

Original Research Paper

Synthesis and Characterization of Eco-Engineered Ternary Iron-Clay-Silver Nanocomposites: A Novel Multifunctional Material

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Abstract

This aim of this study was to develop and characterize a novel ternary clay nanocomposite (TCN) comprising iron nanoparticles, clay, and silver nanoparticles, synthesized through an eco-friendly approach using *Carica papaya* leaf extract as a reducing agent. This eco-engineered nanocomposite was synthesized via a facile and environmentally friendly route using *Carica papaya* leaf extract as reducing agent by leveraging the principles of green chemistry. The nanocomposite's structural, morphological and compositional properties were thoroughly investigated using analytical techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS); Brunauer-Emmett-Teller (BET) and Fourier transform infrared spectroscopy (FTIR). The results revealed a homogeneous distribution of silver and iron nanoparticles within the clay matrix with a mean particle size of 33.5 nm, indicating a strong interfacial interaction between the components. The nanocomposite exhibited high surface area, distinctive morphology, dispersion and functional properties, making it a promising candidate for various sustainable applications, such as wastewater treatment, biomedical devices and environmental remediation. This study demonstrates a significant advancement in the design, synthesis and characterization of multifunctional nanomaterials with promising potentials.

Keywords: novel multifunctional material, clay, silver nanoparticle, iron nanoparticles, eco-engineering

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1. Introduction

Nanotechnology has become a global topic of interest with significant potential for several applications and has undergone significant development in recent times. It deals with the design, synthesis and manipulation of materials on a scale between 1 - 100 nm (Laurent *et al.*, 2010). The significant development of this emerging technology has opened up researches into novel and eco-friendly synthetic routes as well as increased application due to its unique properties like particle size, great surface – to – volume ratio, biocompatibility and stability (Khan *et al.*, 2020), etc. There are different types of nanomaterials (nanoparticles, nanocomposites, carbon nanotubes, graphenes, fullerenes, etc.) as reported by Obadimu *et al.* (2024). Nanocomposite refers to multiphase materials with nanoscale addition in one of the phases (Al–Mutairi *et al.*, 2022). It consists of at least two components made up of continuous matrix and non-continuous reinforcement phases giving rise to combined features of the two materials for improved application (Hassan *et al.*, 2021). Nanoparticles can be engineered into nanocomposites with organic or inorganic materials, with resulting biological, optical, magnetic, adsorptive (Adebayo *et al.*, 2019), mechanical, thermal, or solvent-resistant (Hassan *et al.*, 2021) properties for specifically

tailored applications. Nanocomposites, being heterogeneous in nature can be either binary (two material components) or ternary (three material components). Binary nanocomposites have received wide research attention (Li *et al.*, 2017; Obadimu *et al.* 2024) while the research into ternary composites is still in the early stages and more studies are needed to improve their properties and widen applications (Oluwafemi *et al.*, 2021). Two primary approaches are often available for nanocomposite synthesis; the physical or chemical techniques (which use organic/inorganic reducing agents or electrochemical and physicochemical reducing methods), or the biological synthetic method (Jacob *et al.*, 2022).

Biogenic synthesis of nanocomposites entails synthesis through biological processes utilizing organisms such as bacteria, fungi or plants (Sidhu et al., 2022). Previous studies show that biological entities like yeast (Mandal et al., 2006), algae (Madhavi et al., 2013), fungi (Yehia and Al – Sheikh, 2014), bacteria (Kianpour et al., 2017) and higher plants (Iravani et al., 2016; Herlekar et al., 2014) are good source of reducing, stabilizing and capping agents for biosynthesis of clean, eco - friendly, sustainable and stable nanocomposites. Synthesis of nanocomposites from biological organisms like fungi and bacteria (microbe-based synthesis) is costly and time - consuming whereas synthesis from plant materials do not require expensive and extensive procedures (Nahari et al., 2022). The biogenic synthetic method has numerous advantages over the conventional synthetic methods such as simplicity of synthesis (one-pot synthetic route), elimination of the use of harsh, toxic or expensive chemical substances, high reduction potential, stability and minimum environmental impact (Ohiduzzaman et al., 2024). Plant extracts have been extensively used in biogenic synthesis due to its biodiversity and the numerous secondary metabolites (alkaloids, flavonoids, saponins, tannins, etc.) (Enin et al., 2023) in different plant parts (seeds, roots, stems, leaves, flowers and barks) (Enin et al., 2021) which act as reducing, stabilization and capping agents during the synthesis (Sidhu et al., 2022 and Shaibu et al., 2022). Successful preparation of ternary nanocomposites using conventional physical and chemical methods have been reported by Manikandan et al. (2022), they carried out a biogenic synthesis of TiO₂/ZrO₂/SiO₂ ternary nanocomposite using plant extract.

Carica papaya which belongs to the family Caricaceae is well known for its various nutritional and health benefits. The fruit and leaf extract exhibit antioxidant and antimicrobial properties while their extracts can be used to treat diabetes, indigestion and even for curing open wounds. Biomolecules like caffeic acid, chlorogenic acid, kaempferol, quercitin, carpaine, choline, etc. present in *Carica papaya* are responsible for their reducing, capping and stabilizing properties, making it possible for the formation of nanocomposites (Jacob *et al.*, 2022). Jahangir *et al.* (2023), Alam (2022) and Konjari *et al.* (2015) conducted studies on the use of *Carica papaya* in biogenic synthesis of nanoparticles and nanocomposites leveraging on the abundance of biomolecules in this plant. Also, Mude *et al.* (2009) reported spherical and rod-like shapes and 30 nm size of silver nanoparticles using callus extract of *Carica papaya*. Similar works on the use of *Carica papaya* in the biosynthesis of nanomaterials are presented in **Table 1**. This study aims to develop novel ternary metal nanocomposite materials through biogenic synthesis, providing an environmentally friendly, sustainable and easy one–pot synthetic route, to enhance its importance for various applications.

S/N	Plant Part	Nanoparticle	Biomolecules responsible for reduction	Morphological features	References
1	Leaves	AgNPs	Proteins, Carbonyl compounds	Helical shape, no aggregation	Swapna <i>et al.</i> (2022)
2	Leaves	Fe2O3 NPs	Phenolic compounds, carboxylic acid, secondary alcohols	Crystalline, non- uniform, agglomerated, 21.59 nm in size	Bhuiyan <i>et al.</i> (2020)
3	Shell extract	TiO2 NPs	Phenolics	Crystalline, superficial morphology, spherical shape	Saka et al. (2022)

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Table 1. Continued

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4	Leaves	AgNPs	Phenolic compounds	Crystalline, face-centred cubic structure	Potdar <i>et al.</i> (2022)
5	Peel	AgNPs	Proteins, phenolic compounds	28 nm in size, face- centred cubic structure	Kokila <i>et al.</i> (2016)
6	Leaves	Fe2O3 NPs	Proteins, alcohols, phenolic compounds	Crystalline, 43 nm in size, agglomerated, spherical shape	Usha <i>et al</i> . (2022)
7	Leaves	AgNPs	Alcohols, phenolic compounds, amino acids	Crystalline, face-centred cubic structure, spherical shape, 25 – 50 nm size	Konjari <i>et al.</i> (2015)
8	Callus, Seed, Leaf, juice, peel	AgNPs		Nanorods, triangular shapes, agglomerated, polydispersed, < 100 nm size.	Jahangir <i>et al.</i> (2023)
9	Peel	Iron – doped ZnO NPs		Crystalline, spherical shape, 20.4 nm size	Al-Odayni and Abduh,(2023)
10	Leaves	AgNPs	Alcohols, phenolic compounds	Crystalline, spherical shape, face-centred cubic structure, 5 – 50 nm size	Banala <i>et al.</i> (2015)
11	Leaves	Cu – Ag NPs	Phenols, polyphenols, amino acids, proteins, carbohydrates	Polycrystalline, spherical shape, 20 – 50 nm size	Jacob <i>et al.</i> (2022)
12	Peel	AgNPs	Carboxylic acids, proteins, phenolic acids	Spherical shape, uniform distribution, 15 – 20 nm size	Balavijayalakshmi & Ramalakshmi, (2017)
13	Fruit	AgNPs	Ascorbic acid, phenolic compounds	Well dispersed, 35 – 50 nm size	Firdaus <i>et al.</i> (2017)
14	Leaves	AgNPs	Phenolics, carbohydrates		Patel & Singh, (2020)
15	Leaves	AgNPs		Crystalline, Spherical, 40.8 nm size Rod – like	Syafiuddin <i>et al.</i> (2017)
16	Peel	AgNPs		morphology, crystalline, 70 – 95 nm size	John <i>et al.</i> (2021)

2. Materials and Methods

2.1 Materials

The chemicals for the bench work were analytical grade (AR) reagents, hence, no further purification requirements. These include; silver trioxonitrate V (AgNO₃; 99.80% purity; by Merck, Germany), Iron (III) chloride (FeCl₃; 99% purity; Sigma – Aldrich, U.S.A) and Hydrochloric acid (HCl; 37% purity; Riedel – deHaen, U.S.A.). Other materials include *Carica papaya* (pawpaw) leaves, distilled water and natural clay.

2.2 Collection of Carica papaya Leaf and Extract Preparation

Fresh leaves of *Carica papaya* were collected from Uyo, Akwa Ibom State, Nigeria and identified by a taxonomist from the University of Uyo, Nigeria as shown in **Figures 1a** and **b**. The leaves were thoroughly washed with distilled water to remove impurities and air–dried to remove moisture before crushing into a fine powder

(Kormal & Anya, 2013). A 5.0 g of the leaf was weighed and boiled with 100 mL of distilled water for about 20 minutes at 70 °C and cooled at room temperature. The broth was separated from the leaves by filtration and the pure extract was refrigerated before synthesis (Jacob *et al.*, 2022).



Figure 1. (a) Carica papaya tree and (b) Carica papaya leaves

2.3 Phytochemical Screening

Phytochemical screening of the *Carica papaya* leaves extract was done according to standard procedures, reported by Dubale *et al.* (2023). The presence of different phytochemicals were assessed by colour change or precipitate formation (Swapna *et al.*, 2022).

2.4 Collection and Preparation of Clay material

The natural clay sample used in this study was sourced from Ikot Ebom Itam, Itu, Akwa Ibom State, Nigeria. It was washed, dried, pulverized and soaked in HCl for purification and separation of impurities for four hours (Hu *et al.*, 2022). The soaked clay sample was washed with several times with distilled water, dried and pulverized before being used for the biosynthesis of the TCN.

2.5 Synthesis of Ternary Nanocomposite

The TCN was prepared in a similar method as described by Balachandar *et al.* (2019) and Magdalane *et al.* (2016). A 5.0 g each of the pulverized clay was washed, aged for 2 days and stirred for 6 hours with a 30 mL solution of the precursor (1 mM FeCl₃) and 30 mL of AgNO₃ to form slurry. About 100 mL of the *Carica papaya* leaves extract was then added to the slurry, stirred for 24 hours, allowed to age for 48 hours until a brown colour was observed before filtration. The residue was dried in an oven at 30 °C for 24 hours to form a cake and finally crushed into fine powder.

2.6 Characterization of the Ternary Clay Nanocomposite (TCN)

The absorbance spectra of the synthesized TCN was obtained using UV – visible spectroscopy while surface morphology as well as size and shape were determined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) respectively. Also, surface and porousity characteristics, elemental composition as well as the crystallinity were determined using BET, EDX and XRD respectively. The Fourier – Transform infrared (FTIR) spectroscopy analysis was carried out using Nicolet 370 FT-IR spectrometer obtained at a transmittance mode operated at resolution of 2 cm⁻¹ from 4000 cm⁻¹

3. Results and Discussion

3.1 Physicochemical Analysis

Qualitative phytochemical screening of the *Carica papaya* leaves extract as represented in **Table 2** showed that phytochemicals like alkaloids, flavonoids, glycosides, saponins and tannins are responsible for the reduction of the metal precursors and subsequent stabilization of the ternary nanocomposite. This result is in agreement with the result of phytochemical screening of *Carica papaya* by Nandi *et al.* (2020) and Nduche *et al.* (2019).

S/N	Phytochemical	Test	Result
1	Alkaloids Mayer's Test		+
		Iodine Test	+
2	Anthraquinones	Borntrager's Test	-
3	Flavonoids	Shinoda Test	+
4	Glycosides	Salkowski's Test	+
5	Phenolics	Lead acetate Test	+
		Iodine Test	+
6	Saponins	Frothing test	+
7	Tannins	Ferric chloride Test	+
		Braymer's Test	+

Table 2. Phytochemical screening of Carica papaya leaves extract

(-) Indicates absence (+) indicates presence

3.2 Surface plasmon resonance of TCN

The spectra of clay shows minimal absorption around 250 nm while that of the synthesized TCN shows enhanced absorption peaked around 350 nm and 450 nm for iron and silver nanoparticles respectively in the clay matrix depicted in **Figures 2a** and **b**. This highlights how incorporating nanoparticles like silver and iron into clay materials significantly alters their optical properties, enhancing their absorption in specific regions of the UV-visible spectrum.



Figure 2: Uv-vis spectra of (a) natural clay (b) TCN

3.3 Surface morphology, shape and particle size of TCN

The SEM images of the clay and ternary (Fe – Clay – Silver) nanocomposite prepared from the leaves extract of Carica papya are shown in **Figures 3a** and **b** respectively. The TEM image of the ternary nanocomposite is presented in **Figure 3c** while the particle distribution is in **Figure 3d**. An improved morphology was seen when comparing the SEM images of the natural clay and the TCN. The natural clay shows extensive agglomeration of the particles in a lumpy form while the particles of the TCN were found to be well dispersed with minimal aggregation basically due to the capping and stabilization by the biomolecules from the extract. The slight aggregation is due to the iron–based magnetic interactions as reported by Bhuiyan *et al.* (2020) and agglomeration of clay particles, which is typical in nanocomposites due to strong Van der Waals forces between the clay layers (Jacob *et al.*, 2022). Similarly, the particles exhibit an irregular, granular structure with a non-uniform size distribution as supported by the TEM image. The TEM micro-graph in **Figure 3d**, shows the grains and grain boundaries oriented in different plane outlines indicating the polycrystallinity of the TCN with an average particle size of 33.5 nm. The Light region in the TEM images indicates the porosity of the TCN.

the grains appear darker than others due to diffraction contrast as a result of the different orientations of the particles. These observations are in agreement with the findings of Aswiri *et al.* (2024) and, Mohamad & Hawar, (2022). The possibility of the TCN having more than one geometric shape is primarily due to the different bioactive components in the extract (Obadimu *et al.*, 2024). **Figure 3d** shows the particle size distribution of a TCN, where the majority of particles fall within the 30 - 40 nm range, indicating a narrow distribution that may result from precise synthesis conditions.

3.4 FTIR Analysis

Molecular vibrations were studied using FTIR spectra as presented in **Figure 4a** and **b** for clay and TCN respectively and used to identify the interaction of functional groups in biomolecules with the precursors and clay material in other to evaluate the efficacy of the synthesis and stabilization of TCN. The spectrum for natural clay in **Figure 4a** shows major absorption peaks at 3693.71 cm⁻¹, 3622.34 cm⁻¹, 1625.04 cm⁻¹, 1093.64 cm⁻¹ and 910.40 cm⁻¹. Peaks 3693.71 cm⁻¹ and 3622.34 cm⁻¹ represent –OH vibrations typical of clay while absorption at 1625.04 cm⁻¹ indicates possible adsorbed water on the clay material (Rezender *et al.*, 2018). Peaks at 1093.64 cm⁻¹ and 910.40 cm⁻¹ represent Si – O in-plane stretching and Al – OH – Al bending vibrations of the clay material respectively. This is in agreement with the previous submissions of Oguz *et al.* (2016) and Rezender *et al.* (2018). The spectrum of the TCN in **Figure 4b** shows sharp and intense bands at 3428.81 cm⁻¹, 2921.63 cm⁻¹, 2852.20 cm⁻¹, 1681.62 cm⁻¹, 1384.6 cm⁻¹, 1047 cm⁻¹, 790 cm⁻¹ and 694 cm⁻¹ aside from the ones observed in the clay material. The prominent peaks of TCN are highlighted in **Table 3** depicting the influence of different phytochemicals from the *Carica papaya* extract on the TCN functionalities (Nandini *et al.*, 2020).



Figure 3. (a) SEM image of natural clay mineral (b) SEM image of synthesized TCN (c) TEM image of TCN (d) particle size distribution of TCN



Figure 4. FTIR Spectra of (a) natural clay (b) TCN

3.5 EDX Analysis

The elemental analysis of the clay and the TCN using energy dispersive X – ray spectroscopy is as shown by the spectra in **Figure 5a** and **b**. The EDX spectrum of natural clay (fig.3 a) shows the dominant elements; silicon (Si), oxygen (O) and aluminum (Al). Silicon (40.2%) and aluminum (26.1%) are key constituents of aluminosilicate minerals (quartz, kaolinite and montmorillonite), which form the structural basis of the clay material and is consistent with result of Sabbagh *et al.* (2019). The high silicon content confirms the presence of silica (SiO2), a primary component of clays and other silicate-based materials. Oxygen and aluminum in the clay sample indicates the presence of oxide compounds, particularly silicates and aluminates. This finding supports the identification of the sample as clay, specifically in the form of aluminum silicates such as kaolinite or montmorillonite. These compounds are common in natural clays and contribute to the material's thermal stability, plasticity and ion-exchange properties (Singh *et al.*, 2019; Irabor & Unuigbe, 2023). The spectrum shows no significant impurities, suggesting that the sample is a relatively pure form of aluminosilicate clay. The spectrum of the synthesized TCN using *Carica papaya* leaf extract (**Figure 5b**) highlights the presence of silicon (Si), oxygen

(O), aluminum (Al) as typical constituents of the clay matrix, silver (Ag) and iron (Fe) from the bio-synthesized silver and iron nanoparticles in the TCN. The presence of carbon (C) is due to organic components from the *Carica papaya* leaf extract or carbon-based compounds formed during the synthesis process.

S/N	Observed Peak	Functional Groups	References
	(cm ⁻¹)		
1	3428	-OH stretching vibration of alcohols and	Banala et al. (2015)
		phenols	
2	2921	-CH stretching vibrations of alkyls	Jacob <i>et al.</i> (2022)
3	2852	-CH stretching vibrations of alkyls	Datkhile et al. (2023)
4	1681	-C=C stretching of aromatic functional	Manikandan et al. (2022)
		group	
5	1384	-CN stretch of amines	Balavijayalakshim et al.
			(2017)
6	1047	-C-OH stretching vibration	Mahalingam et al. (2023)
7	790	-CH out - of - plane bending vibrations of	Ullah et al.,
		aromatic phenols	(2024)
8	694	-CX weak vibration of alkyl halides	Alghthaymi et al. (2021)

Table 3. Functional groups observed from FTIR analysis of TCN



Figure 5. EDX spectra of (a) Clay and (b) TCN

3.6 Phase purity and Crystallinity of TCN

The XRD diffractogram of the clay and TCN, **Figures 6a** and **b** as compared with the reflection patterns of the Joint Committee on Powder Diffraction Standards (JCPDS) card no. 04-0783 and 06–0696 reveals key information about its mineralogical composition and crystallinity. The most prominent peak, occurring around 25° (2 θ), is characteristic of quartz (SiO₂) with high intensity suggesting that quartz is a major phase in the sample. Other smaller peaks between 5° and 10° (2 θ) may indicate the presence of montmorillonite or illite, which are typical clay minerals. Montmorillonite, in particular, often shows peaks in this region due to its layered, expandable structure. Additional peaks observed around 12° (2 θ) are likely attributed to kaolinite, it is known for its characteristic peaks at both 12° and 25° (2 θ) as also seen in the result of Obot *et al.* (2021) and Shaibu *et al.* (2022).

The TCN diffractogram in **Figure 5b**, shows significant peaks at around 38.1° (20) and 44.1° (20) corresponding to the (111) and (200) planes of face-centered cubic (FCC) silver (Ag), clearly visible while a peak observed near 44.7° (20), corresponds to the (110) plane of body-centered cubic (BCC) α -Fe (zerovalent iron). However, the peak at 35.5° (20) corresponds to the (311) reflection of magnetite (Fe₃O₄), indicating partial oxidation of the iron nanoparticles (Dadashi *et al.*, 2015; Shaibu *et al.*, 2014).



Figure 6: XRD diffractogram of (a) clay and (b) TCN

3.7 Surface Area Determination

BET Analysis was done to determine the surface characteristics like surface area, pore size and pore volume and the result is presented in **Figure 7**. The plain clay has a surface area of 44.23 m²/g, a pore volume of 0.1032 cm³/g and a pore size of 91.177 Å typical for natural clays. The iron-clay-silver ternary composite exhibits significant changes, with a surface area of 112.03 m²/g, a pore volume of 0.3208 cm³/g and a pore size of 182.004 Å. This sharp increase in surface area and pore volume highlights the synergistic effects of incorporating both iron and silver into the clay, resulting in improved performance in applications requiring high surface area and porosity.



Figure 7: N2 adsorption desorption plot of clay and TCN

4. Conclusion

The synthesis of ternary clay nanocomposite using *Carica papaya* leaves extract, metal precursors and clay as the matrix material was successfully carried out as confirmed by the extensive characterization results. Biological compounds like alkaloids, flavanoids, phenolics, saponins and tannins were found to be present in the extract and perform the roles of reduction, capping and stabilization. The nanocomposite was composed of well-dispersed silver and iron nanoparticles over the clay matrix, which was made up of major quartz, kaolinite and montmorillonite minerals. Further characterization of the synthesized TCN revealed its highly crystalline nature with excellent surface characteristics like surface area, pore volume and pore size. The combination of these materials has offered enhanced properties, such as optical and improved adsorption efficiency, due to the synergistic effects of both silver and iron nanoparticles. The TCN therefore has great potential for various applications, especially in environmental remediation owing to its simple and cost-effective synthesis method and excellent properties.

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