Asian Journal of Natural Sciences (AJNS)
Vol.2, No.3, 2023: 163-172

Modification and Characterization of Polyamide Nanocomposites with Organobentonite Cetyltrimethylammonium Bromide

Barita Aritonang[1*], Ahmad Hafizullah Ritonga[2], Karnirius Harefa[3]
Institut Kesehatan Medistra Lubuk Pakam, Lubuk Pakam
***Corresponding Author:** Barita Aritonang baritaaritonang11@gmail.com

ARTICLEINFO

Keywords: Nanocomposite, polyamide, bentonite, Cetyl Trimethyl Ammonium Bromide

Received : 2 July
Revised : 15 July
Accepted: 20 August

ABSTRACT

Modification of bentonite with Cetyl Trimethyl Ammonium Bromide (CTAB) has been successfully carried out, resulting in the application of organobentonite as a filler. The purpose of this study was to determine the characteristics of the polyamide nanocomposite material before and after the addition of organobentonite filler. Commercial bentonite after being modified with CTAB is organophilic with a particle size of 9.55 nm. The results of the Fourier Transform Infra Red spectrum analysis show that there is a wide and sharp absorption band at wave number 3749.6 cm-1 which indicates the presence of Al-OH groups. The results of Scanning Electron Microscopy analysis of the surface morphology of the polyamide/organobentonite nanocomposite obtained a homogeneous and compatible mixture. The conclusion from the CTAB research results can unite polyamide and bentonite which have different polarities

DOI: https://doi.org/10.55927/ajns.v2i3.4689
E-ISSN: 2986-2787
https://journal.formosapublisher.org/index.php/ajns

INTRODUCTION

In the last few decades, nanotechnology research has developed rapidly in various branches of science and provides very broad benefits for everyday life. One of the studies on the application of nanotechnology that is currently being developed is nanocomposites. Nanocomposite is a new material that is formed by combining two or more compounds by inserting nanoparticles (nanofiller) into the matrix. Nanofiller can be applied to polymers to produce nanocomposite materials with improvements to some of the basic properties of polymers, such as thermal resistance, mechanical properties, chemical resistance, and flammability. The matrix is the basic material for forming composite products that bind and protects the surface of the filler (filler) without chemical bonds. Filler is a filler material that functions to improve the mechanical properties of nanometer impact composites, usually in the form of clay(Nasrollahzadeh et al., 2019)(Othman & Radiman, 2020).

Currently, the use of filler derived from natural materials such as bentonite is being developed because it has a high aspect ratio, plate morphology and is inert (not sensitive to other components), has a large surface area, the material is abundant in nature, and its processing does not require a lot of money and can increase the homogeneity of nanocomposite products. The addition of filler on the nanofiller scale to nanocomposite products aims to overcome resistance to degradation by ultraviolet light, temperature, and humidity, as well as to improve the properties of tensile strength, stiffness, and fire resistance(Sukeksi et al., 2021)(Krasinskyi et al., 2020)(Fisli et al., 2019).

However, the main problem in this research is the difference in the surface properties of bentonite and polyamide. Polyamide (nylon) is a hydrophobic thermoplastic that has a high surface adhesion, abrasion resistance, resistance to pH, and high temperatures, so it is widely used in the automotive, transportation, consumer goods, and electronics industries, while bentonite is a hydrophilic filler that has a high adhesion surface. low so that when used as a filler it can cause agglomeration of mineral clay in a hydrophobic polyamide matrix which tends to form a separation between two immiscible or incompatible phases resulting in poor mechanical and morphological properties(Krasinskyi et al., 2021)(Francisco et al., 2019)(Feldman, 2017).

Therefore bentonite must be chemically modified with surfactants through ion exchange reactions to increase the homogeneity of the polyamide nanocomposite product. One of the surfactants that can be used to modify bentonite surfaces is cetyltrimethylammonium bromide (CTAB). Chemical modification with the CTAB surfactant, this causes bentonite which was originally hydrophilic to become organophilic, this is because the CTAB properties can reduce the polarity of bentonite to become more hydrophobic so that the dispersion ability of the silicate layer becomes wider(Wang et al., 2021)

Previous research on the manufacture of nanocomposites using modified bentonite fillers with various surfactants has been carried out by(Kumaresan et al., 2020) reported that the preparation of polyamide nanocomposites using bentonite filler modified with CTAB had better morphological properties compared to filler without modification.(Mrah, 2022) reported that modification of bentonite with CTAB can improve the morphological properties of poly nanocomposites (3,4-ethylenedioxythiophene)

LITERATURE REVIEW

Nanotechnology has developed in recent years various branches of science and exert a strong influence on various forms of life. The concept of nanotechnology was first initiated by Richard Feynman in 1959. Nanotechnology is an outcome of exploiting the properties of molecules or atomic structures of size nanometers, where extraordinary new properties will be produced through a molecule or nano-sized structure. These are the new features that can be used to create a new technology(Koo, 2019)

METHODOLOGY

The materials used in this study included commercial bentonite, Cetyl Trimethyl Ammonium Bromide (CTAB) (Merck.no 57-09-0), polyamide (produced by PT Titan Petrokimia Nusantara), Aquades, $AgNO_3$. The tools used in this study included a set of glassware, hot plates, magnetic stirrers, ovens, filter paper, filters, mortars, Scanning Electron Microscopy (SEM), X-Ray Diffraction (X-RD), Particle Size Analyzer (PSA), FT-IR Spectrometer.

Organobentonite Preparation

Bentonite is weighed as much as 25 g put into a grinding container and dissolved with 100 mL of distilled water. After that, put the 500 g, grinding ball and put the grinding container into the high-energy ball mill and grind it for 20 hours. The Particle Size Analyzer (PSA) test was carried out by dissolving 1 gram of sample with 50 mL of distilled water in a beaker and stirring with a magnetic stirrer. at 600 rpm for 5 minutes, then the sample was put into the cuvette. Furthermore, the cuvette is inserted into the PSA tool to measure particle size.

Modification of Bentonite with CTAB Surfactants.

Commercial bentonite of 200 mesh size is mixed with 0.2 mol CTAB, then dissolved in 200 mL of distilled water after that it is heated at 80 ^{0}C, then stirred for 1 hour as solution A. After that 50 g of bentonite is added to 800 mL of distilled water, then heated, and stirred at 100 ^{0}C for 2 hours as solution B. After heating and stirring, solution A and solution B were mixed. The mixture was added with distilled water until the volume reached 1500 mL. then heated at 100 ^{0}C for 1 hour. The cleaning mixture uses a vacuum filter, and 2 gr $AgNO_3$ is added to 100 mL of aquabides using a beaker. The purpose of adding $AgNO_3$ solution is to remove bromide. The mixture is filtered using filter paper until it does not change color and becomes dark when using $AgNO_3$, if there is still a change in color it is mixed again with distilled water and filtered again. Then the mixture was dried in the microwave at 100 ^{0}C for 1 day.

Nanocomposite Preparation

Polyamide Post Addition of organobentonite 80 g of polyamide was put into the internal mixer which had been set for mixing conditions (temperature 160 C and rotor speed 60 rpm) for 8 minutes. After 8 minutes, the polyamide will melt, then add 20 gr of organobentonite to it. The mixing process between polyamide and organobentonite was carried out for 4 minutes. After the mixing process is complete, the polyamide nanocomposite is removed from the internal mixer while hot and stored in a plastic container for 24 hours at room temperature.

RESULTS AND DISCUSSION

Particle Size Analysis of Bentonite (PSA).

Bentonite is often used as a filler in composite materials consisting of octahedral and tetrahedral layers, between which there is an interlayer or basal spacing. Commercial bentonite that is not modified with CTAB has a very small basal spacing, based on the results of PSA analysis, a particle size of 8.94 micrometers is obtained, so it is not optimal to be used as a filler. To increase the ability of bentonite as a filler, the basal spacing of bentonite must be enlarged by modifying bentonite with CTAB. After modifying bentonite with CTAB, bentonite which was originally hydrophilic became organophilic, this can be proven from the analysis of the Particle Size Analyzer (PSA) to obtain a particle size of 9.55 nm which can be seen in Figure 1.n this section, you must describe each step taken to complete your research.

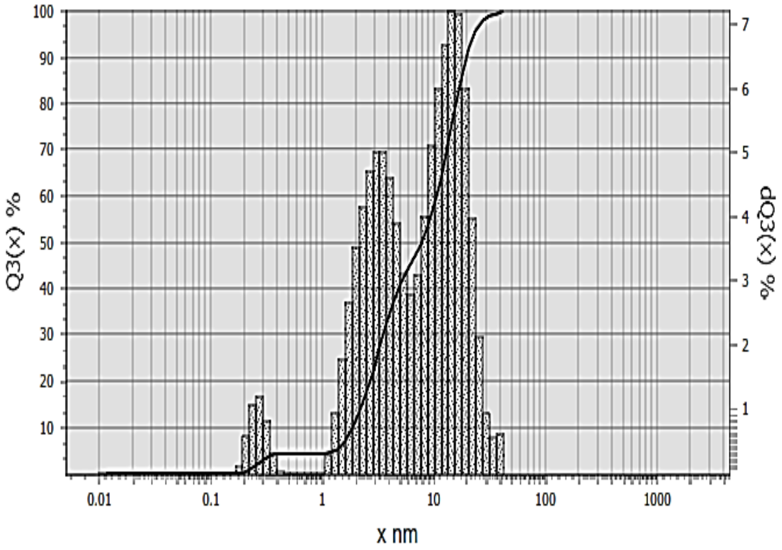


Figure 1. Particle Size Analysis of Bentonite

Based on Figure 1, the smaller the particle size, the greater the surface area. It is expected that with a larger surface area, CTAB bentonite will have better-spreading power compared to micro-sized applications(Feeney et al., 2011; Gatos et al., 2010).

Characterization by X-Ray Diffraction

The results of placing commercial bentonite with X-Ray Diffraction (XRD) in Figure 2 show the presence of montmorillonite (MMT). The peaks indicating the presence of montmorillonite were found at peaks of 18.70^{o}, 20.24^{o}, 22.50^{o}, and 32.54^{o} (Fisli et al., 2019). In Figure 2, after being modified with CTAB surfactant, commercial bentonite which was originally hydrophilic became organophilic, this is what allows intercalation of the interface with the polymer matrix. Based on the results of the XRD spectrum analysis at an angle of 2θ, the typical montmorillonite peaks found in bentonite can be seen at peaks of 18.32°, 20.18°, 22.30° and 32.43°.

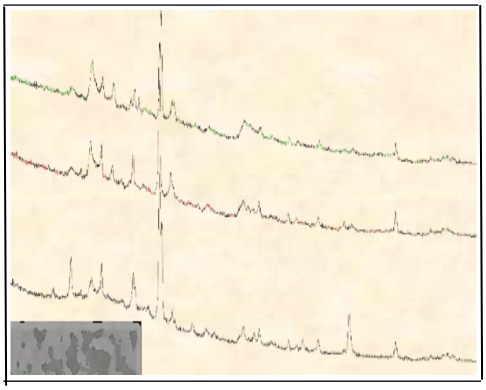


Figure 2. XRD Spectrum of Organobentonite CTAB

Fourier Transform Infra-Red (FT-IR) Analysis of Nanobentonite Before and After CTAB Modification

Commercial bentonite which has been made into nanoparticle size, is then modified with CTAB which is one of the organic cations. In this study, CTAB was used as a surfactant to modify commercial bentonite into organobentonite which has properties from hydrophilic to hydrophobic to maximize the interaction of the nano-alloy to be formed so that when it is mixed with polyamide it becomes compatible (homogeneous). Long alkyl chains of CTAB surfactants with positively charged chain ends and added bentonite which is a negatively charged silicate layer will increase the size of the gallery so that the polymer can spread in the nanoalloy. The results of FT-IR analysis of nano bentonite before and after modification with CTAB can be seen in Figure 3.

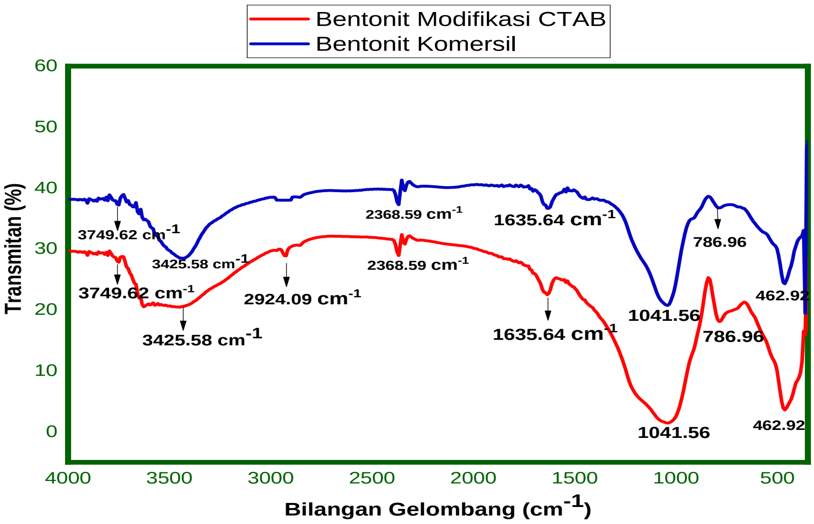


Figure 3. FT-IR Spectra of Nanobentonite Before and After Modified CTAB

In Figure 3, the FT-IR spectra of commercial bentonite that was not modified with CTAB obtained a weak absorption peak with low intensity observed at wave number 3749.62 cm^{-1} indicating the presence of O-H hydroxyl groups from (Al-OH), absorption peaks with high intensity observed at wave number 3425.58 cm^{-1} indicate the presence of octahedral O-H groups, strong and sharp absorption peaks with high intensity is obtained at wave number 1635.64 cm^{-1} indicating the presence of O-H bending vibrations from H-O-H and N-H bending, absorption peaks that expand strongly and sharply with high intensity in the region of wave number 1041.56 cm^{-1} indicating the presence of asymmetric Si-O-Si strain, the absorption peak at wave number 786.67 cm^{-1} indicates stretching vibrations of parallel Si-O bonds, the presence of a strong absorption peak with high intensity at wave number 462.92 cm^{-1} indicates the presence of Si-O-Si bond stretching vibrations. Meanwhile, the FT-IR spectra of commercial bentonite modified with CTAB surfactant obtained a new absorption peak at wave number 2924.09 cm^{-1} indicating an asymmetric stretching vibration of the C-H alkane group of CTAB surfactant. The emergence of new functional groups proves that bentonite has been modified with CTAB surfactants, this is to the results of a study conducted by Alshabanat (2013) who reported that the CTAB spectrum was observed at wave numbers 2850-3100 cm^{-1} (Pohan et al, 2017; Alshabanat et al, 2013; Xue et al,2007).

Scanning Electron Microscopy (SEM) Analysis of Nanobentonite Before and After CTAB Modification.

Surface morphological structure characterization by SEM was used to explore bentonite surface morphology. To determine the morphological structure of organobentonite before and after CTAB modification can be seen in Figures 4a and b.

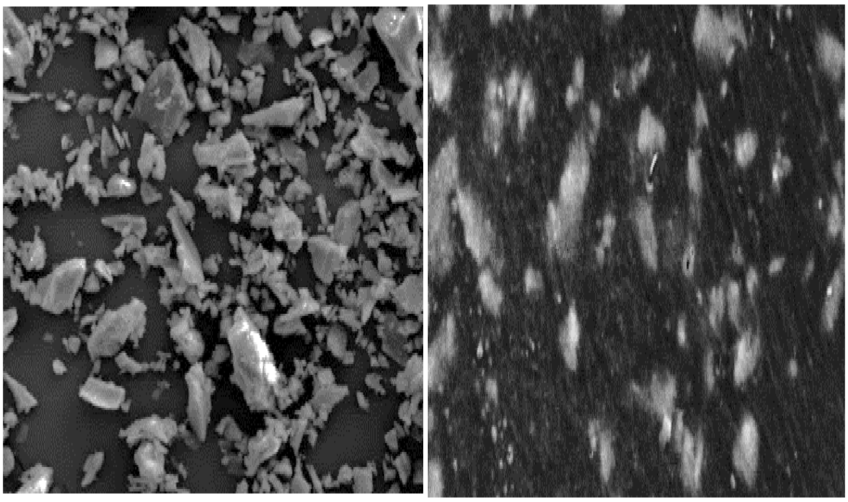
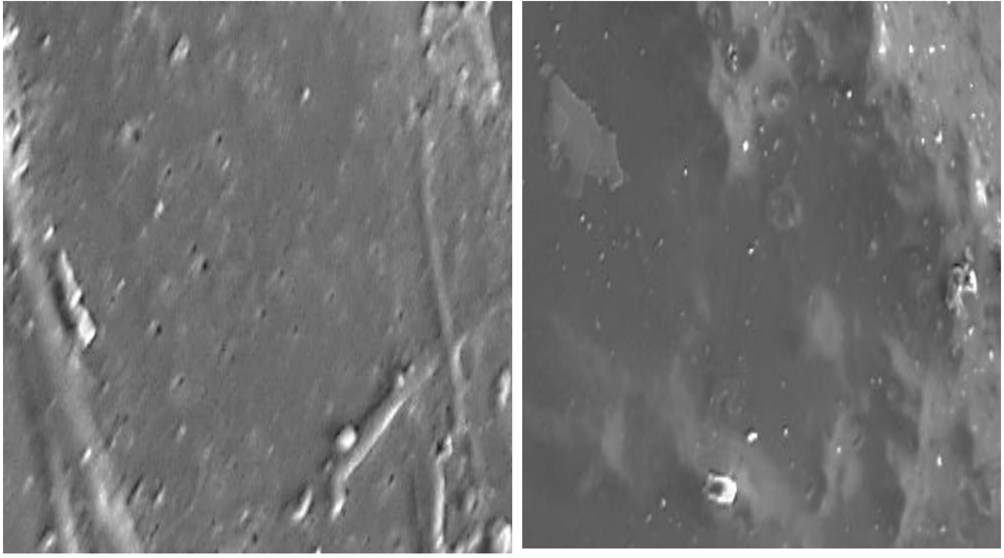


Figure 4. A and B SEM of Nanobentonite Before and After Modified CTAB

Figure 4a shows the surface morphology of bentonite particles before being modified with CTAB, while Figure 4b shows the surface morphology of bentonite particles after being modified with CTAB. Figures 4a and 4b are the morphology of bentonite particles produced using the SEM tool. Visual observations show that the particle size of bentonite is in the range of 9.55 nm. Figure 4a shows the surface morphology of bentonite containing MMT which has unevenly layered pores, there are still clumping pores that cause agglomeration which tends to form separations. This is because nano bentonite has not been modified with CTAB so it is still hydrophilic. Figure 4b shows the surface morphology of bentonite containing MMT which has layered pores that are evenly distributed and no further clumping occurs, this is due to the addition of CTAB surfactant. This study is in line with that carried out by (Ogunlaja & Pal, 2020), who reported that nano bentonite modified with CTAB surfactants could reduce particle agglomeration in the MMT structure.

Scanning Electron Microscopy (SEM) Analysis of Polyamide/Organobentonite Nanocomposites Before and After CTAB Modification

SEM test was performed to analyze the surface morphological structure of the polyamide/organobentonite nanocomposite before and after being modified with CTAB surfactant. To determine the surface morphological structure of the polyamide/organobentonite nanocomposite can be seen in Figures 5a and 5b.



Figures 5. A and B SEM of Polyamide/Organobentonite Nanocomposite Previously and After Modified CTAB

Figure 5a shows the surface morphological structure of the polyamide/organobentonite nanocomposite before CTAB modification. Figure 5b shows the surface morphological structure of the polyamide/organobentonite nanocomposite after CTAB modification. Based on Figure 5a, the results of analysis by SEM of the polyamide/organobentonite nanocomposite surface morphology that was not modified with CTAB produced an incompatible and homogeneous mixture. immiscible resulting in poor mechanical and morphological properties. After modifying bentonite with CTAB surfactant in Figure 5b, a homogeneous and compatible mixture is obtained. It can be seen that the bentonite is dispersed evenly and homogeneously onto the polyamide surface because there are no more porous cavities. This is due to the role of the CTAB surfactant in changing the surface properties of bentonite from hydrophilic to organophilic. The conclusion from the results of the study is that CTAB surfactant can combine two materials with different polarities to mix homogeneously and be compatible.

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of research conducted, CTAB surfactants can change the properties of bentonite which was originally hydrophilic to become organophilic, and can unite polyamide with bentonite which has different polarities to produce a homogeneous and compatible mixture. It can be seen that the bentonite is dispersed evenly and homogeneously into the polyamide surface because there are no more porous cavities.

ADVANCED RESEARCH

This study has limitations in terms of the miscibility of polyamide with bentonite, To overcome this problem, it is necessary to modify bentonite with two or three surfactants.

ACKNOWLEDGEMENTS

We would like to thank the Chancellor, and all the lecturers and laboratory staff of the Faculty of Pharmacy, Lubuk Pakam Medistra Health Institute, who have provided a lot of support and motivation both materially and morally so that this research can be completed properly.

REFERENCES

Alshabanat, M., Al-Arrash, A., & Mekhamer, W. (2013). Polystyrene/montmorillonite nanocomposites: study of the morphology and effects of sonication time on thermal stability. *Journal of Nanomaterials*, *2013*, 9.

Feeney, C. A., & Goldberg, H. A. (2011). Nonautomotive Applications of Rubber–Clay Nanocomposites. *Rubber-Clay Nanocomposites: Science, Technology, and Applications*, 557–574.

Feldman, D. (2017). Polyamide nanocomposites. *Journal of Macromolecular Science, Part A*, *54*(4), 255–262.

Fisli, A., Sumardjo, S., & Mujinem, M. (2019). Isolasi dan Karakterisasi Montmorillonite dari Bentonit Sukabumi (Indonesia). *Jurnal Sains Materi Indonesia*, *10*(1), 12–17.

Francisco, D. L., Paiva, L. B., & Aldeia, W. (2019). Advances in polyamide nanocomposites: A review. *Polymer Composites*, *40*(3), 851–870.

Gatos, K. G., & Karger-Kocsis, J. (2010). Rubber/clay nanocomposites: preparation, properties and applications. *Rubber Nanocomposites: Preparation, Properties, and Applications*, 169–195.

Koo, J. H. (2019). *Polymer nanocomposites: processing, characterization, and applications*. McGraw-Hill Education.

Krasinskyi, V., Suberlyak, O., Kochubei, V., Jachowicz, T., Dulebova, L., & Zemke, V. (2020). Nanocomposites Based on Polyamide and Montmorillonite Obtained from a Solution. *Advances in Science and Technology. Research Journal*, *14*(3).

Krasinskyi, V., Suberlyak, O., Sikora, J., & Zemke, V. (2021). Nanocomposites based on polyamide-6 and montmorillonite intercalated with polyvinylpyrrolidone. *Polymer-Plastics Technology and Materials*, *60*(15), 1641–1655.

Kumaresan, S., Rokade, D. S., Marathe, Y. N., Ingole, P. G., Pawar, R. R., Pol, H. V, & Bajaj, H. C. (2020). Synthesis and characterization of nylon 6 polymer nanocomposite using organically modified Indian bentonite. *SN Applied Sciences*, *2*, 1–11.

Mrah, L. (2022). Synergistic effect of organic clay fillers based on cetyltrimethylammonium bromide in the synthesis of poly (3, 4-ethylenedioxythiophene) nanocomposites. *Polymers and Polymer Composites*, *30*, 09673911221080302.

Nasrollahzadeh, M., Sajadi, S. M., Sajjadi, M., & Issaabadi, Z. (2019). An introduction to nanotechnology. In *Interface science and technology* (Vol. 28, pp. 1–27). Elsevier.

Ogunlaja, S. B., & Pal, R. (2020). Effects of bentonite nanoclay and cetyltrimethyl ammonium bromide modified bentonite nanoclay on phase inversion of water-in-oil emulsions. *Colloids and Interfaces*, *4*(1), 2.

Othman, S. A., & Radiman, S. (2020). Potensi Nanoteknologi. *Advances in Humanities and Contemporary Studies*, *1*(1), 87–100.

Pohan, M. S. A., Sutarno, S., & Suyanta, S. (2017). Studi Adsorpsi-Desorpsi Anion Fosfat pada Zeolit Termodifi-kasi CTAB. *Jurnal Penelitian Sains*, *18*(3).

Sukeksi, L., Grace, M., & Diana, V. (2021). *Characterization of the Chemical and Physical Properties of Bar Soap Made with Different Concentrations of Bentonite as* *a Filler*.

Wang, Y., Jiang, Q., Cheng, J., Pan, Y., Yang, G., Liu, Y., Wang, L., Leng, Y., & Tuo, X. (2021). Synthesis and characterization of CTAB-modified bentonite composites for the removal of Cs+. *Journal of Radioanalytical and Nuclear Chemistry*, *329*(1), 451–461.

Xue, W., He, H., Zhu, J., & Yuan, P. (2007). FTIR investigation of CTAB–Al–montmorillonite complexes. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *67*(3–4), 1030–1036.