Sustainability, Agri, Food and Environmental Research, (ISSN: 0719-3726), 12(2), 2024:
http://dx.doi.org/10.7770/safer-V13N1-art541

A characteristic approach on the synthesis of agro-based nanomaterials and their ability as metal sorbents

Un enfoque característico sobre la síntesis de nanomateriales de base agrícola y su capacidad como sorbentes metálicos

Muthulakshmi Andal N [1*], Preethi G [2], Gohulavani G [3] & Charulatha S [4]

1, 2, 4 - Department of Chemistry, PSGR Krishnammal College for Women, Coimbatore - 641004, Tamil Nadu, India.
3- Department of Chemistry, Ethiraj College for Women, Chennai- 600 008

[*]Author for correspondence: muthulakshmiandal@psgrkcw.ac.in

ABSTRACT

The present study deals with the development of biodegradable/ bio-renewable/ biocompatible nanocomposites functionalized from agro-waste materials (Modified/ Activated) for the removal of environmentally fabricated toxicants. Agro- waste materials: *Azaridachta indica* Nut shell (AINS) and *Prosopis juliflora* barks (PJB) are identified based on their availability, minimal cost and highly effective towards industrial effluents. Two nanocomposites (NCs) are prepared through i) chemical modification (Hydroxyapatite) and ii) Ball Milling (Tungsten Carbide balls). The modified and synthesized NCs are characterized via Fourier Transform, Infra-red Spectroscopy (FTIR), Atomic Force Microscope (AFM) and Scanning Electron Microscope (SEM). The engineered nanocomposites have been effectively employed for removal of Cu(II) / Ni(II) ions and compared with their native precursors through batch equilibration method.

KEYWORDS: biodegradable, agro- waste, toxicants, nanocomposites, characterization

RESUMEN

El presente estudio se ocupa del desarrollo de nanocompuestos biodegradables / bio-renovables / biocompatibles funcionalizados a partir de materiales de residuos agrícolas (Modificados / Activados) para la eliminación de tóxicos fabricados ambientalmente. Materiales de desecho agrícola: La cáscara de nuez de Azaridachta indica (AINS) y la corteza de Prosopis juliflora (PJB) se identifican en función de su disponibilidad, costo mínimo y alta efectividad para efluentes industriales. Se preparan dos nanocomposites (NC) mediante i) modificación química (hidroxiapatita) y ii) molienda de bolas (bolas de carburo de tungsteno). Los NC modificados y sintetizados se caracterizan mediante transformada de Fourier, espectroscopia infrarroja (FTIR), microscopio de fuerza atómica (AFM) y microscopio electrónico de barrido (SEM). Los nanocompuestos diseñados se han empleado eficazmente para la eliminación de iones Cu (II) / Ni (II) y se han comparado con sus precursores nativos mediante el método de equilibrio por lotes.

Palabras Clave: biodegradable, agro-residuos, tóxicos, nanocompuestos, caracterización

INTRODUCTION

Environment and its compartments have been severely polluted by industrial effluents viz., heavy metals, dyes, fertilizers, sewage wastewaters, pesticides etc., which are highly lethal even in trivial amounts (Cook, 2008). Water pollution is an appalling problem, powerful enough, towards the deterioration of the environment (Gambhir et al., 2017). Heavy metal ion have become an ecotoxicological hazard of prime interest and increasing significance, because of their accumulation in living organisms. These ions cause acute chest pain, dizziness, headache, cyanosis, diarrhoea and even death (Madhava Rao et al., 2008). Effluents discharged from dyeing industries are highly colored / toxic to aquatic life. It is estimated that 10–15% of the dyes employed in the textile processing, enter the effluent streams (Garg et al., 2003). On oral consumption, ill effects like toxic methaemoglobin, anemia and cyanosis are caused. In humans, skin contact results in allergic dermatitis. Oral feeding or intraperitoneal and intratesticular administration of dyes in animals produce testicular lesions due to which the seminiferous tubules suffer damage leading to the reduction in the production of spermatogenesis rate (Tiwari, 2012). Excess occurrence of anionic species such as nitrite, nitrate, phosphate, chloride, fluoride and sulphate in water bodies leads to eutrophication resulting in algal bloom and oxygen depletion, in turn causing skin irritation, gastrointestinal illness or neurological damages. Therefore, trapping of these toxic pollutants from their specific outlets is a great challenge for which many methods have been reported.

Adsorption has emerged as a prominent technique for wastewater treatment and is a practical method for bulk separation. Advantages of adsorption techniques include i) toxicants' removal at very low concentrations ii) system operation over a broad pH range (2 -9) iii) simple design and easy operation offer iv) effluent discharge concentrations as per Government regulations. It is adopted as a single stage treatment for pollutants' removal due to its high efficiency by which a substance is transferred from liquid phase to solid surface, further, circumscribed by physical and chemical interactions.

Recently, many studies are focused on the improvisation of this method by modification of low cost/ no cost materials which are categorized as follows

- **i)** Natural minerals and other similar minerals (coal, peat, clays, perlite, red mud) (Zhang et al., 2014)
- **ii)** Industrial wastes (fly ash, furnace slag, bio-gas slurry) (Belgin Bayat, 2002)
- **iii)** Agricultural wastes (coconut shell, soya cake, orange peel, rice husk, hazelnut shell and sometimes their carbonized products) (Pandey et al., 2015)
- **iv)** Animal litters (dung, bones, teeth or their activates) (Rattan et al., 2008)
- **v)** Aquatic debris (algae, molluscs, weeds, chitin - chitosan) (Abdulkarim al., 2014)

Rapid development in nanotechnology has aroused great interest in environmental remediation. Several research studies are being focused on using nanomaterials/ nanocomposites in the sequestration of toxic species from polluted waters. Nanocomposites (NCs) have been reported to exhibit outstanding properties viz., reactivity, high surface area, dispersing ability in aqueous solutions, which significantly differ from their bulk scale counterparts (Laokul et al., 2011).

In this context, two agro based – no cost materials i.e., *Azaridachta indica* Nut Shell (AINS) and *Prosopis juliflora* barks (PJB) have been identified, from which their nanocomposites are synthesized, employing novel methods which in turn enhance their sorptive characteristics against the pollutants.

MATERIALS AND METHODS

Preparation of Treated AINS / NAINSC:

Neem tree, referred as *Azaridachta indica* belongs to family Maliceae, native of India. Neem fruit have hard inner core called nut shells (AINS) shown in Figure 1. These seeds collected from fertilizer manufacturing units in Coimbatore, Tamil Nadu, India. AINS was thoroughly washed with doubly distilled water to remove the impurities, sun dried for a week, powdered using electrical mixer and sieved into 85BSS (0.18 mm) mesh size. The sieved materials were subjected to boiling with 0.1N HCl/ NaOH for 3 hours separately (Saygidger et al., 2005). The boiled materials was soaked in distilled water for 12 hours to enhance swelling property, in turn increase sorption sites for binding. Further, the soaked materials was filtered, dried at 100^{o}C, stored in air tight containers and labeled as TAINS (Figure 2).

Figure 1: AINS

Figure 2: TAINS

A one step co-precipitation method was adopted to prepare the nano hydroxyapatite (Li et al., 2005). Equal amounts of $(NH_4)H_2PO_4$ and $Ca(NO_3)_2$ were mixed, followed by the addition of liquor NH_3 to the contents, until the formation of white nano hydroxyapatite has occurred. As the pH value of the obtained hydroxyapatite was 9, repeated washing with doubly distilled water (DDW), ensured the reduction of pH to neutral condition and air dried. The dried nano powder was then mixed with 0.18mm TAINS in 1:1 ratio and labeled as Nano hydroxyapatite *Azaridachta indica* Nut Shell Composite (NAINSC) (Figure 3).

Figure 3: NAINSC

Preparation of Treated / Activated PJB:

Prosopis juliflora Barks (PJB) belongs to shrub/ small tree of *Fabaceae* family. These barks were collected from Somanur, Coimbatore, cleaned to remove the dirt and dust particles using DDW, sun dried for 12 days, pulverized using stainless steel electrical mixer, further categorized using Scientific Test Molecular sieves, manufactured by JAYANT Scientific Instruments Co., Mumbai. The sieved materials were acid/ base treated, similar to the nut shells. The treated PJB is labeled as TPJB.

Nano particles of TPJB were prepared using Planetary Ball Mill (Model – VBCC /PM/24-13/14). 20 grams of the material were taken in Tungsten carbide (WC) grinding jar along with WC balls and proceeded with the grinding process for continuous 3 hrs with a maintenance of 260 revolutions per minute. Resulting nano- size material is thereafter mentioned as NTPJB. Images of the raw material, its treated and nano size counterparts are depicted in figures 4, 5 and 6.

Figure 4*:* PJB

Figure 5: TPJB

Figure 6: NTPJB

RESULTS AND DISCUSSION

Precursors (TAINS and TPJB) and derived nanocomposites (NAINSC/ NTPJB) were characterized employing advanced techniques viz., FTIR, AFM & SEM.

FTIR Spectra Analysis

FT-IR spectra of TAINS and NAINSC measured using Shimadzu 8400S FT-IR spectrometer are depicted in figures 7 and 8. Appearance of a broad peak for TAINS at 600 cm^{-1} is exhibited as a sharp, deepen peak for NAINSC, confirming the addition of phosphate group in the latter due to the formation of hydroxyapatite. Similarly, peak shift 1249 cm^{-1} (Figure 7) to 1032cm^{-1} (Figure 8) imply the participation of C=O stretching during the synthesis. Also, disappearance of peaks corresponding to 1736 cm^{-1}, 1508 cm^{-1} and 1327 cm^{-1} with respect to C=O stretching, N-O stretching and O-H bending in Figure 8 revealed the binding of TAINS hydroxyapatite.

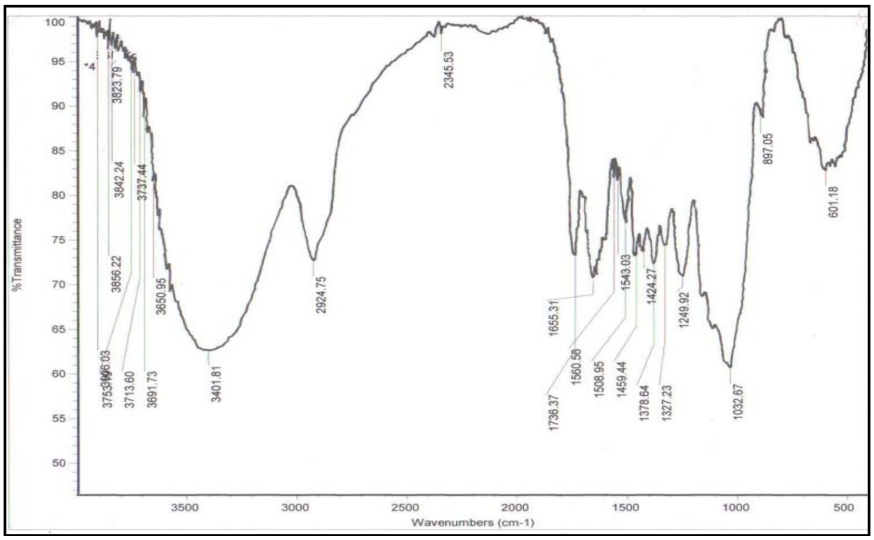

Figure 7: FT-IR Spectra - TAINS

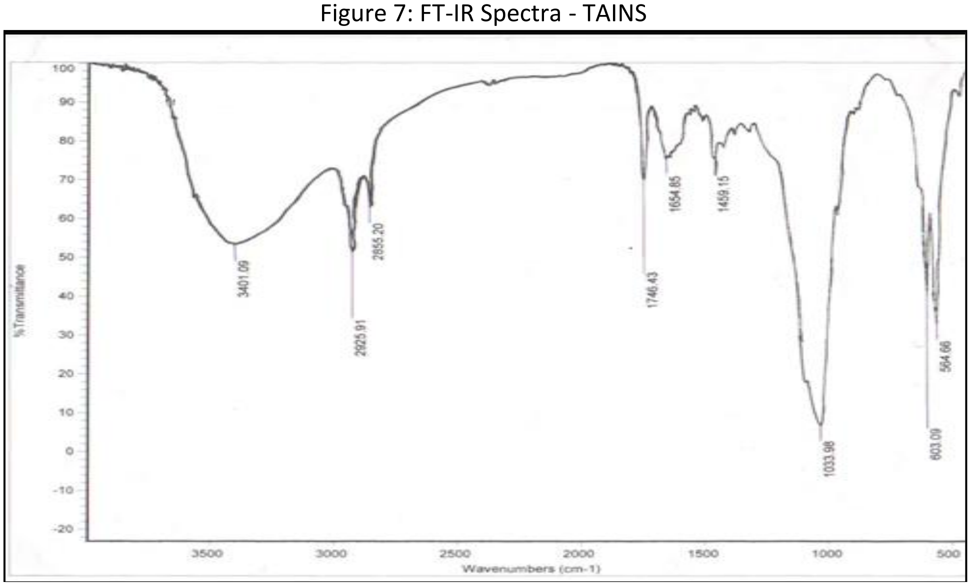

Figure 8: FT-IR Spectra – NAINSC

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Atomic Force Microscopic Analysis:

Individual particle and group of particles can be resolved finer using Atomic Force Microscopic (AFM) NTMDT INTEGRA PRIMA) model compared to microscopic techniques. The synthesized nanocomposites (NAINSC, NTPJB) were analyzed for the confirmation of their nano sizes, the histogram of which is represented in figures 9 & 10. Surface topographic images in 3D patterns (Figures 11 & 12) clearly exhibit sharp peak resolutions, which are reflected as 17.1 nm for NAINSC and 9 nm for NTPJB respectively in the histograms.

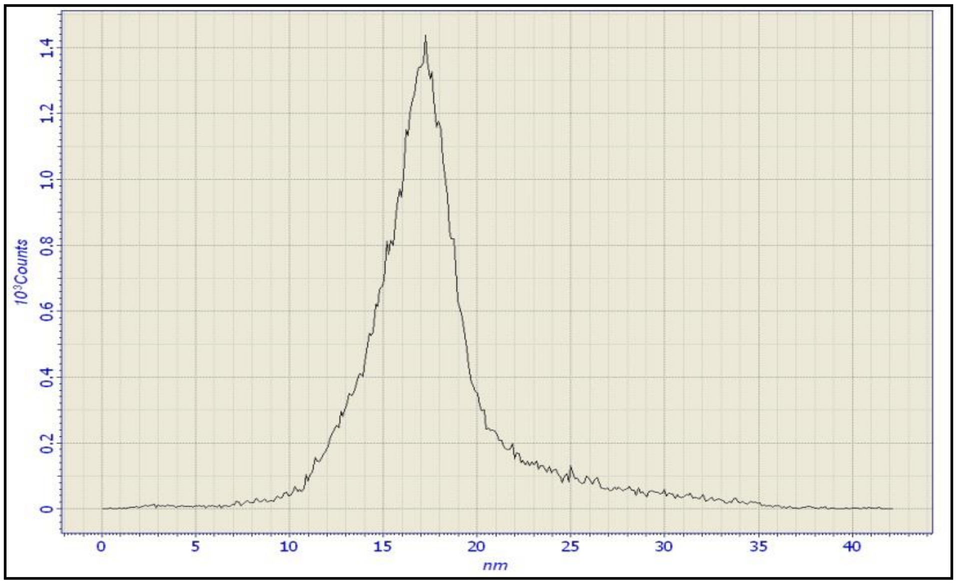

Figure 9: NAINSC

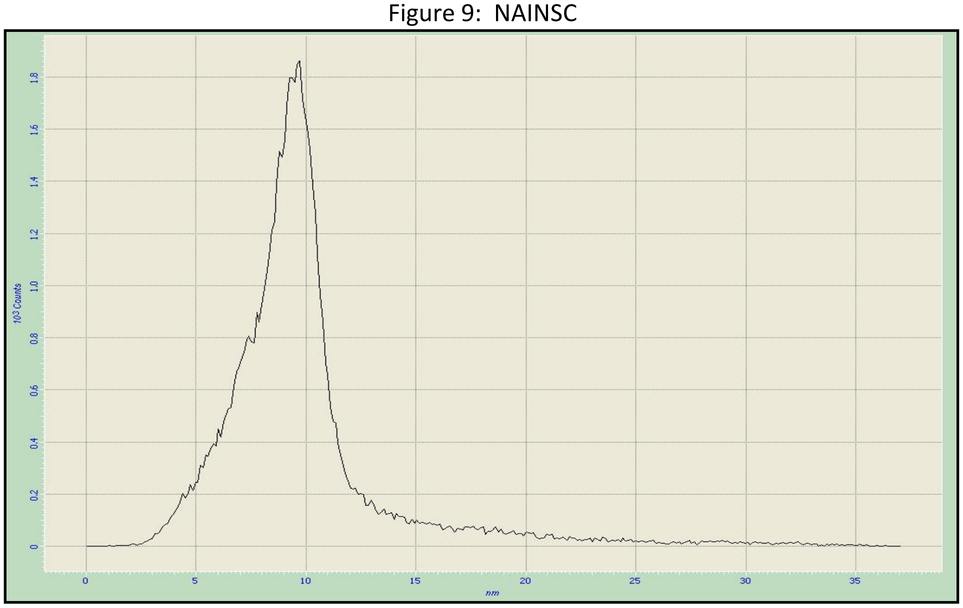

Figure 10: NTPJB

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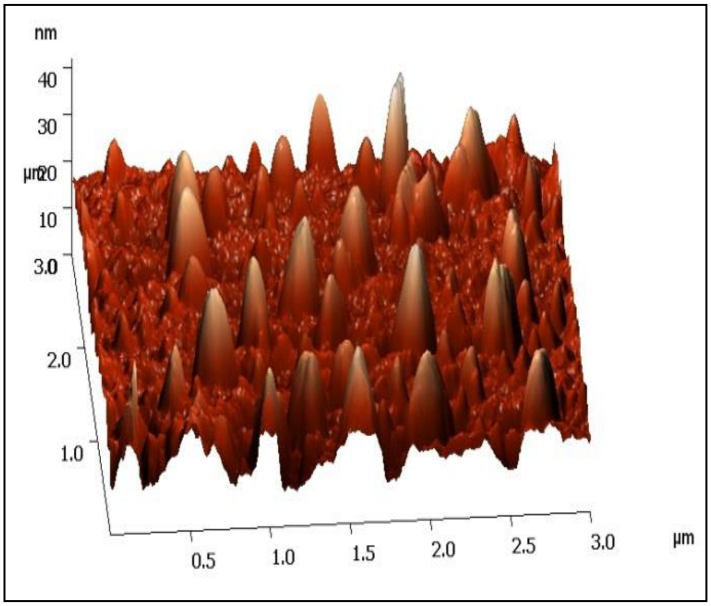

Figure 11: 3 D Surface Topography – NAINSC

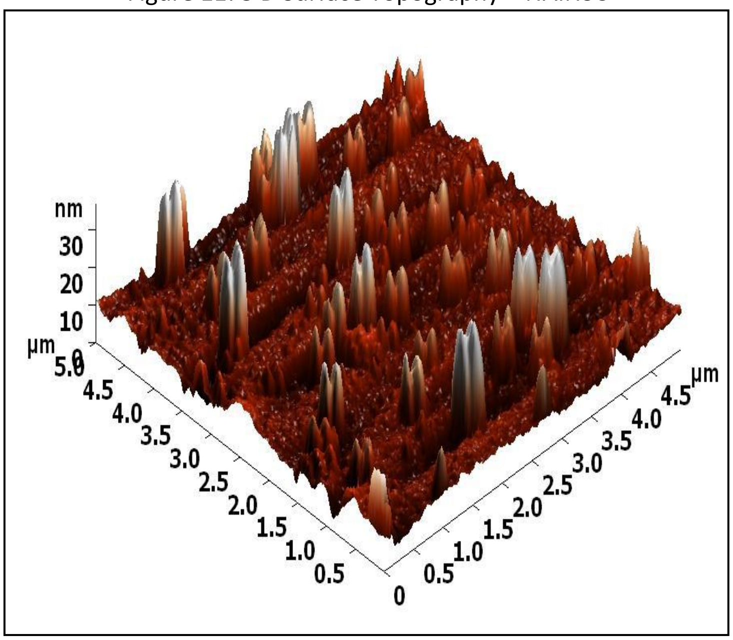

Figure 12: 3 D Surface Topography - NTPJB

Scanning Electron Microscopic Analysis:

Surface morphologies of the precursors and composites were examined using *JOEL JFM 6390* Scanning Electron Microscope. Schematic diagrams (Figures 13 and 15) represent appearance of porous nature with coarse surface texture, whereas those images of nano-sized materials (Figures 14 and 16) exhibited extended formation of pores, leading to better arrangement of surface patterns t0 trap the toxicants in a favorable manner (Liu et al., 2012).

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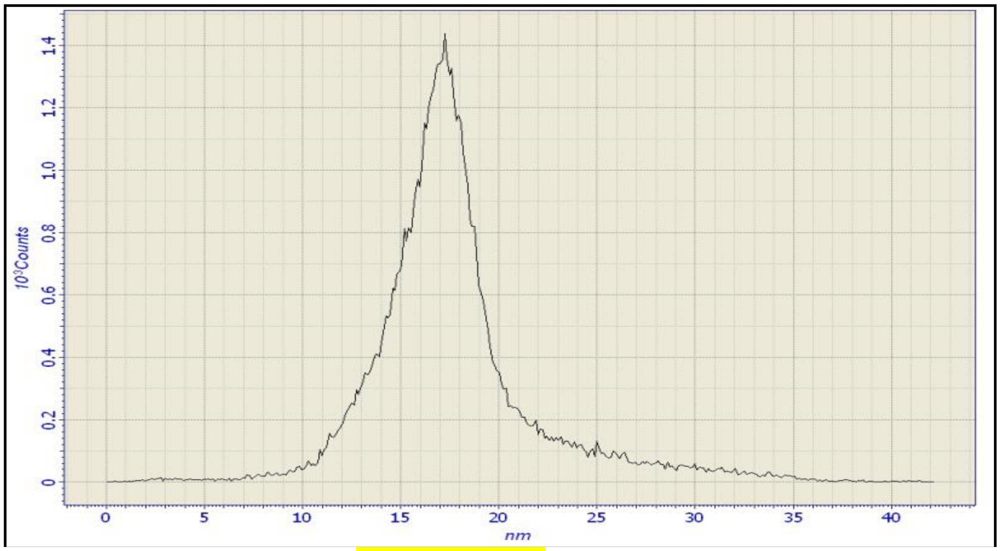

Figure 9: NAINSC

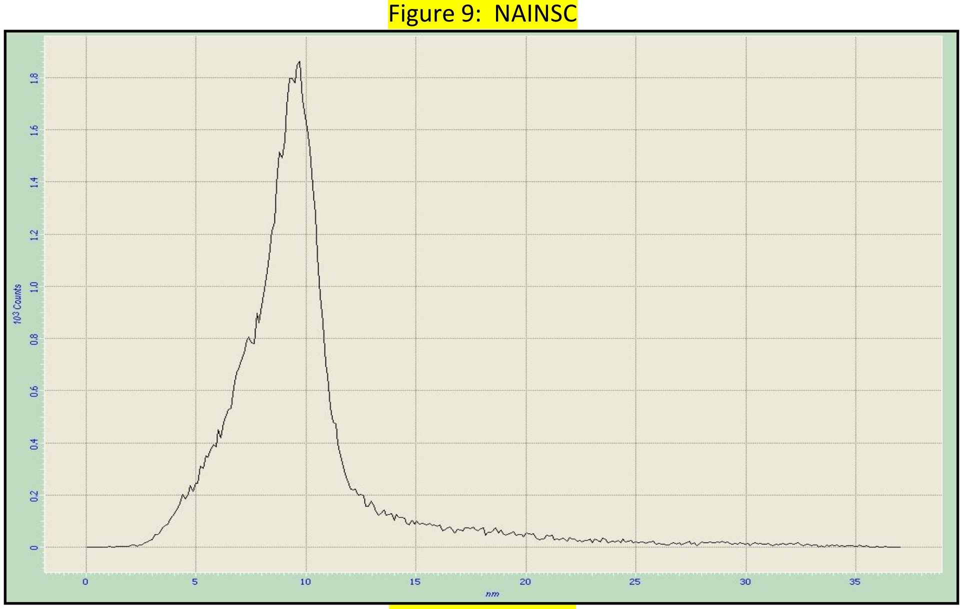

Figure 10: NTPJB

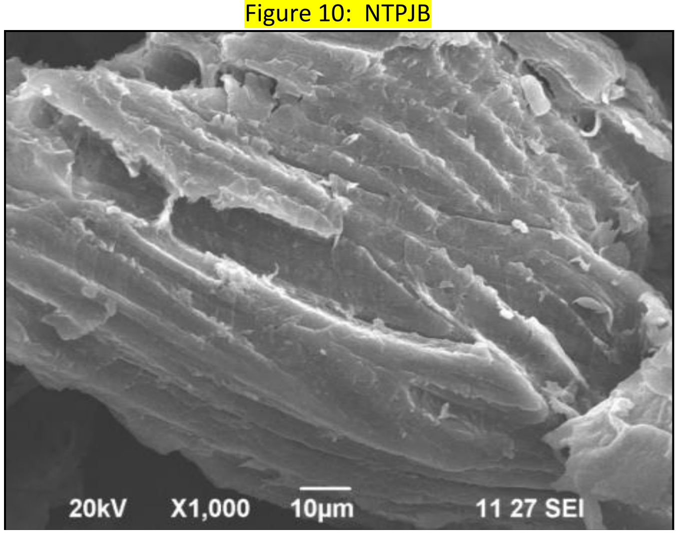

Figure 13: SEM – TAINS

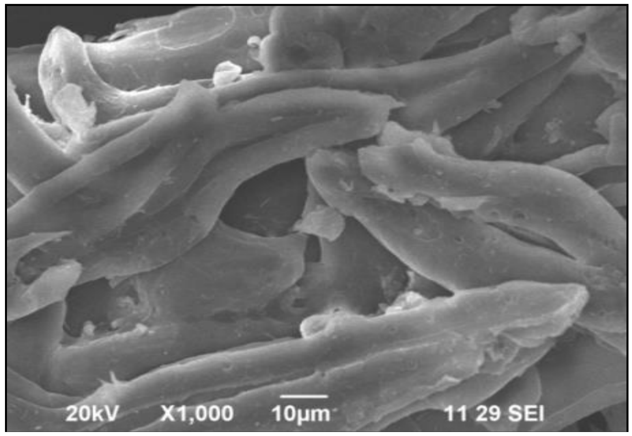

Figure 14: SEM – NAINSC

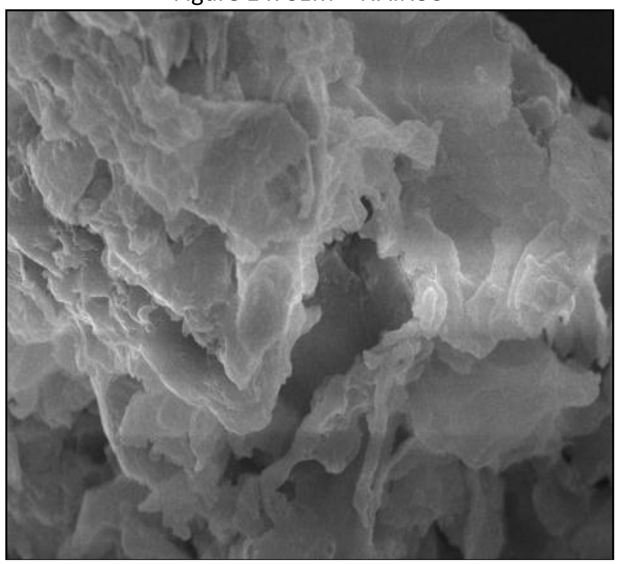

Figure 15: SEM - TPJB

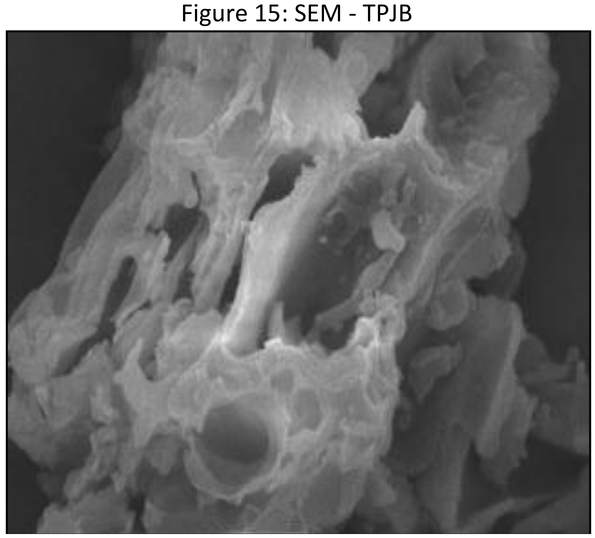

Figure 16: SEM - NTPJB

Efficacies of the treated and nano-sized materials were studied for the removal of divalent metal ions from aqueous solutions at room temperature. NCs derived from the treated sorbents exhibited overall, better sorption characteristics than the latter. However, percentage removal of metal ions (listed in Table 1) were highly dependent on variable conditions of operating factors viz., particle size, initial concentration, dosage, pH and Agitation time. NTPJB exhibited better sorption characteristics when compared to that of NAINSC, which shall be due to reduced nano dimension (9 nm).

Table1: Sorption Efficiency of Synthesized Sorbent Materials – A Comparison

Metal ions	Cu(II)		Ni(II)	
Materials	TPJB	NTPJB	TAINS	NAINSC
Particle size	0.18 mm	9 nm	0.18 mm	17.1 nm
Dosage	1000 mg	100 mg	150 mg	50 mg
Metal Removal	91.40%	99.35%	69.96%	74.53%
Optimized Conditions	Initial Conc.- 1000 mg/L; Agitation Time - 10 mins; pH-7		Initial Conc.- 11 mg/L; Agitation Time – 15 mins (TAINS), 5 mins (NAINSC); pH-2	

As conclusions, Systematic preparation of nanocomposites were carried out employing eco-friendly procedure with seldom use of organic solvents from their treated precursors in the process of chelating toxic metal ions. The raw materials employed were locally available, economically viable and biodegradable in nature. Characterization studies of Nano *Azaridachta indica* Nut shells (NAINSC), Nano *Prosopis juliflora* Barks (NTPJB), of the prepared material reveal presence of functionalized groups (FTIR), notable open pores / enrichment of composite surfaces (SEM) and marked histogram peaks (AFM). The synthesized sorbents show favorable metal up taking capacity. Thenceforth, the NCs' are recommended as potential metal sequestrants from aqueous matrices. Future work is focused on employing these composites for wastewater treatment / purification through biocompatible and environmentally benign synthetic strategy.

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Received: 03th Jule 2021; Accepted: 21th April 2022; First distribution: 28th January 2023.