (NPs) are expensive and hazardous to the environment. There is a growing effort to develop alternative cost-effective and eco-friendly methods for the synthesis of NPs [1-5]. Biosynthesis of NPs using bacteria, fungi, yeast, algae, and plant extracts has more advantages over chemical methods as it is an environmentally benign process, cost-effective, and has the ability of large-scale production over chemical methods [1,2,4-6]. The usage

of plants for the fabrication of NPs could also be suitably scaled up due to the high availability of them [1,2,5,6]. Plants, in the synthesis of NPs, could act as the Reducing and Stabilizing Agent (RSA) [1,2,5,6]. It is revealed that the fresh *Avicennia marina* plant extract contains many biologically active components, such as alkaloids, phenolics, terpenes, flavonoids, carbohydrates, proteins that could be used as RSA to synthesis metal NPs such as silver [1,2,5,6]. The main aspect of current nanotechnology

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research is the development of a reliable green process for the synthesis of metal NPs [7].

Titanium dioxide (TiO₂) and TiO₂-based nanocomposites as photocatalysts have received high attention [5,8-19] due to their unique properties such as non-toxicity, chemical stability, and photostability [5,20,21]. TiO₂ has been used in removing different kinds of organic pollutants such as toxic organic molecules and bacteria from water [5,9-11,13,14,21]. The energy band gap of TiO₂ is relatively high (3.2 eV), and high energy UV irradiation is needed to excite it. The high rate of electron-hole recombination on TiO₂ particles also has made it a low efficient catalyst. Many studies have investigated the photocatalytic activity improvement of TiO₂ by extending the light absorption range from UV to Visible Light (VL) through doping or depositing noble metals [5, 11, 13, 21, 22]. Noble metals could effectively enhance the photocatalytic activity of TiO₂ by decreasing the recombination of photogenerated electron-hole pairs [5, 11, 21, 22]. In this regard, Zhou et al. [23] prepared Ag/AgCl/TiO₂ nanocomposite. Yu et al. [24] reported that the Ag/AgCl on the TiO₂ significantly enhanced the photoactivity and stability under the VL region during the degradation of methyl orange. Zhang et al. [11] studied the effect of Ag/AgCl on the photoactivity of TiO₂ in the VL region. They found out that as-produced nanocomposites had high photoactivity in the VL region to disinfect *Escherichia coli* bacterium. Liu et al. [25] fabricated Ag@AgCl doped TiO₂/sepiolite nanocomposites and showed that the nanocomposite was highly efficient for photodegradation of Methylene Blue under VL. In all these studies, the chemical approach has been performed to synthesize Ag/AgCl@TiO₂ (NPs).

Previous studies reported that extracting solvents significantly influenced the amount of biologically active components of plant extracts, such as alkaloids, phenolics, terpenes, flavonoids, and total phenolic, and consequently led to different applications of them [26-32]. Some studies reported that non-polar solvents were the best for the extraction of active substances while some others reported that alcohol is the best polar solvent for the extraction of active substances from plants. On the other hand, a lot of studies used water as an extracting solvent for the extraction of active substances from plants. There are a lot of studies reporting that the antioxidant, antibacterial, antimalarial and anticancer activities of the plant extracts significantly

depend on the extracting solvents [26-32]. Plant extracts are widely used in different NPs synthesis processes [1, 2, 5, 20, 33-38] so, a systematic investigation comparing the effect of different extracting solvents on the biosynthesis of NPs from plant extracts is important. In the present study, the effect of aqueous and ethanolic extracts of *Avicennia marina* mangrove plant on the biosynthesis of AgCl@TiO₂ nanocomposite was systematically investigated using different characterization techniques. This study seems the first report on the comparative study of the effect of extracting solvents on the novel green biosynthesis method of NPs, here AgCl@TiO₂ as a plasmonic nanocomposite.

EXPERIMENTAL SECTION

Mangrove leaf extraction

Fresh leaves of *Avicennia marina*, a mangrove plant, were collected from the Azini wetland, Hormozgan province in southern Iran. They were thoroughly washed with tap water to remove the adhering salts and other pollutants and finally with double distilled water. The cleaned fresh leaves were shade-dried at ambient temperature for 2 weeks. Dried leaves were powdered by a mixer grinder.

For Ethanolic Extract (EE), powdered leaves and absolute ethanol (C₂H₅OH, Merck) were mixed with a 1:3 weight ratio. The solution was incubated for 24 h at ambient temperature in the dark. Then, the extract was filtered with Whatman No. 1 filter paper. The solvent was then evaporated under a vacuum by a rotary evaporator. The obtained ethanolic leaf extract was dried in an oven at 60°C and then stored in a freezer for further use.

The Aqueous Extract (AE) was obtained according to the procedure reported in our previous study [20]. Typically, powdered leaves and deionized water were mixed with a 1:3 weight ratio and boiled at 100°C for 10 min. After that, the mixture was cooled down and filtered by Whatman No. 1 filter paper. The resulting AE was dried in an oven at 60°C overnight and then stored in a refrigerator at 4°C for further experiments.

Biosynthesis of AgCl/TiO₂ nanocomposite using ethanolic/aqueous leaf extract

The biosynthesis condition is summarized in Table 1. The appropriate amount of dried leaf extract was separately solved in 50 mL of deionized water and then,

Table 1: The initial experimental condition for biosynthesis of samples.

Sample	AE (g)	EE (g)	Extract/AgNO ₃ ratio (R)	AgNO ₃ /TEOT ratio	Crystallite size (nm)
S1	0.07	0	0	0	23.6
S2	0	0.07	0	0	17.0
S3	0.07	0	3.5	0.02	15.7
S4	0.14	0	7	0.02	14.4
S5	0	0.07	3.5	0.02	27.2
S6	0	0.14	7	0.02	9.3

the solution was stirred at 80°C. Then, 7.5mL Tetraethylorthotitanate (TEOT, C₈H₂₀O₄Ti, Merck) was added dropwise to the solution and stirred at 80°C for 30 min. After that, the appropriate amount of silver nitrate (AgNO₃, Merck) was added to the solution under stirring at 50°C for 2 h. Finally, the solution containing the produced NPs was centrifuged (Model: SIGMA 2-16P) at 12,000 rpm, for 20 min, dried at 70°C in an oven overnight, and calcined at 400°C for 5 h.

Characterization of AgCl/TiO₂ nanocomposite

Phase identification and crystal structures of the samples were studied by X-Ray diffraction (PANalytical, X' Pert pro, Netherland) with Cu K α radiation at 40 keV. To study the size and morphology of the synthesized NPs, a Field Emission Scanning Electron Microscopy (FE-SEM) device (TESCAN MIRA3, USA) was used. The band gaps of the prepared samples were calculated based on the measurement of the absorbance spectra of samples obtained using a UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) instrument (Shimadzu, UV-2250, Japan). Bioactive functional groups present in the extract of *A. marina* responsible for the synthesis of NPs and the chemical composition of samples were investigated using a Fourier Transform-Infrared (FT-IR) spectrophotometer (PerkinElmer, Spectrum TWO, USA). The elemental analysis of the synthesized nanocomposite was done by X-Ray Fluorescence (XRF, Oxford Instruments, ED 2000, UK).

RESULTS AND DISCUSSIONS

XRD analysis

The XRD patterns of pure TiO₂ and AgCl@TiO₂ nanocomposite with different Extract/AgNO₃ ratios (R) are shown in Fig. 1. The diffraction patterns of S1 and S2 reveal the formation of the pure anatase phase of TiO₂.

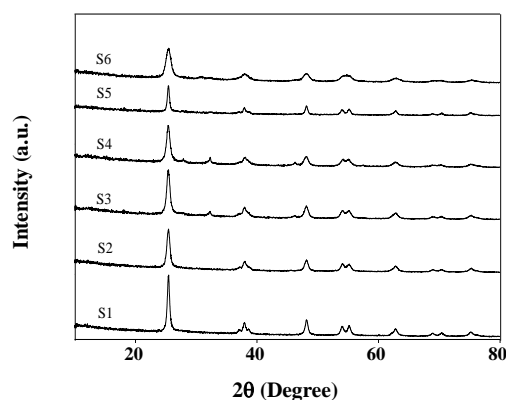


Fig. 1: The XRD patterns of pure TiO₂ and AgCl@TiO₂ nanocomposite with different extract/AgNO₃ ratios.

The strong diffraction peaks at 2 θ equal to 25.32°, 36.99°, 37.79°, 38.58°, 48.05°, 53.96°, 55.08°, 62.69°, 68.762° and 70.287° correspond to the crystal planes of [1 0 1], [1 0 3], [0 0 4], [1 1 2], [2 0 0], [1 0 5], [2 1 1], [2 0 4], [1 1 6] and [2 2 0], respectively [5, 11, 21]. Diffraction peaks corresponding to the AgCl were not identified for S1 and S2 because RSA was absent. When AE of *A. marina* was used as an RSA, S3 and S4 showed new diffraction peaks besides the diffraction peaks of the TiO₂ anatase phase.

These new peaks appeared at 2 θ equal to 27.84°, 32.26°, 46.26°, 54.85°, 57.52°, 67.5°, 74.5°, and 76.8° which were corresponded to the [1 1 1], [2 0 0], [2 2 0], [3 1 1], [2 2 2], [4 0 0], [3 3 1], and [4 2 0] reflections of cubic phase of AgCl [5, 11, 21] on the surface of TiO₂. The diffraction peaks of AgCl gently increased by increasing the R, indicating that the AE, like RSA, is necessary to produce silver species during nanocomposites preparation. Increasing the R-value from 3.5 to 7 increased the AgCl content, by reducing more Ag⁺ and supplying more Cl source. Impurity peaks were not observed in AgCl@TiO₂ nanocomposite diffraction peaks and the AgCl and TiO₂

anatase phases were only identified in products. Therefore, AgCl@TiO₂ nanocomposites were successfully biosynthesized using AE of *A. marina* without adding any chlorine source.

The effect of EE was also investigated with the same R values of AE. XRD patterns of products illustrated that diffraction peaks of AgCl were not observed in the XRD patterns of S5 and S6. This indicated that the amount of Ag species was too low or/and the size of it was too small to be detected by XRD. The results were in line with previous studies. *Vélez et al.* [39] studied the synthesis of silver NPs by reduction of Ag⁺ ions using aqueous or ethanolic Aloe vera extracts as RSA. They reported that the silver NPs obtained using EE had smaller sizes compared with the silver NPs obtained from AE. The difference also might be attributed to the aqueous nature of the initial synthesis solution for the biosynthesis of samples with water as the solvent. Therefore, the nature of biologically active components of AE was stable in the presence of water in the initial synthesis solution.

About the effect of EE, further, observation revealed that some diffraction peaks of TiO₂ in S6 were decreased compared with S5 suggesting that high EE would affect the crystallinity of TiO₂. This revealed that plant extract could influence the crystallinity and also the phase of TiO₂. This was in line with previous studies that reported the synthesis of a different phase of TiO₂ or combined phases of TiO₂ including anatase and rutile phase using different plant extracts [40-44].

The crystallite size of samples was calculated using the Scherrer equation (Eq. (1)).

$$D = \frac{k \lambda}{\beta \cos \theta} \quad (1)$$

Where *D* is the average size of the crystals, *K* is a dimensionless value (it is a constant approximately equal to 0.9), λ is the X-ray wavelength, β is the Full Width at Half-Maximum peak intensity (FWHM), and θ is the Bragg angle. The calculated results showed that the products in this study were Nano-crystalline. By comparing S3 with S4 which were synthesized using AE, and S5 with S6 which were synthesized by EE (Table 1), the results indicated that the crystallite size decreased with increasing the extract/AgNO₃ ratio, which would be due to more nucleation at high ratio compared with the low value of it. At a high extract/AgNO₃ ratio, by increasing the extract

amount as RSA, more Ti⁴⁺ and Ag⁺ species were reduced and more nucleation occurred. The nucleation and crystal growth process play important roles in controlling the crystal size of the NPs. The nucleation is the first stage of the formation of NPs that is generated from nuclei. Nucleation occurs and grows with the aggregation of molecules or ions to the final stable size particles. It is well known that the particle size could be controlled by nucleation and growth procedure of NPs [45-49]. Many studies found out that by increasing the nucleation and its period, the final particle size of NPs [45-49] decreased. Keshmiri and Troczynski reported that the ultra-fine TiO₂ NPs could be obtained by more nucleation through supersaturation phenomena producing monodispersed particles [47]. In the present study, the crystallite size decreased with increasing the extract/AgNO₃ ratio and consequently increasing the extract amount as RSA. By increasing the RSA, more Ti⁴⁺ and Ag⁺ species were reduced and more nucleation occurred. As it was mentioned by previous studies [45-49], more nucleation would decrease the final particle size of NPs. Therefore, the obtained results were in line with previous studies [45-49] as it was expected that the crystallite size of products would be decreased by increasing the extract/AgNO₃ ratio.

FE-SEM analysis

To investigate the size and morphology of the synthesized NPs, FE-SEM studies were performed. Figs. 2a and b show the nanoparticles-aggregated particles of S1 (pure TiO₂) with homogeneous shape and size. Comparing the FE-SEM images of S3 and S4 with S1 (Fig. 2), the particle diameter of S3 and S4 was increased as AgCl was loaded on TiO₂, indicating that with enhancing R values, the size of nanocomposites increased. Larger particles of AgCl@TiO₂ appeared when R was at a high value of 7. The existence of more AE at an R-value of 7 accelerated the formation of TiO₂ and Ag species. By increasing the RSA, more Ag⁺ species were reduced and more nucleation occurred. Therefore, more AgCl was loaded on the surface of TiO₂ and the particle size of nanoparticles-aggregated spheres nanocomposite (S3 and S4) increased compared with the pure TiO₂ (S1). The same observation was reported previously by *Ghasemi et al.* [5] and *Zhang et al.* [21]. They found out that the particle size diameter of TiO₂ increased after loading Ag-AgX (X = Cl, Br) on the surface of pure TiO₂ producing nanoparticle-

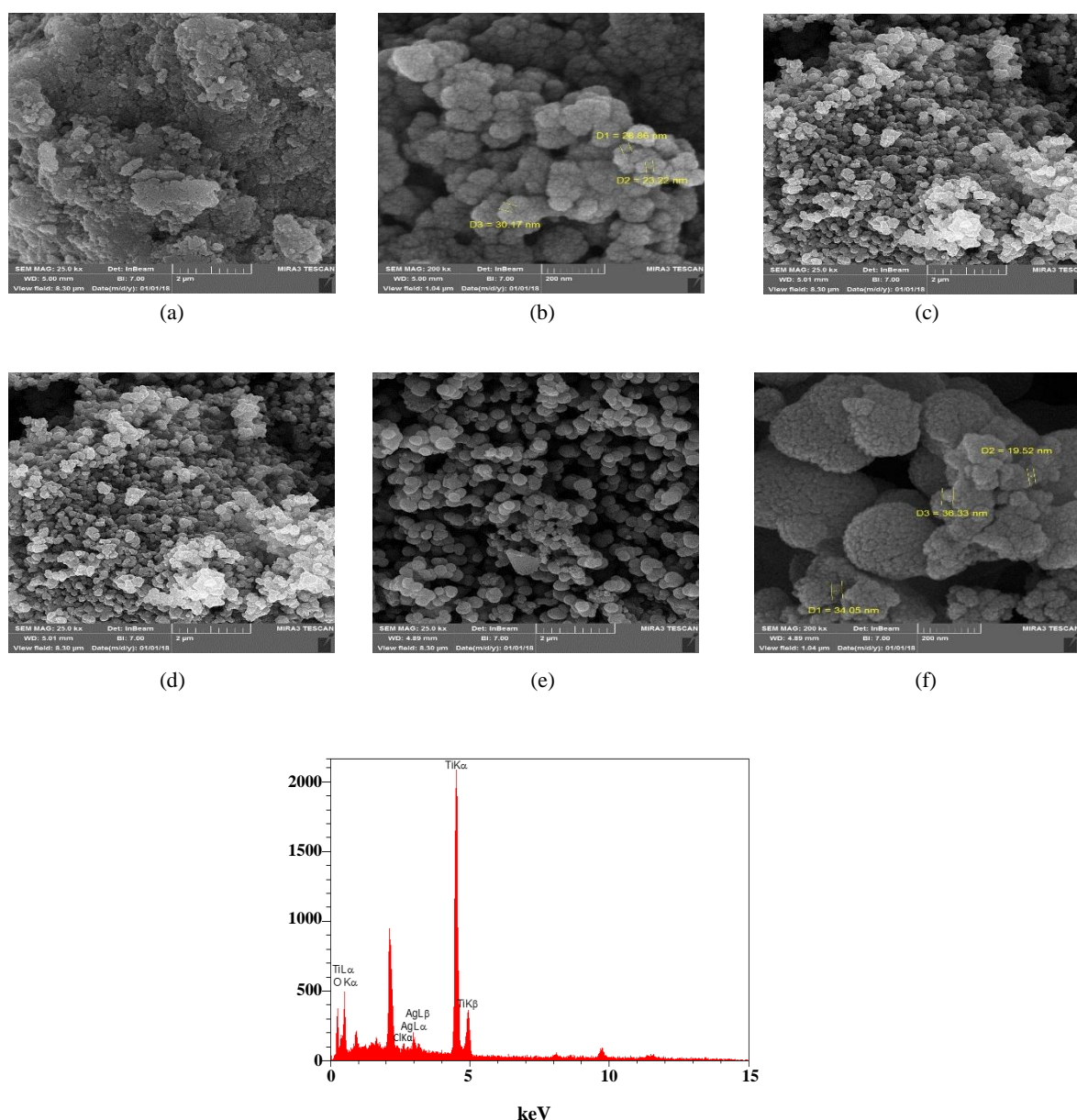


Fig. 2: The FE-SEM images of (a and b) S1, (c and d) S3, (e and f) S4, and (g) EDX of S4.

aggregated Ag–AgX (X = Cl, Br)@TiO₂ microspheres nanocomposite.

The structure of the TiO₂ NPs was not affected by loading AgCl on the surface of TiO₂ and the morphology of S3, S4, and S1 (pure TiO₂) were similar. Results revealed that AgCl species have been uniformly distributed on the surface of TiO₂ NPs. The weight percentage of Ti, O, Ag, and Cl elements of S4 according to Energy-Dispersive X-ray Spectroscopy (EDS) analysis (Fig. 2g) was 33.73, 62.65, 2.51, and 1.10, respectively.

UV-Vis DRS analysis

The different optical and chemical compositions of TiO₂ and biosynthesized AgCl@TiO₂ came from loading AgCl on the surface of the pure TiO₂ influencing the band gap and optical properties of final biosynthesized AgCl@TiO₂. Therefore, there was a need to investigate and compare the optical properties of biosynthesized AgCl@TiO₂ with a pure TiO₂. Among S1–S6 and according to the XRD patterns of products, diffraction peaks of AgCl just were observed in the XRD patterns of S3 and S4. Therefore, S4

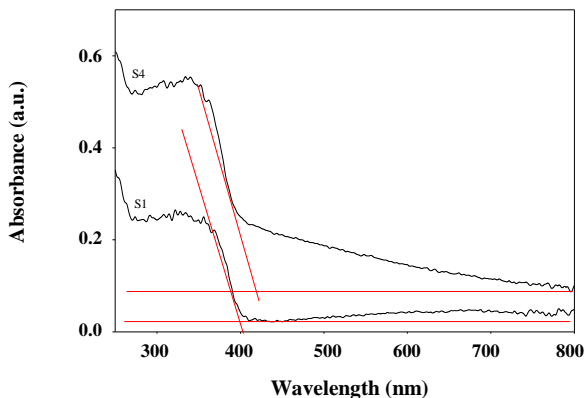


Fig. 3: The UV-Vis DRS spectra of S1 and S4.

as biosynthesized AgCl@TiO₂ by AE of *Avicennia marina* with better characteristic peaks on XRD pattern was selected for other analyses, and S1 was selected as pure TiO₂ to be compared with biosynthesized AgCl@TiO₂ (S4) because the AE of *Avicennia marina* was used for S1 similar to S4. The absorption edge of pure TiO₂ NPs (S1) and S4 was at 399 and 420 nm. As can be seen in Fig. 3, the absorption intensity of biosynthesized AgCl@TiO₂ was boosted both in the UV and VL region and displayed stronger absorption compared with the UV-Vis DRS spectra of pure TiO₂ (S1). This could be due to the surface plasmonic resonance of loaded AgCl on TiO₂ that significantly influenced the light absorption of S4. The band gap energy of S1 and S4 samples was calculated by Eq. (2) [50].

$$\text{Band gap energy (E)} = \frac{hC}{\lambda} \quad (2)$$

Where h is Planks constant and equal to 6.626×10^{-34} Joules sec, C is the speed of light and equal to 3.0×10^8 meter/sec, λ is the cut-off wavelength in meter scale. The cut-off wavelength was the intersection point with the wavelength axis on the absorbance spectra and tangent edge [5, 51, 52]. As the absorption edge is 399 and 420 nm for S1 and S4, the band gap energy of them was calculated to be 3.12 and 2.95 eV, respectively. The decrease of the band gap of biosynthesized AgCl@TiO₂ compared with the pure TiO₂ could be due to the surface plasmonic resonance of loaded AgCl on the surface of TiO₂ that significantly influenced the light absorption of it.

FT-IR analysis

Fig. 4 shows the FT-IR spectra of biosynthesized pure TiO₂ (S1) and AgCl@TiO₂ (S4) NPs. FT-IR spectra show an absorption band at about 3428.34 cm^{-1} which was attributed to H-bonded hydroxyl stretching due to the water adsorbed on the surface of products [36,53,54] and/or the phenols (O-H group) of phenolic compound in the plant extract [55]. The band at 2345.53 cm^{-1} was related to ammonium ion absorption frequency N-H stretch [5, 56]. The band at 1625.47 cm^{-1} was due to the presence of alkene group C=C stretch and amine I, II NH band [56]. The biosynthesized samples also showed the presence of bands due to aromatic rings (1508.05 cm^{-1}), Aliphatic fluoro compounds absorption frequency C-F stretch (1127.04 cm^{-1}), Aliphatic chlorine compounds absorption frequency C-CL (734.90 cm^{-1}), carbonyl group absorption frequency (2059.85 cm^{-1}), aromatic rings absorption frequency C=C-C stretch and methylene C-H (1459.86 cm^{-1}), and aliphatic group (996.88 cm^{-1}). The band at 1084.16 cm^{-1} was due to the presence of amine I, C-N stretch [5,6,56]. FT-IR spectra illustrated the presence of reducing agents of metal ions in the extract such as polyphenols, flavones, and terpenoids [5,6,56,57]. The mentioned reducing agents are proved to have a good potential activity to convert the aldehyde groups to carboxylic acids in the metal ions. The presence of the enzymes was also confirmed by the presence of amide groups in samples. Enzymes could play a role as RSA in the biosynthesis of the metal ions [5,6].

The stretching vibration of Ti-O-T (T=Ti or Ag) was observed as broadband from 859 to 1087 cm^{-1} . The peaks beneath 810 cm^{-1} are ascribed to the stretching vibrations of Me-O bonds like O-T-O or T-O (T=Ti or Ag) [9, 51]. The typical stretching vibrations bands of Ti-O were observed in the range of 543 - 616 cm^{-1} [58]. The band at 531 was ascribed to the Ti-O-Ti/Ti-O framework vibration [59]. In S4, by loading Ag species on TiO₂, the Ti-O-Ti/Ti-O stretching bands shifted to lower wavenumbers.

The band ascribed to the presence of Ag species was identified at 562 - 575 cm^{-1} by Adamczyk and Rokita [58]. As the Me-O stretching vibrations bands, Ti-O-Ti vibration overlapped with Ag-O stretching [9,51]. The shifting and disappearance of stretching bands at 500 - 1140 cm^{-1} in the FT-IR spectrum of S4 compared with that of S1 illustrated that S4 is not just a simple physical mixture of Ag and TiO₂ species and confirmed

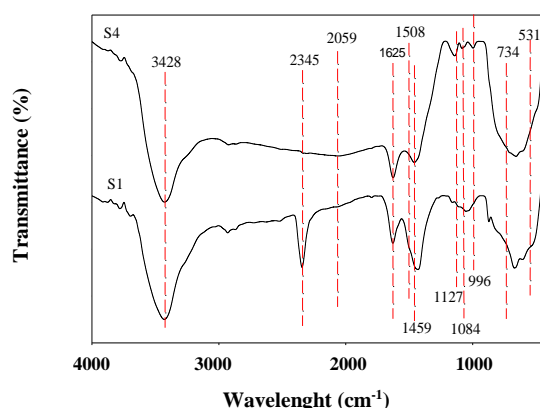


Fig. 4: The FT-IR spectra of S1 and S4.

the molecular-level combining of Ti–O and Ag–O domains in the nanocomposite [58]. The weight percentage of Ti, Ag, and Cl of S4 was 44.2, 10.9, and 1.02, respectively based on XRF analysis.

The leaf extract was used as an RSA and as a chlorine source, and AgCl@TiO₂ was successfully biosynthesized without adding any extra chlorine source during the whole green synthesis process. Chlorinated aliphatic compounds (C–Cl) in the extract which were confirmed by FT-IR analysis would be responsible for the synthesis of AgCl in the structure of AgCl@TiO₂ nanocomposite. It could be a benefit and merit of *A. marina* extract that can be used for the green synthesis of valuable AgCl@TiO₂ nanocomposite without using any extra chlorine source.

CONCLUSIONS

In this study, the comparative effects of different kinds of extracts (aqueous and ethanolic) and different concentrations of extracts were investigated on the biosynthesis of AgCl@TiO₂ NPs. AgCl@TiO₂ nanocomposite was successfully synthesized using *A. marina* AE. XRD results illustrated the presence of AgCl and TiO₂ phases without any impurity in the synthesized samples using AE. XRD confirmed that the extract was necessary for the biosynthesis of AgCl@TiO₂ NPs and with increasing R-value from 3.5 to 7, the AgCl content of products increased, by reducing more Ag⁺ and supplying more Cl sources. FE-SEM images showed that the biosynthesized nanocomposite had a spherical shape. It also revealed that Ag species were uniformly distributed on the surface of TiO₂. The results illustrated that the *A. marina* aqueous leaf extract had the potential to

biosynthesize AgCl@TiO₂ nanocomposite with a band gap energy of 2.95 and enhanced light absorption in the UV and VL region by combining Ag–O and Ti–O domains at the molecular level. Therefore, the use of *A. marina* mangrove plants for the biosynthesis of NPs could be suitably scaled up due to their high availability.

Conflict of Interest

There is no conflict of interest in the publication of this article.

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