https://dx.doi.org/10.4314/dujopas.v10i2a.16
ISSN (Print): 2476-8316
ISSN (Online): 2635-3490
Dutse Journal of Pure and Applied Sciences (DUJOPAS), *Vol. 10 No. 2a June 2024*

Synthesis and Spectroscopic Analysis of Illite Clay - Silica Nanocomposite

Elisha Karu[1], Buhari Magaji[1] Adamu Baba Moh'd[1] and Ahmed Shehu[2]

[1,] Department of Chemistry,
Faculty of Science,
Gombe State University,
Gombe State,
Nigeria.

[2]Federal College of Horticulture
Dadin Kowa,
Gombe State,
Nigeria.

Email : elishakaru@gsu.edu.ng

Elisha Karu - Orcid id: 0000-3001-9008-9958
Buhari Magaji - Orcid id: 0000-0002-2413-3890
Adamu Baba Mohd - Orcid id: 0009-0003-0281-5713
Ahmed Shehu - Orcid id: 0009-0008-8035-076X

Abstract

Illite clay silica nanocomposites (ICSiO2NCPs) were successfully synthesized from two samples Illite-clay and silica, and the silica was synthesized from rice husk using Sol-Gel Method. The prepared ICSiO2NCPs was characterized using UV-visible, FTIR, SEM and XRD analysis. The FTIR spectroscopy revealed the vO-H, vSi-O-Si, and vSi-OH stretching vibrations at around 3440, 798 and 913 cm^{-1} respectively and also the Si-O, C-H O-H, and Si-O-Si deformation modes at 531, 1384, 1633 and 472 cm^{-1} respectively. The XRD analysis showed face centered cubic (FCC) structures with an average crystal size of 63.6 7nm. SEM analysis showed irregular spherical shape particles fused together at various sizes that are agglomerated at higher magnification. In the UV-visible analysis the wavelength of maximum absorbance was observed at around 400 nm characteristic of silica and ascribed to the wavelength of surface plasmon resonance phenomenon. .

Keywords: Illilite clay silica Nanocomposite, FTIR, UV-Visible, XRD and SEM Analysis

INTRODUCTION

Rice husk is known as a complex organic substance containing cellulose (50 %), lignin (25 – 30 %), silica (15 – 20 %) and moisture (Babaso and Sharanagouda 2017). Cellulose basically a polymer has the same unit structure as starch except that cellulose is β – glucose while starch is α –glucose. On the other hand lignin is a carbohydrate and an irregular compound. The fact that there are the OH, and CO functional groups attached to the benzene ring in their structures is useful in the interpretation of the IR spectra of illilite silica composite.

Author for Correspondence

China and India contribute about 33 % and 23 % of the global production of rice respectively, (Soltani *et al.,* 2015; Babaso and Sharanagouda 2017). Prior to May 2023 the Federal Government of Nigeria lifted the importation of 43 items including rice, growing of rice in the Savannah zone of the country had led to tremendous investments in rice production including the Northeast geographical zone. Rice husk (RH) is a major by-product of rice milling and is available as an abundant waste in most rice growing areas.

Illite clay has the formula $(K.H_3O)(Al.Mg.Fe.)_2(SiAl)_4O_{10}[(OH)_2.(H_2OI]$ and consists of 2:1 layers or tetrahedral – octahedral – tetrahedral layers bonded together by large interlayer of potassium.

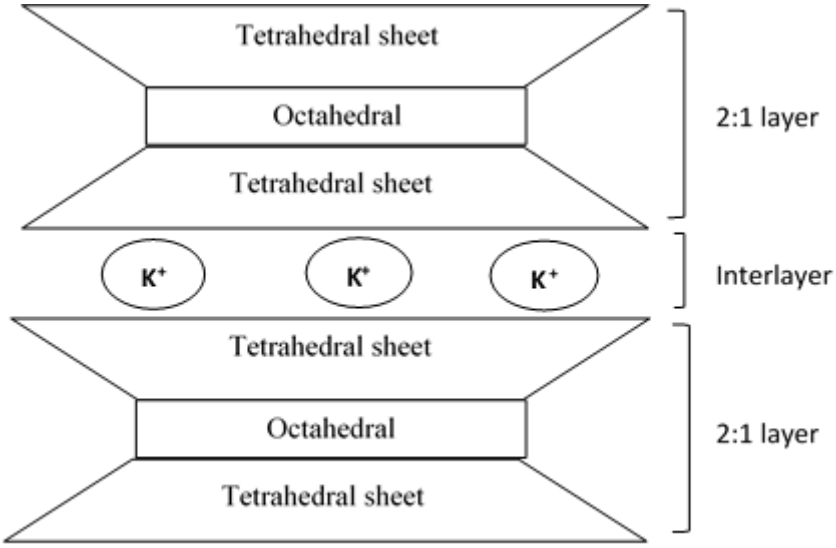

Figure 3 Illite layering structure

Dongmin *et al.,* (2010) had demonstrated the preparation of silicon powders from rice husk ash whereby Na_2CO_3 was used as the silica extraction agent that resulted into a high yield (72.52 %) content of silica. In this study the silica content of RH was enriched with Illite clay.

The characterisation of silica related compounds is well documented in literature. For example Xu *et al* (2005) synthesized and characterized iron oxide-coated silica. The IR absorption bands for Fe-O and Si- O bonds were found to be at 1100, 798, and 960 cm^{-1}. A similar study by Waseem *et al* (2009), reported the synthesis and characterization of SiO_2 by sol-gel method and its characterization by X-Ray diffraction studies (XRD), Fourier Transform Infrared Spectroscopy (FTIR). Like the work by Xu, *et al*. (2005) the FTIR analysis revealed all the required bands indicative of the successful synthesis of silica particles. Zulfigar and his coworkers (2016) reported the characterization of silica nano particles from bentonite, using series of thermal and acid treatment processes to lower the alumina likely to be present and to also increase the silica content. AAS, X – ray fluorescence, scanned electron microscopy etc. were used to characterize the silica nano particles. Also Hameed *et al* (2016) synthesized mesoporous silica nanoparticles and used it to prepare zero valent iron supported on the mesoporous silica nanoparticles.

The broad aim of this work is to synthesize, characterize the illite silica composite NPs ($IOSiO_2NCPs$) by the sol – gel method.

MATERIALS AND METHODS

Chemicals and reagents

$Ni(NO_3)_2.6H_2O$, $Cd(NO_3)_2.4H_2O$, $Pb(NO_3)_2.6H_2O$ NaOH , 68 % HNO_3 , 35 % HCl and KOH. All Chemicals and reagents used in this study were of analytical grade except NaOH and KOH and were used as supplied.

Preparation of solutions

Stock solutions of $Pb((NO_3)_2$, $Cd((NO_3)_2$ and $Ni((NO_3)_2$ solutions were prepared by standard procedure as described by Yahaya *et al* (2022) by dissolving in distilled water 1.5980, 2.103 and 4.9530 g respectively in 1 L volumetric flask and various concentration were prepared by serial dilution method from the stock solutions by using the formula below

$$C_1V_1=C_2V_2 \quad (1)$$

Where C_1 is the concentration of the stock solution, V_1 is the volume of the stock solution to be used. C_2 is the concentration of the dilute solution to be prepared and V_2 is the volume of the dilute solution to be prepared.

Preparation of 0.1M of NaOH

0.1 M NaOH solution was prepared by dissolving 4.00 g of NaOH pellets in about 1000 cm^3 of distilled water in 1000 cm^3 volumetric flask and the solution was made to mark with distilled water.

Preparation of 0.1M of HNO_3

0.1M of HNO_3 was prepared by diluting 6.3 cm^3 of 68 % HNO_3 in 1000 cm^3in volumetric flask and diluted to mark with distilled water.

Preparation of 10% HCl

10% HCl was prepared by diluting 28.57 cm3 of 35 % HCl with 78.43 cm^3 distilled water in 100 cm^3 volumetric flask.

Preparation of 7% KOH

7% KOH was prepared by dissolving 35 g of KOH into 500 cm^3 volumetric flask and made to mark with distilled water.

Collection of Samples and preparation

The illite clay was collected from along Futuk – Alkaleri road in Alkaleri Local Government Area of Bauchi State, Nigeria. The sample was grounded into powder using mortar and pestle, and then sieved using 120 mesh size sieve. Also some rice husks (RH) were collected from a rice mill in Gombe Metropolis. They were cleaned three times thoroughly with tap water and then rinsed with distilled water to removes adhering soil and dirt. It was then dried in an oven at 80 ^oC for four hours.

Preparation of Illite Clay

The illite (clay) was washed three times with tap water then with distilled water and dried in an oven at 120 ℃ for three hours until constant weight was obtained and then air-dried for two hours. The illite clay was grounded into fine powder using pestle and mortar.

Production of Silica from rice husk

The silica from the RH was prepared following a procedure previously reported by Setyawan *et al.,* (2021). The RH was washed with hot water to remove contaminants of water-soluble organic matter present. The RH was first soaked in hot water of about 80 °C for 2 hours and

then rinsed four times. The RH was dried at room temperature followed by extraction of the silica using an alkali extraction method as reported by Sembiring *et al.,* (2014) with little modification using sieve cloth instead of filter paper. 50 g of dried RH was mixed with 500 cm^3 of 7% KOH solution in a 1 L glass beaker. The mixture was boiled for 90 min, and then allowed to cool to room temperature for 24 hrs. The mixture was filtered to obtain silica (silica sol). To obtain solid silica, the sol was acidified by adding 10% HCl solution drop by drop with constant stirring until the pH is 7 after which the sol was converted into the gel. The gel was allowed to mature for three days and then rinsed 7 times repeatedly with distilled water to remove the excess acid until a clear sol was obtained. The gel was oven-dried at 110 °C for eight hours and afterwards ground into powder using pestle and mortar. The experiment was done in triplicate giving an average yield of 14 g.

Characterisation

Fourier Transform Infrared (FTIR) Spectra

Following a KBr pellet technique as reported by Stuart (2004), about 5 mg of sample was weighed and placed in an agate mortar. It was ground into fine powder and 250 mg of the suspending matrix (KBr) in the form of fine power was added and stirred using a spatula. The Powder was transferred into a dice and placed in a disk press and pressed into a disk. The disk was removed and placed into a disk holder of the FTIR machine. Alkaline halide like KBr is favaourably used in IR spectra analysis, because it does not absorb in the IR region. FTIR machine was calibrated with polystyrene film (polystyrene standard).

FTIR spectra was acquired using FTIR Perklin-Elmer spectrophotometer version 10-03-09 model at the Pharmacy Department Gombe State University on the synthesized silica alone from rice husk, illite clay silica nanocomposite ($ICSiO_2NCPs$) as well as rice husk and the spectrum superimposed on one to determine the functional groups present in the samples.

Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD Studies

The SEM and XRD analyses were done at the National Research Institute of Technology Zaria, Nigeria in order to determine the morphology, size and the average crystalline size using the Debye Scherer equation (2). The Debye Scherer equation of the synthesized nanoparticles.

$$D = K\lambda/\beta COS\theta \quad (2)$$

Where D = Particles size

K = Constant volume

λ = X-ray wavelength

β = Line broadening at half the maximum intensity

θ = Braggs angle (in degree

UV-Visible Spectroscopy

Ultra-violet spectroscopy of nanomaterial is usually undertaken to ascertain the wavelength of maximum absorbance often referred to as the Surface Plasmon Resonance excitation.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR infrared spectra are given under Fig. 3.1 while the absorption frequencies are tabulated in Table 1

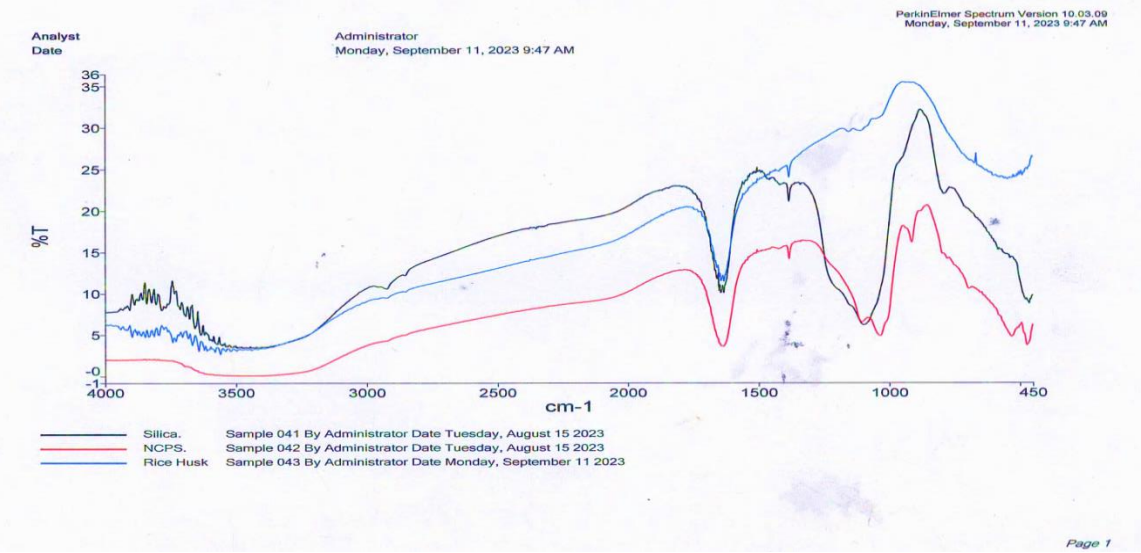

Figure 1 IR Spectra of Silica, ICSiO2NCPs and Rice husk

Table 1 The FTIR Absorption Frequencies (cm^{-1}) for Silica from RH, Illite-clay silica Nano composite (NCPs) and Rice husk (RH).

Silica from RH	NCPs	RH	Literature	Reference	Assignment
3439br	3392br	3443br	3300 – 3427	Cheng *et al* (1998), Waseem *et al* (2009), Xu *et al* (2005)	vOH stretching vibration probably from water, and phytochemical such as phenol, carboxylic acid.
2925m	n.o	n.o	2852-2957	Ombaka O. (2016)	CH-CH3 stretching,
1633vs	1633vs	1633vs	1633-1638vs	Cheng *et al* (1998), Waseem *et al* (2009), Xu *et al* (2005)	Bending or deformation mode of OH (δOH) from water.
1384w	1384w	1384w	1420 & 1380	Budnyak *et al* (2015)	C-H bending vibrations
1098w	1104w	n.o	1098 &1100	Cheng *et al* (1998)	Asymmetric stretching vibration (vSi-O-Si)
n.o	913w	n.o	911-913	Ombaka O. (2016) Waseem et al (2009), Xu et al (2005)	Si-OH stretching vibration vOH(Si-OH)
789w	798w	n.o	798	Waseem *et al* (2009).	vSi-O-Si Symmetric stretching
n.o	531w	546	555-950	Oufakir *et al* (2017)	Si-O Bending vibration
463w	472w	488	465-794	Kepdie *et al* (2023) Ombaka O. (2016)	Si-O-Si deformation mode (δSi-O-Si)

Note: **vs** = strong, **v** = strong, **m** = medium, **w** = weak, **br** = broad, **sh** = shoulder, **n.o** = not observe

A broad peak is observed at around 3441 cm^{-1} in both the spectra of pure silica and the silica obtained from rice husk nanosilica (SiNCP) composite. This was assigned to OH stretching vibration probably from water or the phytochemical from the rice husk such as phenol, carboxylic acid etc. However three prominent peaks were noted as characteristic in the IR spectra of silica via the asymmetric silicon-oxygen-silicon vibrations v_{as}(Si-O-Si), symmetric silicon-oxygen-silicon vibration v_s(Si-O-Si) and silicon-hydroxide stretching vibration v(Si-OH). These are reported (Waseem *et al*., 2009 and Cheng *et al*. 1998, Xu *et al*. 2005, and Panwar *et al*. 2014) to occur at about 1100, 798 and 960 cm^{-1} respectively. A very weak absorption peak observed at 463 cm^{-1} that appeared in the silica but not observed in the silica composite was assigned (Kepdieu *et al*.; 2023) to the Si-O-Si bending or deformation mode.

XRD Analysis

X-ray diffraction (XRD) studies is another common characterization technique for nanoscale materials. Analysis of a sample by XRD provides important information that is complementary to various microscopic and spectroscopic methods. Fig. 3.2 shows the XRD analysis of Illite clay-silica nanocomposites. A strong diffraction peak is observed at 2θ value = 26.86° corresponding to the plane of hkl (111) which shows Face Centered Cubic (FCC) cell. The average crystal size was determined by Debye-Scherrer equation.

$D = K\lambda\beta\cos\theta$ (2)

where

D = particle in nm,

K is a constant (Sherrer constant = 0.9),

λ is the wavelength of the X–ray radiation,

θ is Bragg's angle and

β is Full Width Half Maximum (FWHM).

The calculated mean crystal size was found to be 63.67 nm. This result is in agreement with the findings by Zulfigar *et al.,* (2016).

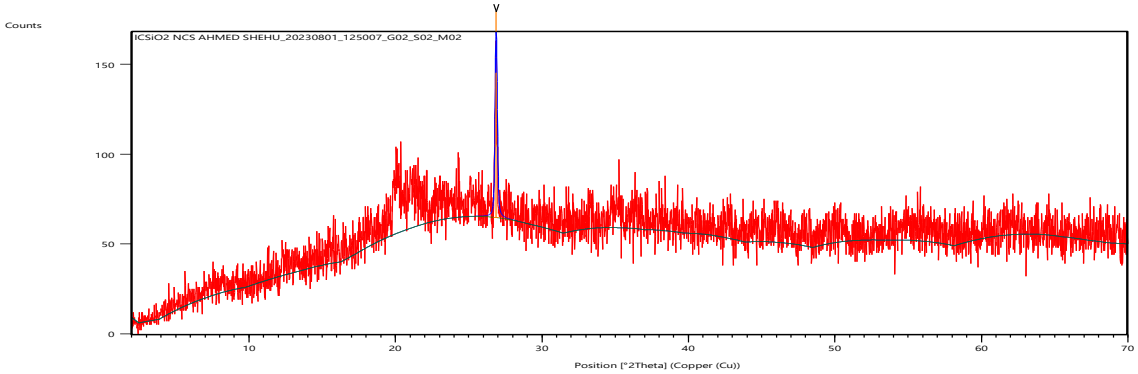

Figure 3.2 showing the XRD analysis result for Illite clay-silica nanocomposites

SEM Analysis

Scanning Electron Microscopy (SEM) technique is widely used to characterize nanoparticles. It basically determines the size, shape and surface morphology with direct visualization of the nanoparticles.

The SEM result obtained for the illite clay- silica nanocomposites is shown in Fig. 3.3. An irregular spherical granular like morphology is observed. The result obtained is in agreement with the literature report by Tahir *et al.,* (2010) which shows spherical and granular like morphology.

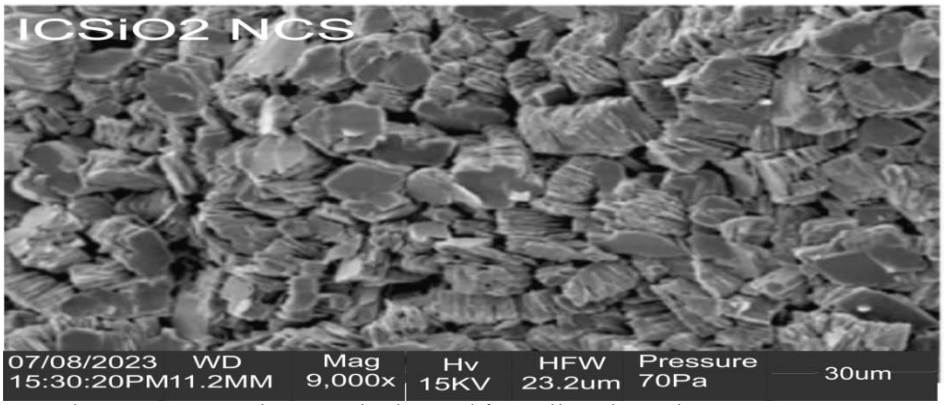

Figure 3.3 showing SEM Analysis result obtained from Illite clay-Silica nanocomposites

UV-Visible Spectroscopy

The UV-visible spectrum of $IOSiO_2NCPs$ is shown in Fig. 3.4.

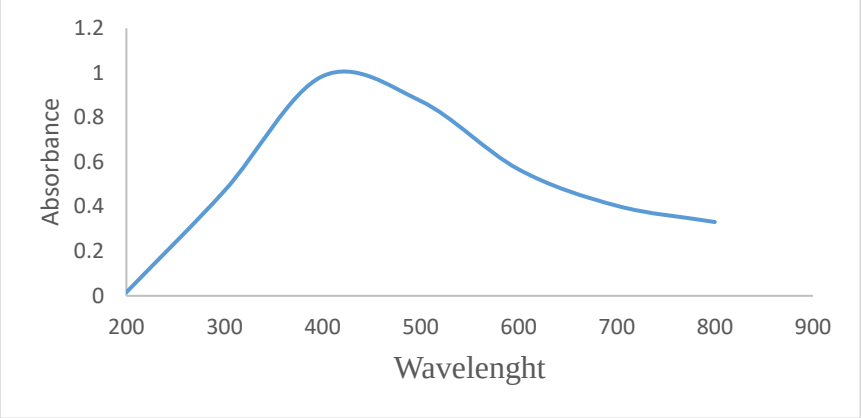

Figure 3.4 UV-visible of Illite-clay silica nanocomposite ($ICSiO_2NCPs$)

The presence of $IOSiO_2NCPs$ on the silica nanoparticles was also confirmed by UV–vis spectroscopy. The $IOSiO_2NCPs$ showed a peak with maximum absorbance at 400 nm, characteristic of silica (Panwar *et al*., 2014) indicating the presence of silica on the $IOSiO_2NCPs$ generally ascribed to the Surface Plasmon Resonance (SPR) phenomenon.

CONCLUSION

The Nano composite ($ICSiO_2NCPs$) was successfully synthesized from rice husk through sol-gel method, and was characterized by UV-visible spectroscopy, FTIR, SEM and XRD analysis. The UV-visible spectrum showed a maximum absorbance at 400 nm characteristic of silica (Panwar *et al*. 2014) while the FTIR spectra clearly showed three prominent peaks at 1100, 798, and 960 cm^{-1} also characteristic of silica that was in agreement with literature reports (Cheng *et al*. 1998 and Xu *et al*. 2005). The nanocomposites crystallized in the Face Centred Cubic cell (FCC) and the SEM analysis revealed an irregular granular spherical pattern of morphology.

Acknowledgement: We wish to acknowledge the analyses done at the Centre for Energy Research of Ahmadu Bello University Zaria, Nigeria for the XRD and SEM; and the Financial support granted to Ahmed Shehu by the College of Horticulture Dadin Kowa, Gombe Nigeria to undertake the project.

REFERENCES

Babaso, P. N. and Sharanagouda, H., (2017). Rice Husk and Its Applications: Review, *International Journal of Current Microbiology and Applied Sciences;* 6(10): 1144-1156

Cheng, Z. H., Yasukawa, A., Kandori, K., & Ishikawa, T., (1998). Dongmin, A., Y. Guo, Y. Zhu and Wang, Z. A., (2010). Green route to preparation of silica powders with rice husk ash and waste gas. *Chemical Engineering Journal*. 162(2): 509-514.

Dongmin, A., Y. Guo, Y. Zhu and Wang, Z. A., (2010). Green route to preparation of silica powders with rice husk ash and waste gas. *Chemical Engineering Journal*. 162(2): 509-514.

Hassan P. B., Rezan O. Rasheed R. O., and Zargoosh K. (2022). Cadmium and Lead Removal from Aqueous Solution Using Magnetite Nanoparticles Biofabricated from Portulaca oleracea Leaf Extract. *Journal of Nanomaterials.* 2022, Article ID 1024554, 18.

Hameed, A. K., Dewayanto, N., Dongyun, D., Nordin, M.R. and Rahim, M.H., (2016) Kinetic and Thermodynamics of Methylene Blue Adsorption onto Zero Valent Iron

Supported on Mesoporous Silica, *Bulletin of Chemical Reaction Engineering & Catalysis,* 11(2):250-261.

Kepdieu J. M., Djangang C. N., Njimou J. R.; Maicaneanu S. A., and Mache J. R., (2023). Low-cost pathways to synthesize silica-smectite clay-based composites. *362-376* https://doi.org/10.212033 - 23 - 02569 – 2.

Lata, S., and Samadder, R., (2014). Removal of heavy metals using rice husk: a review. *International Journal of Environmental Research and Development.* 4:165-170.

Panwar, K., Jassal,M., and Agrawal A. K., (2014). In situ synthesis of Ag–SiO_2 Janus particles with epoxy functionality for textile applications.*Particuology*.714: 1-7.

Pindiga N. Y., Walid A. H., Abdullateef Olalekan Abdullahi A. O., Mohammad A. B.(2022). Kinetic, Equilibrium and Thermodynamic Study of the Adsorption of Pb (II) and Cd (II) Ions from Aqueous Solution by the Leaves Biomass of Guava and Cashew Plants. *Online Journal of Chemistry***.** 2022(2): 23-38.

Sembiring, S Simanjuntak, W Manurung, P Asmi, D and Low, I M. (2014) Synthesis and characterisation of gel-derived mullite precursors from rice husk silica *Ceram. Int.* 40(5): 7067–7072.

Setyawan N., Hoerudin, and Yuliani, S., (2021). Synthesis of silica from rice husk by sol-gel method. *Earth and Environmental Science.**733** (2021) 012149* 1-7 doi:10.1088/1755-1315/733/1/012149.

Shwetha, M. K., H. M. Geethanjali and Chowdary, K., (2014). A great opportunity in prospective management of rice husk. *International Journal of Commerce and Business Management.* 7(1): 176-180.

Soltani, N., Bahrami, A., Pech-Canul, M. I. and Gonzalez, L.A., (2015). Review on the physicochemical treatments of rice husk for production of advanced materials. *Chemical Engineering Journal*. 264: 899-935.

Stuart, B., (2004). Infrared Spectroscopy: Fundamentals and Applications. John Wiley & Sons, Ltd p 46-47.

Tahir, H., Hammed, U., Sultan M. and Jahanzeb, Q., (2010) Batch adsorption technique for the removal of malachite green and fast green dyes by using montmorillonite clay as adsorbent. *African Journal of Biotechnology.* 9(48): 8206-8214.

Waseem, M., Mustafa, S., Naeem, A., Shah, K. H., Shah, I., and Haque, I., (2009). Synthesis and Characterization of Silica by Sol-Gel Method. *J Pak Mater Soc* 3 (1):19-21

Xu,Y., Axe, L., (2005). Synthesis and characterization of iron oxide-coated silica and its effect on metal adsorption. *Journal of Colloid and Interface Science* 282 (2005) 11–19

Yahaya N. P., Deedat A. A., Madugu Y. D., and Abubakar A. (2022). Kinetic, Equilibrium and Thermodynamics Study of the Ad-sorption of Pb(II), Cu(II) and Ni(II) from Aqueous Solution using *Mangiferaindica* Leaves. *Online Journal of Materials Science***.** 2022**(**1): 16-29.

Zulfiqar, U., Subhani, S.T., and Husain, W., (2016). Synthesis and characterization of silica nanoparticles from clay. *Journal of Asian Ceramic Societies*; 4(1):91-96.