



## Original Article

# Organo-Clay Composites of Intercalated 4-Methylaniline and Its Schiff Base Derivative: Preparation and Characterization

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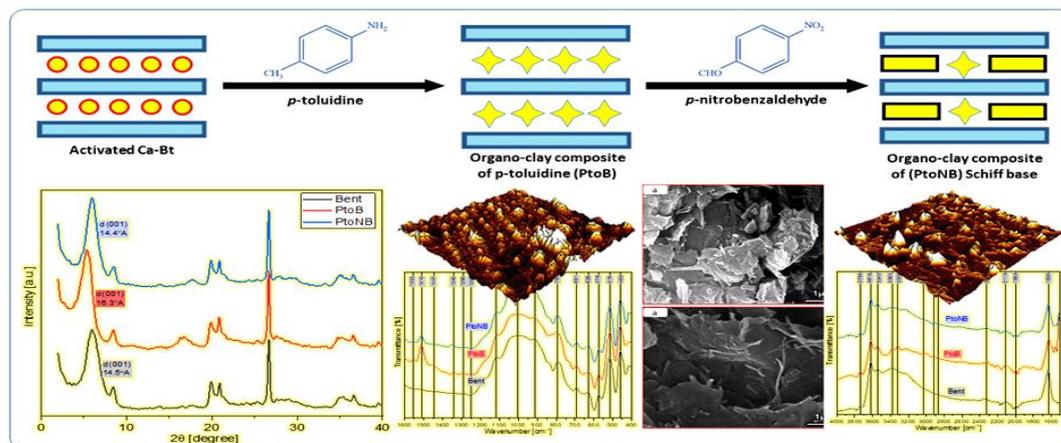
Intercalation

Organo-clay composite

## ABSTRACT

4-methylaniline and its Schiff base derivative were intercalated into the Bentonite clay interlayers in a solid state reaction followed by a condensation reaction to produce two organo-clay composites. X-ray diffraction was used to identify the changes in basal spacing of montmorillonite layers which exhibited noticeable alteration before and after the formation of the composites. FT-IR spectra, on the other hand, were utilized for identifying the structural compositions of the prepared materials as well as the formation of the intercalated Schiff base derivative. The surface morphology of the composites was examined by Scanning Electron Microscopy SEM and Atomic Force Microscope AFM, which reflected some differences in the surface of prepared composites as the particle size decreased with the Schiff base formation.

## GRAPHICAL ABSTRACT



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## Introduction

Clay minerals are the most abundant and widespread materials in both terrestrial and aquatic environments that have massive surface area per mass unit [1]. Therefore, these material are used extensively in industrial processes and removal of pollutants due to the strong biogeochemical effects of their surface reactions in both soil and water molecules [2].

However, one of the most known clay minerals is the bentonite clay that contains mainly montmorillonite and other components with its unit cells made of two tetrahedral silica sheets with octahedral alumina sheet located in the center of silica sheets; in-between these unit cells, water molecules and inorganic ions are flooding [3, 4].

Schiff bases, on the other hand, are considered as one of the most important types of organic molecules due to their variety of applications in many fields. More specifically, Schiff bases that have aromatic moieties are found to be connected with asymmetric catalysis, which can be attributed to the variety of behaviors of their electronic and steric properties [5]. Moreover, the biologically active Schiff base complexes are utilized as ligands in the transition metal complexes, which have many usages such as radio-pharmaceuticals for targeting cancer cells [6], biological macromolecules [7], catalysts [8], dioxygen carriers [9], as well as agrochemical agents[10].

Furthermore, the intercalation of organic molecules into the clay interlayers represent one of the most widespread agricultural, environmental and industrial reactions in the earth. As the inorganic ions are exchanged by organic ions where organic ions or molecules are transferred from the solution right to the clay surface, which accumulate the polar and nonpolar molecules on the surface clay mineral. Typically, chemical or physical bonds are formed between the organic molecules and the clay

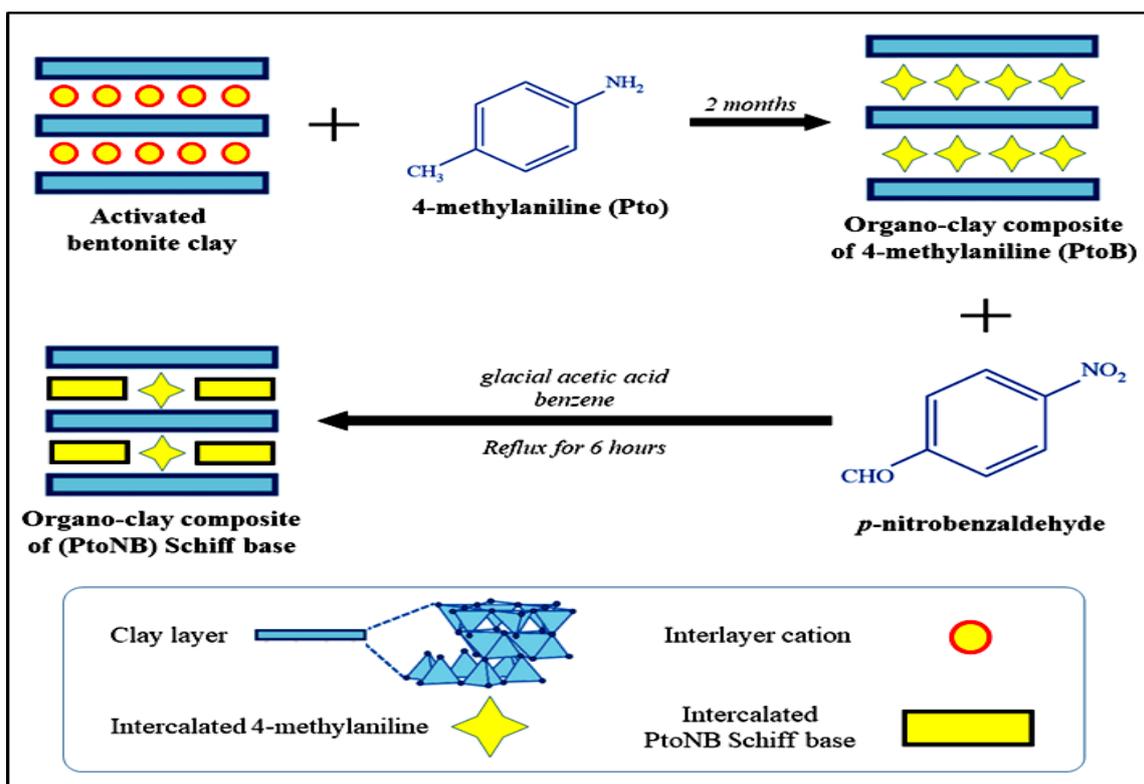
surface in order to form organo-clay composites. These intercalating reactions and their mechanisms have been studied and reviewed widely, especially during the last century [11, 12].

## Materials and Methods

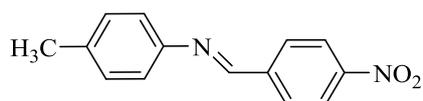
Local bentonite clay was supplied from the Iraqi Geological Survey, which was then modified and acidly activated, according the procedure recorded in our previous study [13]. 4-methylaniline (Pto) and 4-nitrobenzaldehyde was supplied from Sigma alderch.

### *Preparation of the organo-clay composites*

Aniline derivative (Pto) was intercalated into the interlayer of modified clay through solid state reactions. The clay powder and Pto were grounded using an agate mortar and a pestle at room temperature for one hour in a 4:1 ratio, respectively, accompanied by adding several drops of deionized water. However, the mixture was left for two months to allow the guest molecules to penetrate the interlayer of host material as the organo-clay composite of 4-methylaniline "PtoB" was formed with reddish brown color that indicated the intercalating process (Figure 1). After that, 10 gm of the prepared PtoB in a powder form was dispersed in 80 mL of benzene solvent. Further, 16.50 mmol of 4-nitrobenzaldehyde was dissolved in 20 mL of the solvent and acidified by several drops of 1 N of glacial acetic acid. Both the suspended solutions of PtoB and 4-nitrobenzaldehyde were reflexed for six hours under 80°C. Moreover, the yielded material was left to be cooled down and settled, followed by filtration and drying overnight. Figure 1 illustrate the preparation of PtoB and PtoNB organo-clay composites. However, the Schiff base prepared in the clay mineral interlayers had a chemical structure as depicted in Scheme 1.



**Figure 1:** Schematic illustration of the preparation of organo-clay composites of PtoB and PtoNB



**Scheme 1:** Chemical structure of Pto-NB Schiff base compound

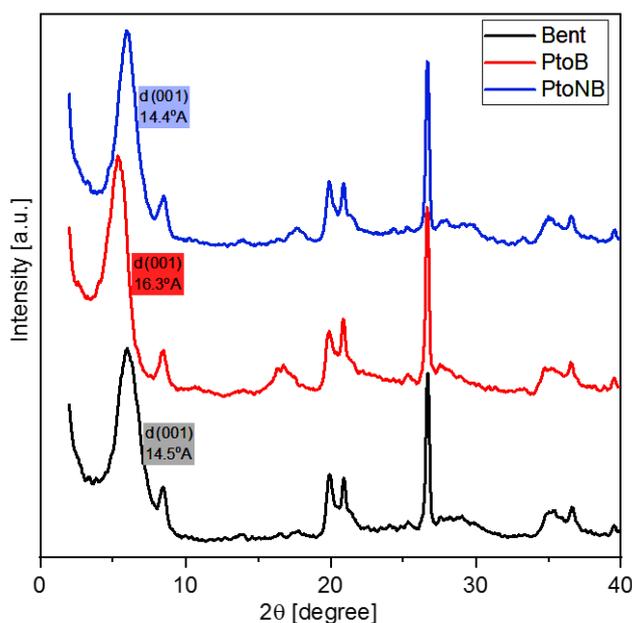
#### Samples characterization

The diffractograms of the prepared materials was recorded by using XLab 6100 model of Shimadzu X-ray diffractometer, whereas FTIR spectra were recorded on Alpha II model of Bruker FTIR spectrometer with the aid of ATR module with the spectral range between 400 and 4000  $\text{cm}^{-1}$  while the spectral resolution was 2  $\text{cm}^{-1}$ . The investigation of surface structure of prepared materials was carried out using Atomic Force Microscope, JPK NanoWizard-II model of BRUKER AFM. On the other hand, high resolution images of the shape and surface of the prepared material were obtained by using the AIS2300C model of SERON Scanning Electron Microscope with 3.0 nm resolution. The diffused reflectance spectra were recorded by utilizing DH-S-BAL model of AvaLight spectrometer with deuterium

halogen source with the range of wavelength (500-2500 nm) aided with dichroic filter.

#### Results and Discussion

Most of the reflections obtained from the XRD diffractograms were almost identical compared with the diffractogram of bentonite clay reported in a previous work [13]. Nevertheless, there were changes which occurred at montmorillonite reflection, located at (5.4-6.1) range of  $2\theta$ , including relative variation in the position of the peaks, changes in the basal spacing  $d(001)$  as well as different relative intensities of the peak as illustrated in Figure 2. These changes can be attributed to the presence of organic compounds, which put a stress upon the structural frame of montmorillonite atoms such as aluminum, silicon, and oxygen alongside the calcium ions.

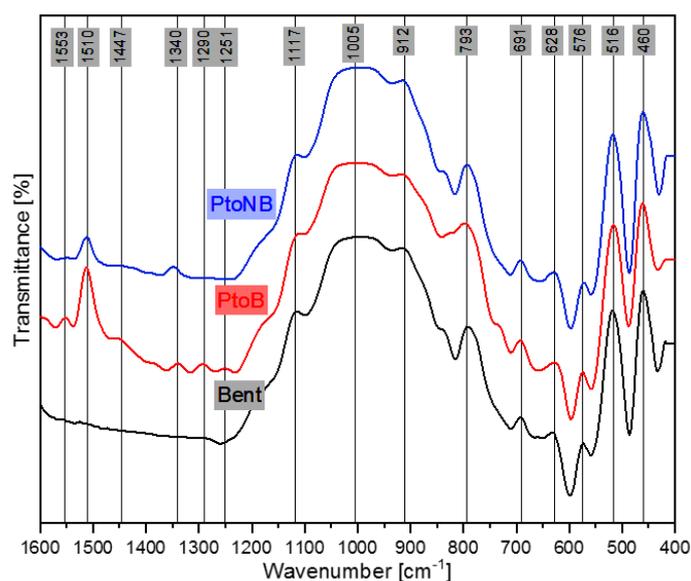


**Figure 2:** XRD diffractograms of (bent) modified clay and organo-clay composites of PtoB and PtoNB

The basal spacing of the modified clay and its composites exhibited noticeable changes specifically for montmorillonite reflection, as the layers expanded to 1.8 Å when (Pto) compound was introduced to clay interlayers because of the high polarity of (-NH<sub>2</sub>) groups. However, when Schiff bases were yielded in-between the clay layers, the basal spacing reduced considerably for value that was similar to the clay alone or even lower than that. This shrinking can be attributed to reducing the polarity of the compound and the ability of creating hydrogen bonds.

FTIR spectra of the prepared composites show some distinctive vibrational bands in the low

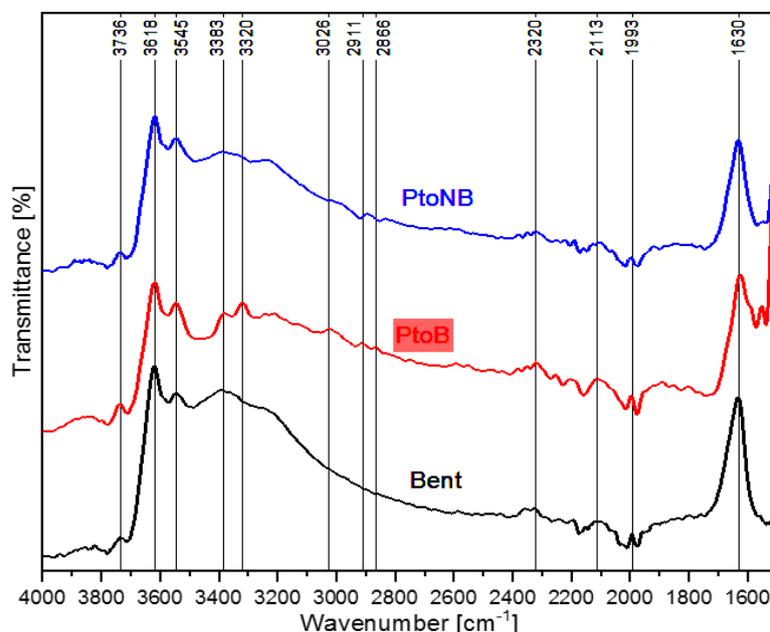
frequency region (1600-400 cm<sup>-1</sup>) as illustrated in Figure 3 and the high frequency region (4000-1600 cm<sup>-1</sup>) as illustrated in Figure 4. The sharp band recorded at 3734, 3619, 3545 and 1632 cm<sup>-1</sup> are assigned to Al-O-Al stretching, O-H stretching of silanol group, HO-H stretching of the water molecules and OH asymmetric stretching of water respectively. However, two peaks appearing at 3383 and 3320 cm<sup>-1</sup> in the PtoB spectrum can be assigned to the N-H stretching vibration, which then disappeared in the PtoNB spectrum due to formation of CH=N group.



**Figure 3:** FTIR spectra of Bentonite clay (Bent) and organo-clay composites of (PtoB) and (PtoNB) in the low frequency region (1600-400 cm<sup>-1</sup>)

The low frequency region, on the other hand, shows some bands which are characteristic for the prepared composites such as the sharp band appears at  $1004\text{ cm}^{-1}$  which is the characteristic band of silicate layer of montmorillonite mineral representing the triplet degenerate stretching (in-plane) vibration ( $\nu_3$ ) of Si-O bond [14], while  $792\text{ cm}^{-1}$  band corresponds to  $\nu_1$  mode of

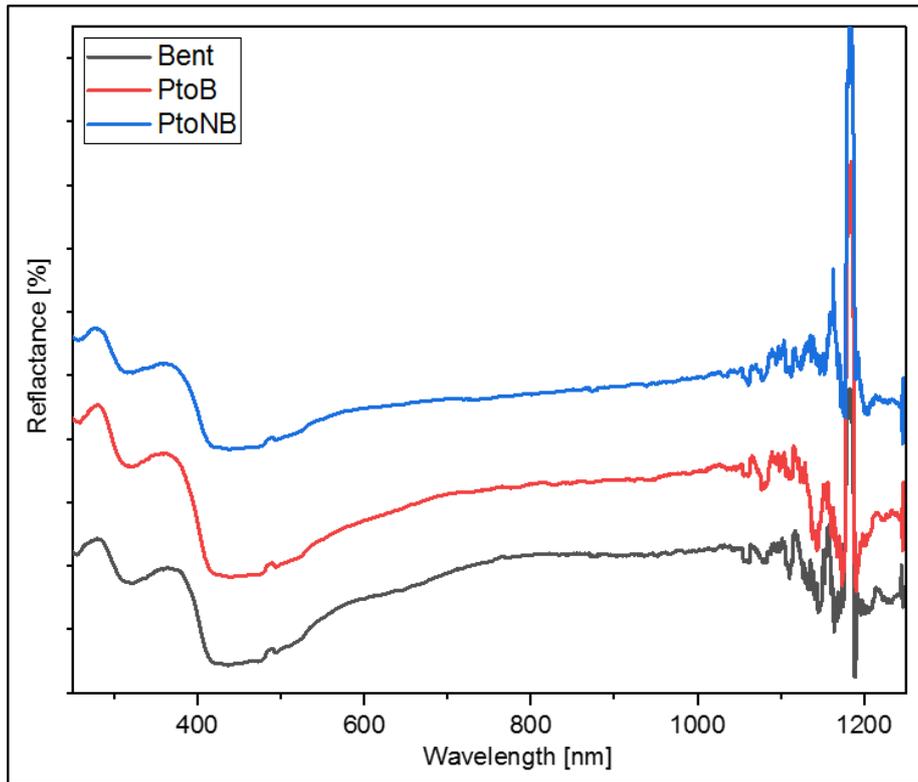
vibration which indicates a partial removal of the degeneracy [15]. However, the band at  $905\text{ cm}^{-1}$  is assigned to hydroxyl deformation mode of Al-OH or Al-OH-Al. The observed band at  $517\text{ cm}^{-1}$  represents the deformation mode ( $\nu_2$ ) of Al-O-Si group, however, the deformation mode of Si-O-Si group is assigned at  $460$  and  $432\text{ cm}^{-1}$  bands.



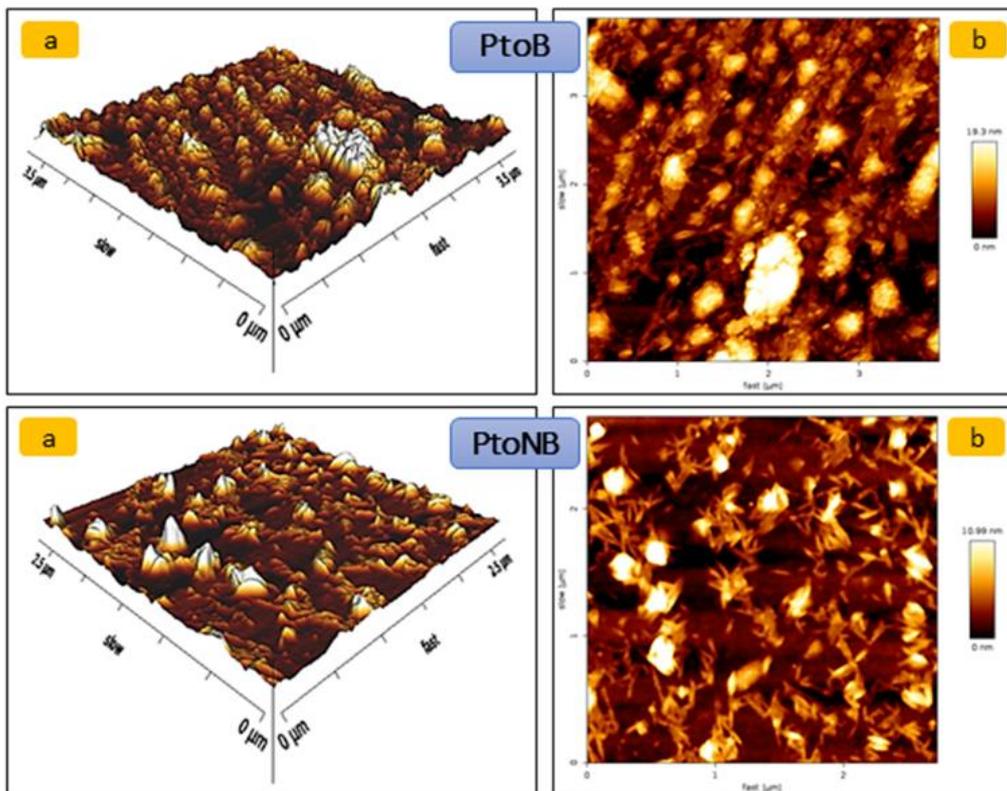
**Figure 4:** FTIR spectra of Bentonite clay (Bent) and organo-clay composites of (PtoB) and (PtoNB) in the high frequency region ( $4000\text{-}1600\text{ cm}^{-1}$ )

The vibrational band at  $1553\text{ cm}^{-1}$  which appeared in the PtoB spectrum and disappeared in the PtoNB spectrum is representing the deformation mode of  $\text{NH}_3^+$  group. The other bands at  $1510$ ,  $1447$ ,  $1340$  and  $1251\text{ cm}^{-1}$  are assigned to C—C aromatic stretching,  $\text{CH}_2$  bending, C—N stretching and C—N—H bending vibrations, respectively. Moreover, some changes toward the higher or lower wavenumbers compared with (bent) bands can be noticed. These changes can be attributed to the incorporation of the organic molecules into bentonite layers. In addition, the diffused reflectance spectra (Figure 5) exhibit no distinctive bands for the prepared composites that indicate the absence of complex formation for both the (Pto) and its Schiff base derivative with the exchangeable cations in the interlayers of the clay.

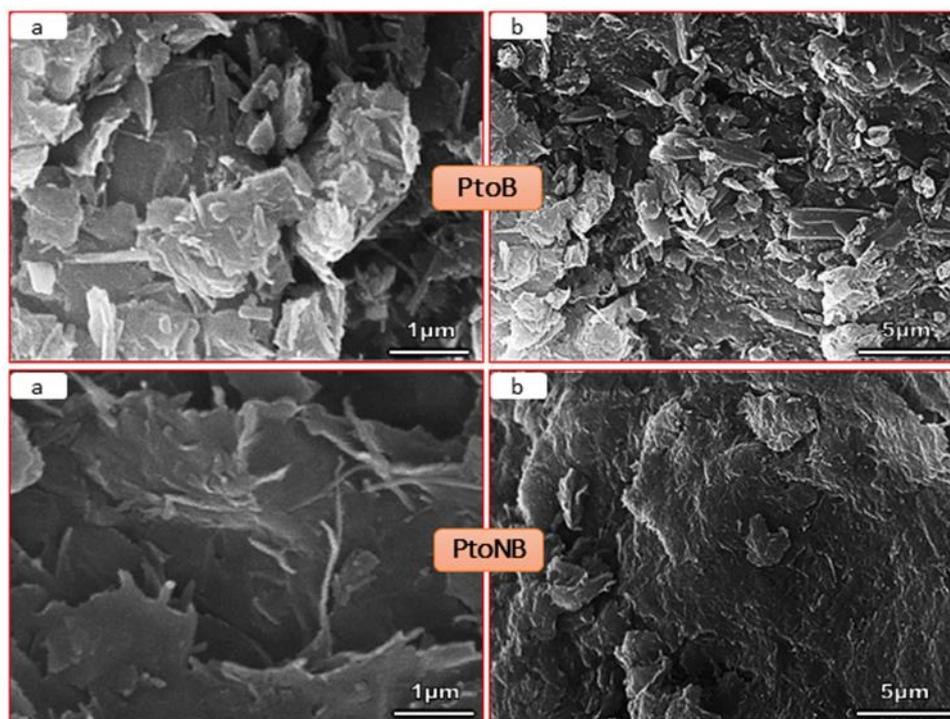
The SEM images of prepared organo-clay composites of PtoB and PtoNB are depicted in Figure 7. The particles appeared with irregular spherical shapes that can be attributed to the close-packed sheets of organo-clay layers. While some sheet fragments appeared in  $1\text{-}5\text{ }\mu\text{m}$  scale images for PtoB composite, which can be attributed to some exfoliated montmorillonite layers, PtoNB composite showed featureless surface. These explanations can be in a good agreement with the AFM 3D and 2D images where the surface of PtoB (Figure 6) exhibited up to  $19\text{ nm}$  as a height of the particles, whereas it was only up to  $11\text{ nm}$  for PtoNB composites (Figure 6). On the other hand, certain pattern of particles' arrangement can be seen in the three-dimensional images that somehow indicates nano-scale arrangement for the prepared composites particles.



**Figure 5:** Diffused reflectance spectra (bent) activated Ca-Bt, (PtoB) and (PtoNB) clay-organic composites of p-toluidine and PtoNB Schiff base respectively.



**Figure 6:** AFM surface images in (a) 3-Dimensions and (b) 2-Dimensions of PtoN and PtoNB



**Figure 7:** SEM images of PtoN and PtoNB at scale of (a) 1µm and (b) 5µm

## Conclusion

The organo-clay composites of 4-methylaniline and its Schiff base derivative have been successfully prepared and characterized by different techniques. The basal spacing of prepared materials has increased with introducing 4-methylaniline for the clay mineral, whereas forming Schiff base derivative has caused noticeable decrease in that spacing. On the other hand, the FTIR spectra of the prepared materials have shown the characteristic bands of the 4-methylaniline and its Schiff base derivative providing an evidence of Schiff base formation. SEM and AFM images illustrate some surface features of the prepared materials and their particle shapes and sizes.

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## Authors' contributions

Based on the recommendations of the international Committee of Medical Journal Editors, all authors met the criteria of authorship.

## Conflict of Interest

We have no conflicts of interest to disclose.

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