



Preparation and characterization of *Theobroma cacao* pod-modified feldspar composite for possible metal adsorption in wastewater management

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Abstract

In this study modified feldspar composite (MFC) was prepared from the combination of *Theobroma cacao* pod (TCP) and feldspar (FS) using calcination method. The *Theobroma cacao* pod-feldspar sample was first Na-modified by treatment using 0.1M NaOH solution before calcination in the muffle furnace at 300°C to complete the process of composite preparation. The *Theobroma cacao* pods (TCP), feldspar (FS) and modified feldspar composite (MFC) were characterized using XRF, X-ray diffraction (XRD), Brunauer Emmett and Teller (BET) analysis, scanning electron microscopy (SEM) and Fourier transforms infrared spectroscopy (FTIR). The results showed that the cation exchange capacity of the modified feldspar composite (30.66 ± 0.21 meq/100 g) was 5 times higher than that of raw feldspar (6.42 ± 0.45 meq/100g). More so, the novel biohybrid material, MFC has a surface area of 53.60 ± 0.3 m²/g and particle size of 105.4 ± 0.18 . The XRD patterns revealed that after the modification process, there is only slight shift in the position of some diffraction peaks of feldspar and the composite material indicating the retention of the crystalline properties of the feldspar in the novel composite (MFC). FTIR results showed that some functional groups present in the two starting materials were also available on the surface of the composite (MFC) indicating that the intercalation of TCP biomass into feldspar surface was successful. Owing to its improved cation exchange capacity and eco-friendliness, the modified feldspar composite (MFC) has a good potential application as adsorbent for heavy metals in wastewater treatment besides other industrial explorations.

Keywords: *Theobroma cacao* pod-feldspar; Calcination; Intercalation; Characterization; wastewater

1. Introduction

Biohybrid composites are a new class of materials obtained from the dispersion of high quality ratio of aluminosilicate particles in a biopolymeric matrix exhibiting distinguished interface with improved mechanical, thermal and physico-chemical properties compared to the pristine constituent materials [1]. Biohybrid composite materials attract the interest of both scientific and engineering communities due to their extensive use in a wide range of application fields from environmental remediation to biomedical uses [1]. The incorporation of inorganic particles into biopolymer matrices has long been studied and the results showed improved mechanical, thermal, and better polymer properties combining organic and inorganic moieties in the novel composites produced [2]. At the microscale, the inorganic particles have improved significantly the stability and other properties of biocomposites even with a small intercalation [3]. In recent years, considerable research attention in material science has been focused on the synthesis of hybrid materials from synergistic combination of aluminosilicate and agrowaste materials for enhancement in thermal stability, gas barrier properties and mechanical strength of the composites. By adding just a small quantity of

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aluminosilicate mineral to the biopolymer matrix, the composite materials exhibit good heat resistance, char properties, and reduced weight loss when subjected to calcination/pyrolysis [4].

Intercalated biopolymer/aluminosilicate composite on nanoscale molecular level have display interesting characteristics resulting from the sub-micron diameter, fine cross-linked porous network and high surface-to-weight ratio compared to ordinary polymeric structures [1]. These characteristics enhanced surface reactivity and make the reinforced composites useful for numerous applications such as adsorbents, filler in industrial and medical devices. For most engineering and industrial applications, composites owing to their thermal stability and mechanical strength are used as carbon nanotubes (CNTs) and single or hybrid aluminosilicate fillers [1]. Besides these applications, the high adsorption capacity and cation exchange capacity of most composite material have made their intensive use for industrial purposes and adsorbent in wastewater treatment [5].

Cocoa (*Theobroma cacao*) is an important agricultural and economic crop. As the consumption of cocoa bean and chocolate-related products (e.g., cakes, beverages and powders) became more and more widespread around the world, these significantly resulted in the spread of cultivation of cocoa, including Central/South America, West Africa and Southeast Asia [5]. It is one of the key economic crops cultivated in Nigeria. As the third largest producer of cocoa in Africa and one of the highest cocoa producer in the world, the production capacity of Nigeria was reported to have reached about 385,000 tonnes per annum on the cultivable area of 966,000 ha with an appreciable increase of about 215,000 from year 2000 production level [5, 6]. Cocoa beans are the primary economic part of the cocoa fruit and are the principal ingredients in the manufacture of chocolate and other derived products such as cocoa liquor, cocoa butter, cocoa cake and cocoa powder. The implication of this is that as the cocoa production industry is expanding, the *Theobroma cacao* pods (TCP) which are the main by-products of cocoa processing are discarded as wastes hence constituting environmental pollution. *Theobroma cacao* pod (TCP) is a lignocellulose waste consisting of cellulose 19.7-26.1%, hemicellulose 8.7-12.8% and lignin 14-28% [6]. Cellulose and hemicellulose are polymerized from monosaccharides, which can be converted into sugar under certain conditions. Lignin is a macro component of a molecule that binds covalently with cellulose and hemicellulose. However, based on its chemical composition to create valuable products, cocoa pod husks have been explored as food antioxidants, dietary fibers, animal feed, as a precursor in the activated carbon production, fertilizer, adsorbent in water purification and natural filler thermoplastic composites [7].

Feldspar is crystalline aluminosilicate minerals and appertains to the tectosilicate group that characterized by a larger density framework of layered silicate structure. It is the greatest and most abundant rock-forming mineral in the earth crust. It constitutes about 60% of igneous rocks. The mineralogical composition of feldspar consist of minerals such as orthoclase (KAlSi_3O_8), albite ($\text{NaAlSi}_3\text{O}_8$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). In a considerable ratio of Feldspar ores, K-Feldspar (KAlSi_3O_8 , microcline or orthoclase) and Na-Feldspar (albite, $\text{NaAlSi}_3\text{O}_8$) exist in the similar matrix [7]. It has a formula Si_4O_8 but up to two of Si (VI) may be replaced by Al (III) with the charge deficiency balanced by large univalent cation [8]. The feldspar surface is composed of negative and positive sites. The positive charges are Na^+ ions in albite and K^+ ions in orthoclase, and the negative sites are nonpolar siloxane groups or polar silanol groups. The inorganic cations on the internal and external surfaces of feldspar (e.g. Na^+ , K^+ and Ca^{2+}) could be replaced by organic functional groups, such as hydroxyl, carbonyl, carboxyl and methylene groups, through ion exchange that enhances the adsorption capacity as the feldspar surfaces has been modified. The surface properties of feldspar can be greatly modified with TCP through ion-exchange mechanism and hence the surface area is enhanced [5, 9].

Indeed, numerous reports available on use of materials such as biosorbents, aluminosilicate minerals and biopolymer/clay composites for heavy metal removal from aqueous solution [10]. Clay/aluminosilicate material is a popular adsorbent, because different clays easily exchange ions with the environment and, thus, efficiently remove heavy metals from waste water (Unuabonah et al., 2013). In contrast, there are virtually limited research reports on utilization of feldspar-biobased composites in adsorption studies [7, 9].

Obviously, the chemistry of feldspar requires new approaches for the production of feldspar-based composite materials useful for metal adsorption and thus wastewater treatment purposes. This research work is aimed at the preparation and characterization of modified feldspar composite (MFC) from synergetic combination of agro-waste (TCP) and aluminosilicate (feldspar) for possible application as adsorbent for heavy metals in wastewater treatment.

2. Material and methods

2.1. Collection and preparation of Adsorbents

2.1.1. *Theobroma cacao* pods (TCP)

The *Theobroma cacao* (Cocoa) pods were collected from cocoa plantations in Ifetedo town, Osun State. The TCP samples were washed thoroughly with tap water and then distilled water to remove dust and dirt. The samples were sun-dried and then oven-dried at 70°C for 72h to remove moisture. The dried TCP was ground in a mortar into powder. The powdered sample was sieved in a 0.230 mm sieve and stored in a pre-cleaned dry air-tight plastic container [4, 6].

2.1.2. Feldspar Sample (FS)

The feldspar sample was obtained from the Federal Institute of Industrial Research Oshodi (FIIRO), Lagos, Nigeria. The sample was pre-treated by suspension in deionized water for 24 h and the suspension was carefully decanted to obtain the feldspar [9]. The organic matter in the sample was removed by adding 30% hydrogen peroxide solution with stirring until effervescence ceased. The mixture was decanted and washed with deionized water to remove all traces of hydrogen peroxide and then oven dried at 105 °C [11]. The sample was ground, sieved through a 230 mm mesh size sieve and stored in a pre-cleaned dry air-tight plastic container for subsequent studies [12].

2.1.3. Modified Feldspar Composite Adsorbent (MFC)

Equal weight of feldspar and *Theobroma cacao* pods (50 g each) were weighed into a 500 mL beaker and 300 mL of 0.1M NaOH was added. The content was thoroughly stirred and heated in an oven at 150 °C until dryness [12]. The samples of the dried mixtures were weighed into crucibles and calcined at 300 °C for 6 h. The resulting dark powdery material was washed with deionized water to remove residual NaOH from the surface of the composite and subsequently oven-dried at 105°C to remove all moisture. The dried sample was stored in an airtight container [9]. It was subsequently referred to as Modified Feldspar Composite (MFC).

2.1.4. Selection of Optimum *Theobroma cacao* pod/Feldspar Percentage Combination in the Composite preparation

In order to select the optimum percentage combination of feldspar (FS) and *Theobroma cacao* pod (TCP) in the novel composite (MFC), five different combos were prepared which comprise of 10% TCP and 90% FS (10FCP–90FS), 20% TCP and 80% FS (20TCP–80FS), 30% TCP and 70% FS (30TCP–70FS), 40% TCP and 60% FS (40TCP–60FS) and 50% each of TCP and FS (50FCP–50FS). The procedure was followed so as to optimize the preparation of the composite (MFC) adsorbents [5].

2.2. Characterization of adsorbents

The pH of the adsorbents was determined (pH-80-HM DIGITAL). The cation exchange capacity (CEC) of TCP, FS and MFC samples were determined using the ammonium acetate method as reported by Unuabonah *et al.* (2013). Na⁺ and K⁺ were determined using AES (Agilent PG 10T), while Ca²⁺ and Mg²⁺ were determined by atomic absorption spectrophotometer (SHIMAZU 360H Model). The summation of the exchangeable cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺) gave the cation exchange capacity (CEC) (5, 18).

The functional groups present in the adsorbents (TCP, FS and MFC) were obtained using Shimadzu 8400S FTIR spectrometer operating on Platinum-Attenuated Total Reflectance (ATR) method. The samples were mounted on a diamond crystal disc and recorded with 20 scans in the frequency range of 4000 - 400 cm⁻¹ with a resolution of 2 cm⁻¹ [11, 13, 19].

The surface morphologies of the adsorbents were analyzed using scanning electron microscopy (SEM), Philips XL30 model. After gold coating (Philip J1050 sputter coater), the samples were placed in the SEM sample chamber where the micrographs of the TCP, FS and MFC were scanned and recorded at 32 scan and 15keV (Hossain, 2013; Dawood, 2018).

The XRD spectra for TCP, FS and MFC were obtained using Agilent X-ray diffractometer with Ni filtered CuK α radiation at ($\lambda = 1.5406 \text{ \AA}$, 40 mA and 40 kV), a diffracted-beam graphite monochromator, and a detector [15]. The X-ray diffractograms of TCP, FS and MFC were recorded by step scanning from 1.5° to 50° (2 θ) at 0.02° s⁻¹ [9, 15]. XRF analysis technique was used in this study to determine the chemical composition of the TCP, FC and MFC adsorbents using Bruker AXS S4 Pioneer model X-ray fluorescence (XRF) Spectrometer with 60 kV energy of the X-ray tube [7, 9, 15].

Brunauer, Emmet and Teller (BET) results for specific surface area and porosity of adsorbents were obtained from adsorption/desorption isotherm of N₂ at 77 °K [5, 13, 16].

All experiments were carried out in triplicate for all the adsorbents prepared in the study.

3. Results and discussion

3.1. Test for the performance of modified feldspar composite (MFC) for metal Adsorption

The composite adsorbents were utilized for the adsorption of the metal ions from the aqueous solution at metal concentration 100mg/L as shown in Figure 1. It was observed that an increase in percentage adsorption and adsorption capacity of the metal ions with increase in the amount of TCP in the composite were obtained. However, 50TCP–50FS recorded the highest percentages for Pb (96.8%), Cd (90.2%), As (94.5%) and Cr (80.7%) respectively. In general, the increase in metal adsorption with TCP concentration is possibly due to increase in the number of active binding sites on the MFC and improved heterogeneous nature of the adsorbent. The 50TCP–50FS composite adsorbent was chosen and utilized in this study for adsorption due to its relatively higher adsorption potential recorded than the other composite mixtures.

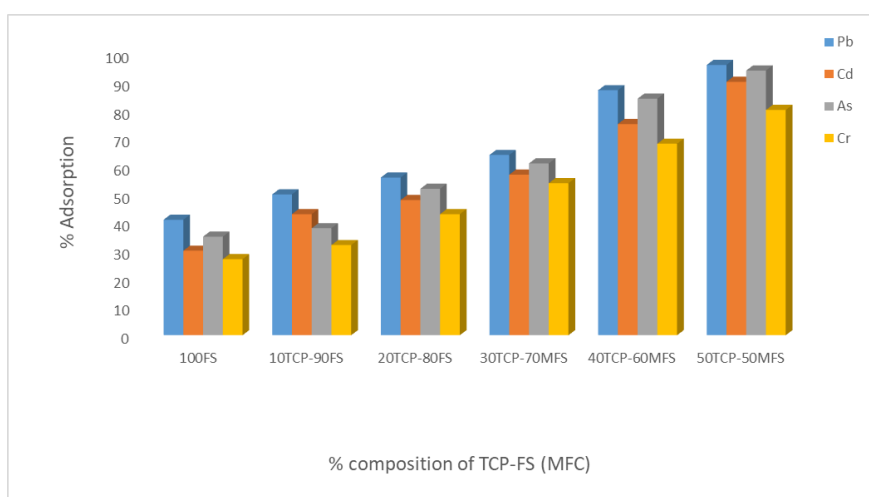


Figure 1 Optimization of Theobroma cacao- feldspar mixtures and calcination on the adsorption of Pb (II), Cd (II), As (III) and Cr (VI) from solution

3.2. Characterization of adsorbents

3.2.1. pH and cation exchange capacity (CEC)

The pH and Cation Exchange Capacity (CEC) of the TCP, FS, and MFC were presented in Table 1.

Table 1 The pH and Cation Exchange Capacity of the TCP, FS, and MFC

Adsorbents	pH	Exchangeable cations (meq/100g)				CEC (meq/100g)
		Ca	Mg	K	Na	
TCP	7.08±0.12	3.34±0.3	3.74±0.11	1.41±0.7	0.64±0.08	9.13 ± 0.09
FS	4.95±0.36	1.08±0.1	0.45±0.02	3.31±0.4	1.58±0.23	6.42 ± 0.45
MFC	7.60±0.01	5.57±0.9	3.85±0.00	13.88±0.5	7.36±0.99	30.66± 0.21

pH was measured as 4.95 ± 0.36 for the FS and 7.08 ± 0.12 for the TCP while the pH of MFC adsorbent was 7.60 ± 0.01. The CEC of the adsorbents was calculated from the summation of exchangeable cations (Mg²⁺, Ca²⁺, K⁺ and Na⁺) of the adsorbents. From the results, MFC had the highest value for CEC (30.66 ± 0.21 meq/100g) compared to TCP (9.13 ± 0.09

meq/100g) and FS (6.42 ± 0.45 meq/100g). This implies that MFC, a composite resulting from the combination of FS and TCP has improved ion-exchange capacity from the surface modification process.

3.2.2 Fourier Transform Infrared (FTIR) spectroscopy analysis

The infrared spectra of TCP, FS, and MFC were shown in Figure 2 (a, b, and c). FTIR spectra of TCP showed several absorption peaks between the scanning frequency ranges of 4000–500 cm^{-1} . The peak exhibits a broad and strong –OH band at 3479 cm^{-1} indicating the presence of hydroxyl, phenolic or carboxylic –OH stretching vibration as typical of cellulose and lignin (i.e. free hydroxyl groups in the polysaccharide structure of its wall). The strong band at 3408 cm^{-1} is a –N–H stretching indicative of vibration associated with N- substituted amide. The two sharp absorption bands at 2923 and 2854 cm^{-1} showed the presence of C–H stretch likely from aliphatic (methyl and methylene) groups. The sharp band appearing at 1747 cm^{-1} is characteristic of typical C=O stretch bond from either a free acid or esterified carboxyl group. However, a distinct absorption band at 1651 cm^{-1} is assigned to a C=O stretching vibration of carbonyl group. The strong band appearing at 1380 cm^{-1} suggests a carboxylate ester. Moreover, the prominent band at 1057 cm^{-1} is associated with the C–O bond or –C–C– stretching such as glycosidic linkage which are characteristic of polysaccharides. Similar observations have been reported by [5], [6] and [18].

Table 2 X-ray fluorescence analysis of feldspar (FS), *Theobroma cacao* pod (TCP), and MFC

% Oxide	FS (%)	TCP (%)	MFC (%)
SiO ₂	63.20 ± 0.45	0.20 ± 0.36	60.20 ± 0.50
Al ₂ O ₃	16.00 ± 0.33	0.05 ± 0.45	10.90 ± 0.01
Na ₂ O	5.13 ± 0.12	0.13 ± 0.21	6.13 ± 0.00
K ₂ O	9.76 ± 0.88	2.76 ± 0.11	10.76 ± 0.35
CaO	2.17 ± 0.10	1.17 ± 0.45	2.17 ± 0.77
Fe ₂ O ₃	0.49 ± 0.00	0.49 ± 0.21	0.40 ± 0.14
TiO ₂	ND	ND	ND
MgO	1.37 ± 0.99	0.37 ± 0.01	1.37 ± 0.31
LOI	0.06 ± 0.46	6.06 ± 0.41	0.06 ± 0.22

ND = below detectable limit

The FT-IR spectra of feldspar (FS) exhibit a strong band at at 3670 cm^{-1} indicatives of the presence of hydroxyl group (–OH stretching vibration) lying between the octahedral sheets in the feldspar mineral surface. This peak at 3670 cm^{-1} is characteristic of –OH group residing at the surface of the layer that form weak hydrogen bonds with oxygen of the Si–O–Si bonds on the lower surface of the next layer. The absorption peaks noticed at 3447 and 1637 cm^{-1} are H–O–H stretching and bending vibrations from absorbed water. The strong peak at 1366 cm^{-1} is suggestive of Si–O stretching vibration band. Bands at 1067 and 952 cm^{-1} correspond to the Si–O and Al–OH in plane bending vibrations, respectively. The peaks at 993 and 767 cm^{-1} were attributed to SiO₂ and Al–OH deformation. The two medium but weak peaks at 615 and 559 cm^{-1} indicate the presence of Si–O stretching as well as –OH bending vibration respectively. FT-IR spectra analysis confirmed that the aluminosilicate material composed of feldspar [7, 8, 9].

For the MFC adsorbent, as it could be seen (Figure 2c), changes in the absorption bands of the feldspar after TCP modification were observed in the spectrum which is an indication of the successful modification of the adsorbent. The absorption band of the TCP/feldspar (MFC) appearing at 3432 and 3696 cm^{-1} has been enhanced, which resulted from vibration bands of TCP (O–H and N–H stretching) overlap with the bands of feldspar (–OH stretching of H₂O). The bands at 2928, 2849 cm^{-1} and 1380 cm^{-1} related to the intercalated TCP (–CH₂ stretching and C–H bending on methyl and methylene groups) are seen in the spectra of the bio-based (MFC) composite [5, 9]. The Si–O bending vibration observed at 1034 cm^{-1} showed a significant shift when compared to that of the raw feldspar. This suggests that the peak position is perhaps one of the active sites for interaction of the feldspar with the TCP biomass [17, 18]. The band at 1626 cm^{-1} attributed to the deformation vibration of the protonated amine group (–N–H) of TCP was also observed in the MFC. The intensity of the band at 1626 cm^{-1} of the MFC spectra has increased with a pronounced band shift from the original constituent materials, indicating the first NH–CO group stretching vibration of TCP overlap with –OH bending vibration of H₂O in the interlayer of feldspar. More so, corresponding to the vibration bands of silicates, and other adsorption bands are relatively similar to those of the feldspar sample with only slight shift indicating the MFC adsorption active

sites responsible for binding of metal ions [3, 5, 17]. Overall, FTIR spectra confirmed that the MFC is indeed a composite consisting of feldspar (FS) and *Theobroma cacao* pod (TCP).

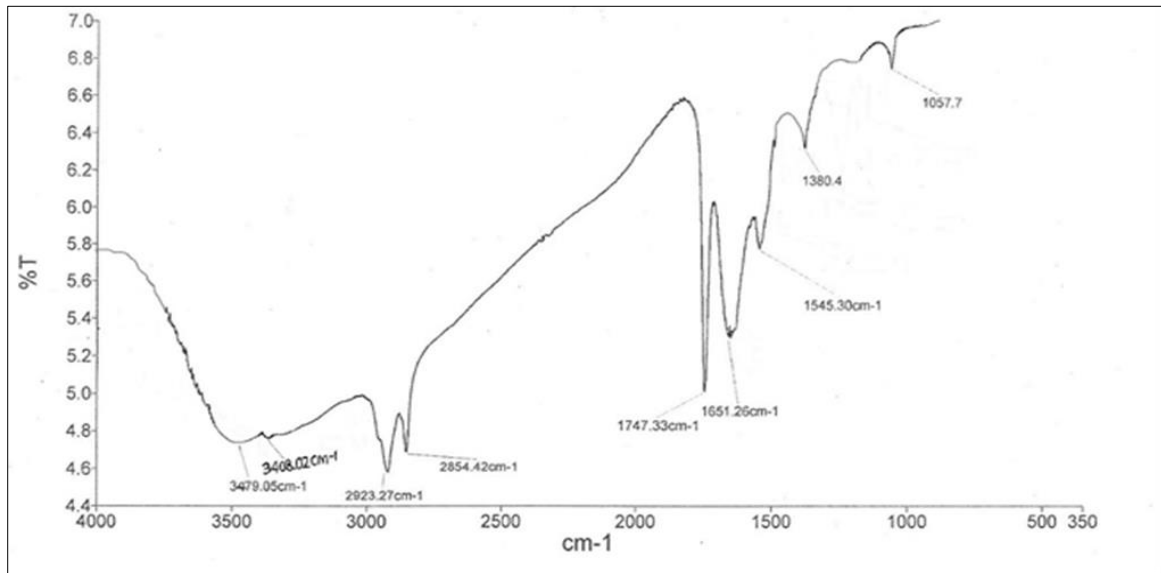


Figure 2(a) FTIR Spectra of *Theobroma cacao* pod (TCP)

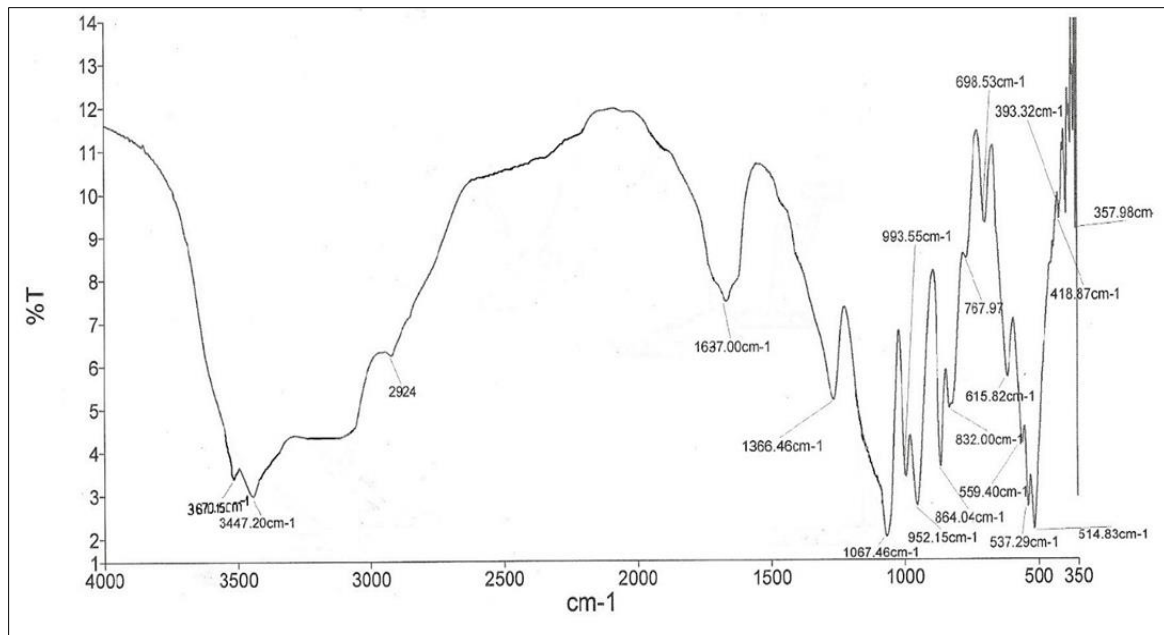


Figure 2(b) FTIR Spectra of unmodified feldspar (FS)

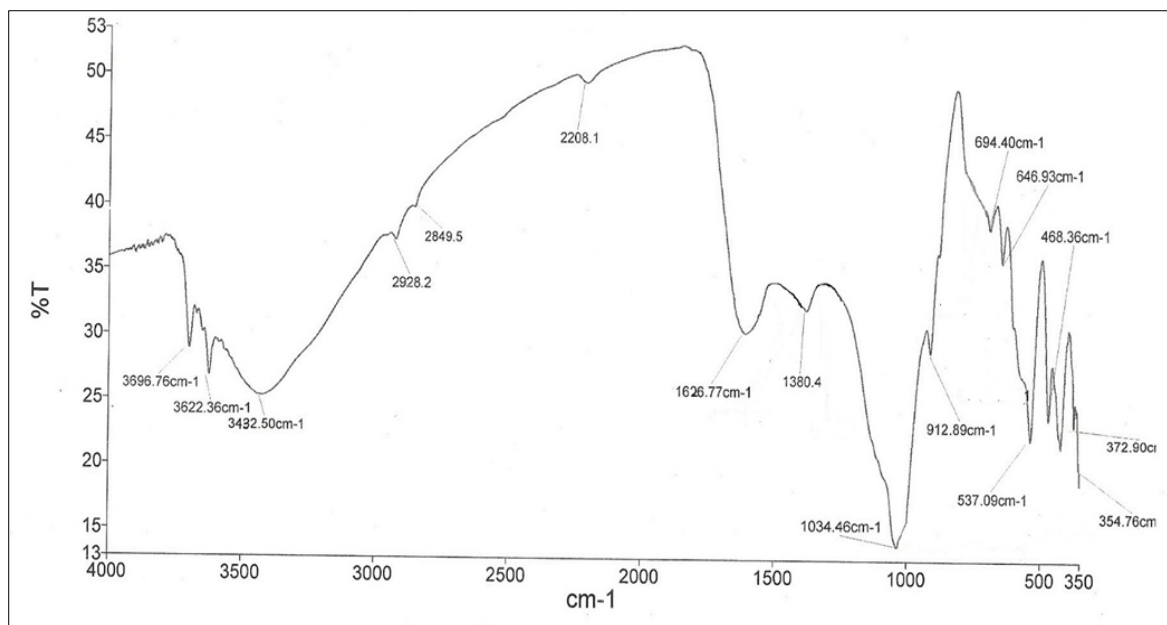


Figure 2 (c) FTIR Spectra of modified feldspar composite (MFC)

3.2.3 X-ray Fluorescence (XRF) Analysis

Table 2 showed the results obtained from X-ray fluorescence (XRF) analysis of the adsorbents. XRF detected only a slight change in the Si/Al ratio before and after modification of the feldspar. MFC has a higher silica to alumina ratio (5.52) than the FS (3.95) which might be associated with the leaching of silicon and aluminum by base treatment during the surface modification process [5, 9]. From XRF results, it was observed that the percentage composition of K is higher than Na and Ca in the feldspar sample, suggesting an orthoclase (K- feldspar) [5, 8]. XRF also finds a number of other elements (Fe, Ca and Mg) that are typical of the raw feldspar [5, 8, 9, 18]. XRF did, however, detected the elements only at low levels in TCP except for K and Ca which are essential minerals.

3.2.4 X-ray diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis of the FS sample showed that it is a feldspar containing orthoclase, microcline and quartz (Figure 3). This suggests that the feldspar has two variety (phases) of K-feldspar minerals; the orthoclase (O) and microcline (M) [5, 9]. The reflections at 20.08° (2θ) (3.83 \AA , 201) and 25.6° (2θ) (3.11 \AA , 002) could be assigned to that of orthoclase and microcline minerals respectively. The reflections at 20.08° (2θ) (3.83 \AA , 201), 25.6° (2θ) (3.11 \AA , 002) and 27.80° (2θ) (2.89 \AA , 040), 30.44° (2θ) (2.67 \AA , 131) indicated that the crystals of the feldspar sample used in this study were partly monoclinic and partly triclinic [5, 9]. The reflection at 26.60° (2θ) is from quartz (3.00 \AA , 131), which is also present in the raw material. The XRD pattern of feldspar showed typical diffraction peaks at $2\theta = 13.25^\circ$ (6.6 \AA) and 14.40° (6.14 \AA), whereas, after incorporating with TCP, these peaks shift to lower angles and even disappear. The disappearance of the feldspar reflection at $2\theta = 14.40^\circ$ and the appearance of a new reflection at 11.25° 2θ in the XRD pattern of MFC composite showed that intercalation has occurred (Yazdani *et al.*, 2014). These results suggested that the order along the crystallographic c-axis of feldspar is slightly disturbed by the reaction between the TCP and the FS. The rest of the crystal structure is not affected by the MFC preparation process, indicating that the crystallography of the individual aluminosilicate layers is not affected. Similar observation was reported [5, 9, 10]. The XRD patterns of the TCP with two broad and overlapping reflections essentially indicate a low order structure. Correspondingly, the XRD patterns of the MFC have increased intensity than those of the FS indicating that the incorporation of TCP via calcination cause little orderliness in the resulting MFC material, presumed by disturbing the interlayer geometry between individual feldspar mineral layers. This likely confirmed the disordered intercalation in MFC composite as reported [4, 5, 19].

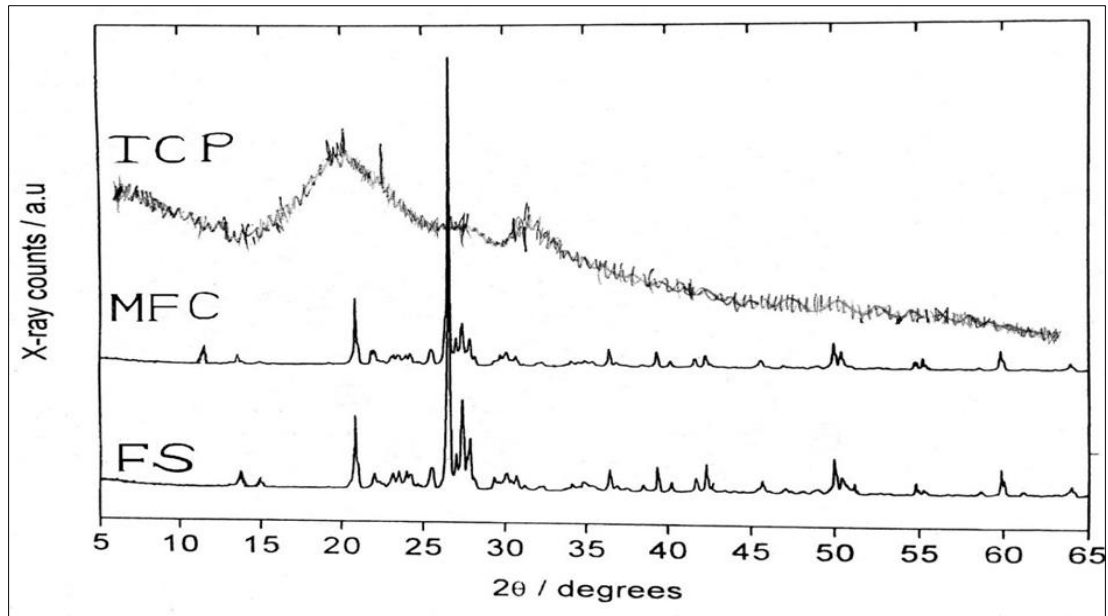


Figure 3 XRD patterns of TCP, FS and MFC adsorbents

3.2.5 SEM Analysis

Figure 4 (a, b and c) showed scanning electron microscopy (SEM) of the TCP, FS, and MFC respectively. The SEM is used to examine the surface morphology and the porous nature of the material responsible for adsorption of metal ions. The SEM images supported the XRD results, as there was no significant morphological disparity between the FS and MFC. Both adsorbents are porous, consisted of considerable number of heterogeneous pores, irregular surface and particle aggregation of various shapes and sizes with relatively flat facets, which is typical of feldspar mineral [2, 8]. The presence of pores helps in the diffusion of metal ions into the adsorbents during the adsorption of metal ions from solution [5, 17]. Also, the SEM image of FS and MFS showed some white clumps or particles on the surface, these were probably due to the presence of non-clay minerals like potassium, magnesium, sodium and calcium [5, 20]. From the image of MFC (Figure 4 c), it was observed that the bio-based composite smaller particle sizes compared to the raw feldspar.

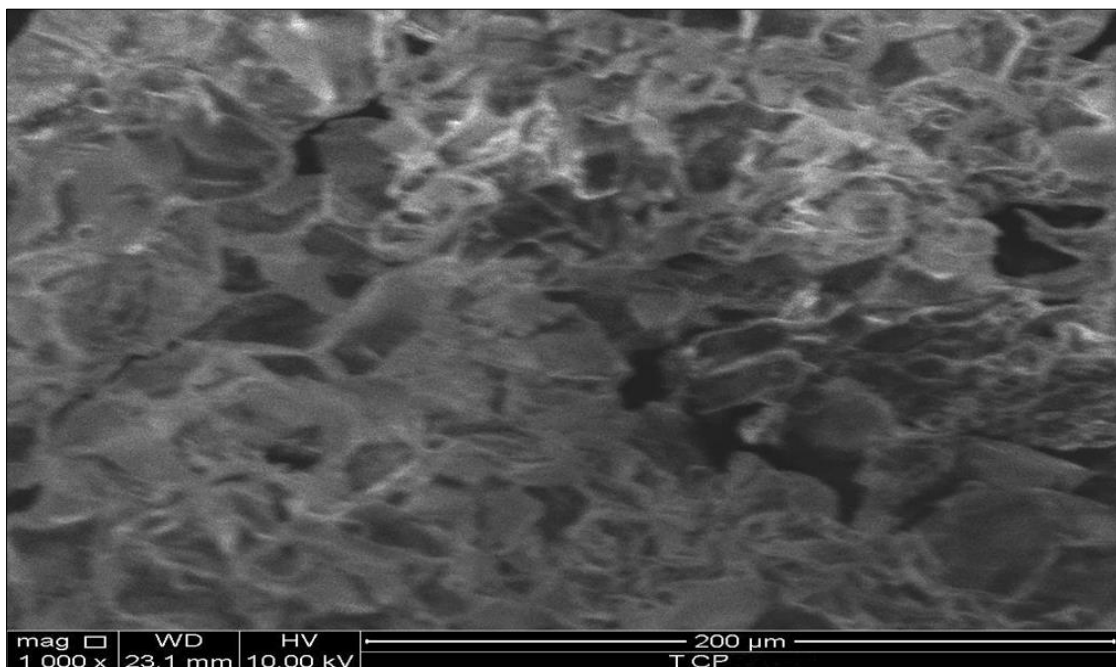


Figure 4 (a) Scanning Electron Micrograph of TCP

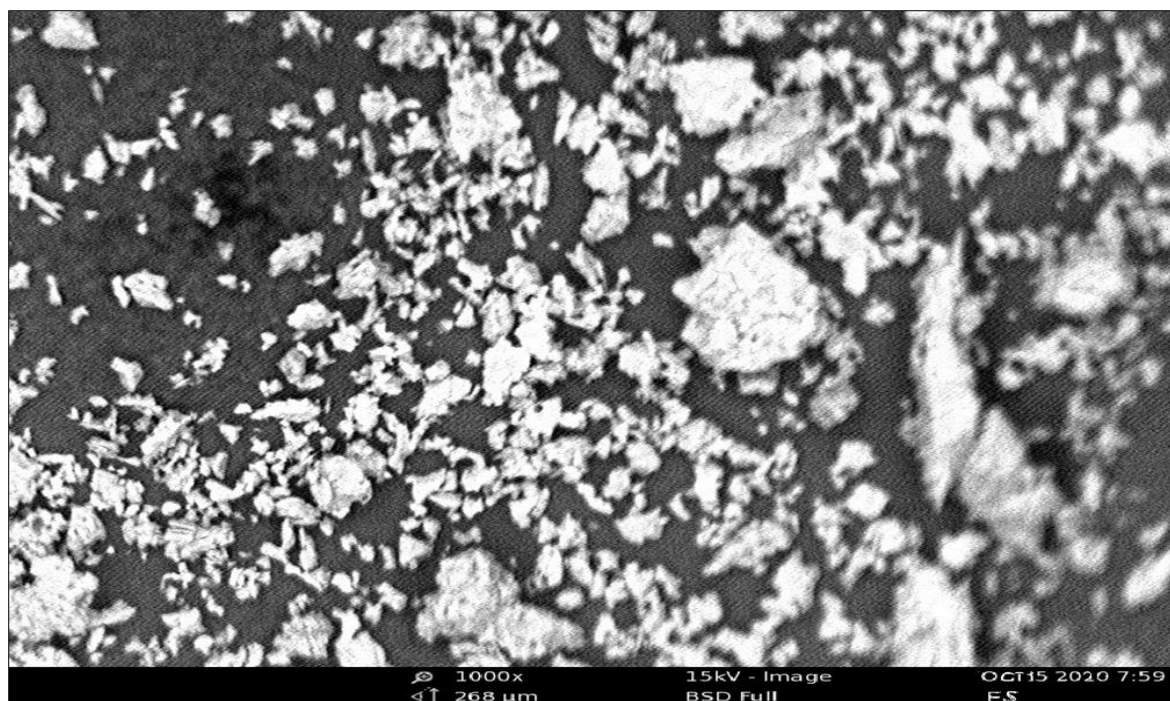


Figure 4 (b) Scanning Electron Micrograph of FS

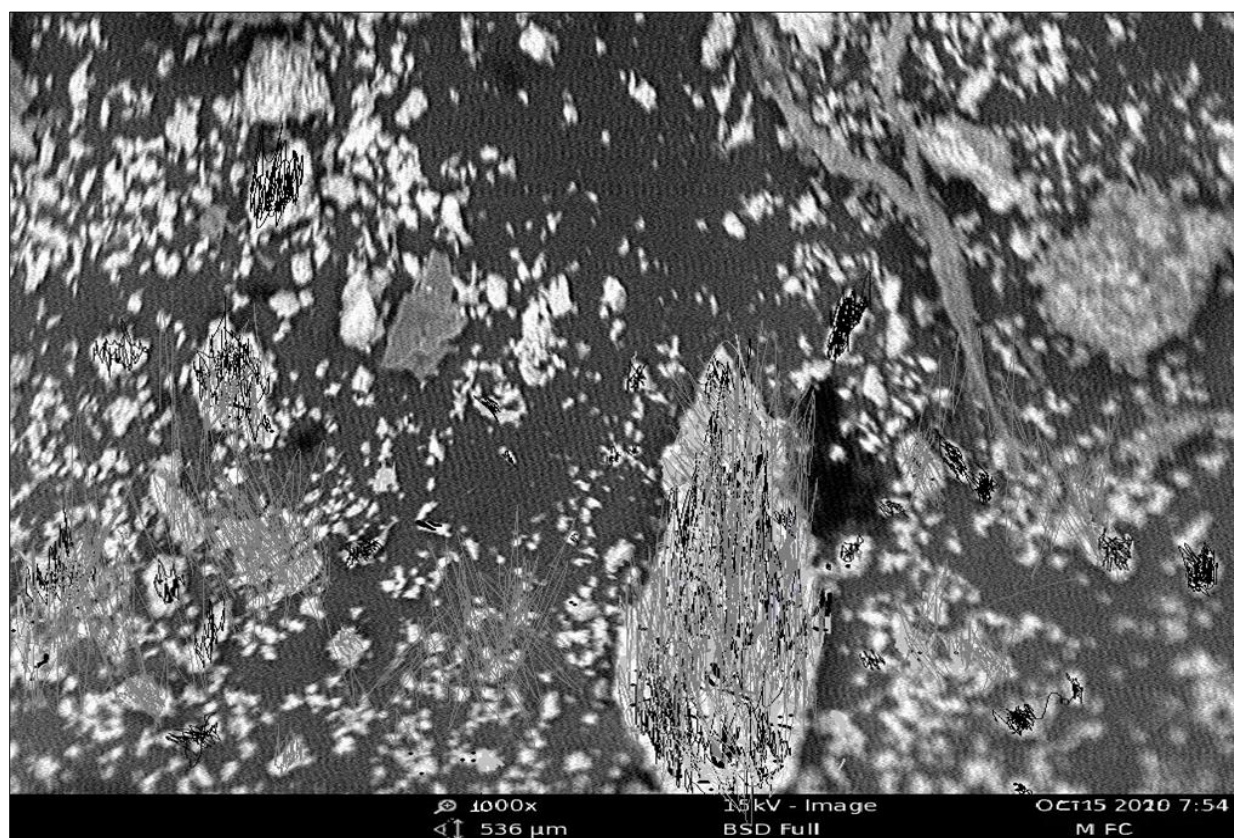


Figure 4 (c) Scanning Electron Micrograph of MFC

3.2.6 BET Surface Area and Particle size Analysis

The results of cation exchange capacity (CEC) (Table 1) and the surface area (SA) (Table 3) supported the FTIR, XRF, XRD, and SEM images. The results reflected the similarities and differences between the FS and MFC. The MFC adsorbent

showed an increased specific surface area ($53.60 \pm 0.3 \text{ m}^2/\text{g}$) compared to FS ($21.56 \pm 0.1 \text{ m}^2/\text{g}$) and TCP ($15.36 \pm 0.1 \text{ m}^2/\text{g}$), suggesting that the new material has the smallest particle sizes. This is supported by the results of particle size analysis of the adsorbents in which the particles sizes decreased from a mean size of $162.8 \pm 0.16 \mu\text{m}$ (FS) and $217.6 \pm 0.12 \mu\text{m}$ (TCP) to $105.4 \pm 0.18 \mu\text{m}$ for the MFC adsorbent. Finally, the CEC increased from $6.42 \pm 0.45 \text{ meq}/100\text{g}$ (FS) and $9.13 \pm 0.09 \text{ meq}/100\text{g}$ (TCP) respectively to $30.66 \pm 0.21 \text{ meq}/100\text{g}$ (MFC) upon functionalization. The narrow pore diameter ($8.571 \pm 0.11\text{nm}$) indicated a micropores dimension as improvement from feldspar mesopores ($30.65 \pm 0.03\text{nm}$). These mesopores were responsible for transporting metal ions into the micropores of MFC, consequently improving the adsorption capacity of the MFC [5, 18, 19].

Table 3 The Specific surface area, particle size and pore volume results of TCP, FS and MFC

Parameters	FS	TCP	MFC
Specific surface area (m^2/g)	21.56 ± 0.10	15.36 ± 0.10	53.60 ± 0.30
Average pore diameter (nm)	30.65 ± 0.03	10.28 ± 0.50	8.571 ± 0.11
Total pore volume (cm^3/g)	0.470 ± 0.00	0.651 ± 0.00	0.253 ± 0.05
Particle size (μm)	162.8 ± 0.16	217.6 ± 0.12	105.4 ± 0.18

Overall, FTIR, XRF, XRD and SEM confirmed that the composite (MFC) was essentially identical to the feldspar (FS) starting material; a tectosilicate with only slight modification. These observations were reported in a similar studies by [4, 5, 9, 20].

4. Conclusion

Feldspar and its composite with *Theobroma cacao pod* (MFC) were prepared and characterized for physicochemical parameters such as the pH and cation exchange capacity (CEC). The instrumental techniques used were FTIR, XRF, XRD, SEM and BET for surface properties analysis. The FTIR, XRF and XRD results showed that the major functional groups and elements on both samples are OH, methylene groups and potassium (K), silica and alumina due to the chemical structure of the feldspar and its composite. The SEM analysis revealed that both FS and the agro-based modified feldspar composite (MFC) are porous, consisted of considerable number of heterogeneous pores, irregular surface and particle aggregation of various shapes and sizes. In addition to this, high porosity was observed with both materials. The surface areas of feldspar and composite were found to be $21.56 \pm 0.10 \text{ m}^2/\text{g}$ and $53.60 \pm 0.30 \text{ m}^2/\text{g}$ respectively. Furthermore, the sizes of the composite particles were about $105.4 \mu\text{m}$ as revealed by the particle size analysis. The characterization results for the novel composite from synergetic combination of feldspar and TCP indicated that the MFC has the potential applications for environmental and industrial utility such as polymer fillers, ion-exchangers and adsorbents in wastewater treatment.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare that they have no known competing financial interest or personal relationships that could appear to influence the work reported in this paper.

References

- [1] Saif, Muhammad Jawwad., Asif, Hafiz Muhammad and Muhammad Naveed. Properties and Modification Methods of Halloysite Nanotubes: A State-of-the-Art Review. *J. Chil. Chem. Soc.* 2018; 63(3): 4109-4125.

- [2] Dang VBH, Doan HD, Dang VT, Lohi A. A Study on Heavy Metal Adsorption Using Shrimp Shell. *Journal of Bio-resources Technology*. 2009; 10(5): 211-223.
- [3] Ogbu IC, Akpomie KG, Osunkunle AA, Eze SI. Sawdust-kaolinite composite as efficient sorbent for heavy metal ions. *Bangladesh J. Sci. Ind. Res.* 2019; 54(1): 99-110.
- [4] Sanusi KA, Babayo AU, Isyaka MS. Evaluation of the Application of Modified Feldspar Clay for Adsorption of Pb+2 and Cu+2 in Aqueous Media: Equilibrium and Thermodynamic studies. *Journal of Environmental & Analytical Toxicology*. 2016; 6 (2): 02-09.
- [5] Sanusi, K. A., Yahaya, Y., Ambrusa, M. M., Rabiou, A. K., and Hamed, A. M. Optimization of Adsorption of Pb (II) and Cr (VI) from Aqueous Solution using Modified Feldspar Composite: Isotherm and Kinetic Studies. *International Journal of Engineering Science Technologies*. 2021; 5(4), 18-53.
- [6] Olu-Owolabi B, Oputu OU, Adebowale KO, Ogunsolu O, Olujimi OO. Biosorption of Cd²⁺ and Pb²⁺ ions onto mango stone and cocoa pod waste: Kinetic and equilibrium studies. *Scientific Research and Essays*. 2012; 7(15):1614-1629.
- [7] Yazdani M, Bahrami H, Arami M. Preparation and Characterization of Chitosan/Feldspar Biohybrid as an Adsorbent: Optimization of Adsorption Process via Response Surface Modeling. *The Scientific World Journal*. 2014; 20(14): 1-13.
- [8] Awala HA, El Jamal MM. Equilibrium and kinetics study of adsorption of some dyes onto feldspar. *Journal of Chemical Technology and Metallurgy*. 2011; 46(1): 45-52.
- [9] Unuabonah IE, Gunter C, Weber J, Lubahn S, Taubart A. Hybrid Clay: A New Highly Efficient Adsorbent for Water Treatment. *Journal of Industrial and Engineering Chemistry*. 2013; 132: 252-255.
- [10] Ofomaja AE, Unuabonah EI, Oladoja NA. Competitive modeling for the biosorptive removal of copper and lead ions from aqueous solution by *Mansonia* wood sawdust. *Journal of Bioresource Technology*. 2010; 101(11): 3844-3852.
- [11] Adebowale KO, Unuabonah IE, Olu-Owolabi BI. The effect of some operating variables on the adsorption of lead and cadmium ions on kaolinite clay. *Journal of Hazardous material*. 2005; 134: 130-139.
- [12] Olu-Owolabi BI, Alimoh H Alabi, Emmanuel I Unuabonah, Paul N Diagboya. Calcined bentonite-biomass composites for removal of aqueous metal ions. *Journal of chemical and engineering technology*. 2016; 4: 1379-1383.
- [13] Singh Rimmy, Rachna Bhatia. Optimization and Experimental Design of the Pb²⁺ Adsorption Process on a Nano-Fe₃O₄-Based Adsorbent Using the Response Surface Methodology. *ACS Omega*. 2020; 5: 28305-28318.
- [14] Hossain MA. Development of novel biosorbents in removing heavy metals from aqueous solution. PhD Thesis, School of Civil and Environmental Engineering, Faculty of Engineering and Information Technology, University of Technology, Sydney (UTS) Sydney, Australia. 2013; 57-65.
- [15] Salih AM. The purification of industrial wastewater to remove heavy metals and investigation into the use of zeolite as a remediation tool. A thesis submitted in partial fulfilment of the requirements of the University of Wolverhampton for the degree of Doctor of Philosophy. 2017; 31-33.
- [16] Dawood SA. Synthesis and Characterization of Biomass and Clay Mineral Based Adsorbents for the Removal of Cationic Dye and Metal Ion from Wastewater by Adsorption. Faculty of Science and Engineering, WA School of Mines: Minerals, Energy and Chemical Engineering. Thesis is presented for the Degree of Doctor of Philosophy of Curtin University. 2018; 57-69.
- [17] Akpomie KG and Dawodu FA, Montmorillonite-rice husk composite for heavy metal sequestration from binary aqua media: a novel adsorbent, *Transactions of the Royal Society of South Africa*. 2014b; 54: 32-39.
- [18] Chukwuemeka-Okorie Helen O, Peter N Ekemezie, Kovo G Akpomie, Chisom S Olikagu. Calcined Corn-cob-Kaolinite Combo as New Sorbent for Sequestration of Toxic Metal Ions from Polluted Aqua Media and Desorption. *Frontiers in Chemistry*. 2018; 273(6): 1-13.
- [19] Anusa R, Ravichandran C, Sivakumar EKT. Removal of heavy metal ions from industrial waste water by nano-ZnO in presence of electrogenerated Fenton's reagent. *International Journal of Chem Tech Research*. 2017; 10(7): 501-508.
- [20] Ozdes Duygu, Celal Duran, Hasan Basri Senturk. Adsorptive removal of Cd(II) and Pb(II) ions from aqueous solutions by using Turkish illitic clay. *Journal of Environ. Management*. 2011; 92: 3082-3090.

- [21] Sanusi KA, Babayo AU, Isyaka MS. Evaluation of the Application of Modified Feldspar Clay for Adsorption of Pb²⁺ and Cu²⁺ in Aqueous Media: Equilibrium and Thermodynamic studies. *Journal of Environmental & Analytical Toxicology*. 2016; 6 (2): 02-09.
- [22] Singh Rimmy, Rachna Bhatia. Optimization and Experimental Design of the Pb²⁺ Adsorption Process on a Nano-Fe₃O₄-Based Adsorbent Using the Response Surface Methodology. *ACS Omega*. 2020; 5: 28305–28318.
- [23] Unuabonah IE, Olu-Owolabi BI, Adebowale KO, Ofomaja AE. Adsorption of lead and cadmium ions from aqueous solutions by tripolyphosphate-impregnated kaolinite clay. *Journal of Colloids and surfaces*. 2007; 82: 202-211.
- [24] Unuabonah IE, Gunter C, Weber J, Lubahn S, Taubart A. Hybrid Clay: A New Highly Efficient Adsorbent for Water Treatment. *Journal of Industrial and Engineering Chemistry*. 2013; 132: 252-255.
- [25] WHO. Guidelines for drinking water quality by World Health Organization, Geneva, Switzerland. 2000.
- [26] Yazdani M, Bahrami H, Arami M. Preparation and Characterization of Chitosan/Feldspar Biohybrid as an Adsorbent: Optimization of Adsorption Process via Response Surface Modeling. *The Scientific World Journal*. 2014; 20(14): 1-13.