

Purification of Iranian bentonite, for organoclay synthesis to use in clay/polymer composite

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ABSTRACT:

Polymer-based composites modified with organoclay are economically beneficial candidates for varieties of applications. Different types of impurities accompany montmorillonite phases in various bentonites, which impact the quality and price of organoclay and final composite. To achieve organoclay for clay/composite applications, eight Iranian raw bentonites from different geographic locations were selected as the candidates and characterized by X-ray diffraction (XRD). Iranian bentonite (IB) was chosen due to its high purity and lower cristobalite amount than other samples. It was purified by centrifugation or sedimentation methods using sodium hexametaphosphate (NaHMP) dispersant. The cation exchange capacity (CEC) was measured for bentonite before and after purification by sedimentation, showing an impressive increase from 6.944 eq/g to 12.128 eq/g, confirming successful purification. Organoclay was prepared using purified bentonite (sedimentation method) with two surfactants (cetyltrimethylammonium



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bromide (CTAB) and octadecylamine), while the amount of octadecylamine was optimized. Purified bentonite and organoclay were characterized by XRD, scanning electron microscopy (SEM), and X-ray fluorescence (XRF). The results indicate that most of impurities were removed after purification, and the interlayer space of organoclays increased to 35 Å in the optimized sample, prepared with an amount of octadecylamine, twice the CEC in purified bentonite. The prepared organoclay was used to improve low-density polyethylene (LDPE) polymer properties. Clay/polymer composite properties were studied by field emission scanning electron microscopy, thermogravimetric (TG) analysis, and tensile test. Organoclay was fully dispersed in the low-density polyethylene (LDPE) matrix and sample with 5%wt of organoclay, where T_i (the temperature at which 10% of the sample is decomposed) and $T_{50\%}$ (the midpoint of degradation) were 17°C and 13°C higher than in polyethylene, respectively. Additionally, the sample residue with 5%wt of organoclay in 600°C was 43.4%. The tensile strength of polyethylene increased from 8.67 MPa to 9.03 MPa in the sample with 5%wt of organoclay.

Keywords: Bentonite, Purification, Organoclay, Clay/polymer composite, montmorillonite

INTRODUCTION:

Phyllosilicates comprise several tetrahedral (T) and octahedral (O) sheets that stack on each other to make various types of phyllosilicates. One of the most common and swelling phyllosilicates is smectite, which includes T-O-T sheets (2:1 clay) and many interlayer cations such as Na^+ , Ca^{2+} , and Mg^{2+} (Forbes & Chryss, 2017). Clays are layered materials whose tetrahedral and octahedral sheets arrangement and interlayer charge determine their type and structure. Clays are mainly separated into three groups named 1:1 (Kaolinite), 2:1 (Smectite), and 2:1:1 (chlorite) (Uddin, 2008). Smectites are classified into several species based on their chemical composition and the types of

exchangeable interlayer cations they contain, such as montmorillonite, beidellite, nontronite, and saponite (ROSS & HENDRICKS, 1943). Montmorillonite is a well-known and highly promising material for scientists and industrial technologists (Pacuta *et al.*, 2006) due to its beneficial and important properties (Golubeva *et al.*, 2013).

Bentonite soils, containing montmorillonite as the dominant mineral, find applications in various industries, from casting and drilling mud to nanomaterials and medicine. They are also used in food processing and cosmetics owing to their chemical stability, decontamination, and moisturizing properties (Gong *et al.*, 2016a). Because of the low cost, layered structure, and surface charges, they can be added to the polymer varieties to improve their organoclay qualities. To prepare the organoclay, the clays should be exfoliated; however, bentonite, besides montmorillonite, contains several minerals that are impurities. Typical impurities found in bentonite include cristobalite (or Opal-c), quartz, calcite, feldspar, mica, and illite. The presence of these impurities alongside smectite diminishes the quality for industrial applications (Boylu *et al.*, 2010). These impurities hinder the exfoliation process, thereby limiting the expected enhancement from bentonite incorporation and may even degrade its properties. On the other side, although the purification process can remove undesirable phases, it increases the price. It sensibly reduces the overall yield of bentonite (Bahranowski *et al.*, 2017). Thus, selecting the proper raw material from the various bentonites with fewer unwanted impurities, which can be omitted with the lowest cost and higher yield, is commercially favorable.

Bentonite mines mainly originate from the alternating weathering of volcanic ash and some pre-existing minerals (Galán, 2006), for example, weathering silicates such as feldspar and mica (Zhou & Keeling, 2013). Bentonite deposits are centers where smectites can be found and they are located in many countries such as the USA, Germany, Greece, Spain, Turkey, and Iran. Iran is among the

eight leading countries in this field, with over 70 bentonite deposits and 420,000 tons of annual bentonite production (Modabberi *et al.*, 2019). Iranian bentonite deposits can be divided into six geological structural parts, and in each region, there are several deposits located with different qualities for different applications (Modabberi *et al.*, 2015).

Bentonites are divided into two main groups depending on the dominant interlayer cations: sodium and calcium bentonite. Impurities in bentonite inhibit industrial applications, so purification is essential for developing bentonite applications and adding value to the raw material (Boylu *et al.*, 2010).

There are several methods for bentonite purification (Thuc *et al.*, 2010). Finer grain size is needed to achieve better results from purification processes (Gong *et al.*, 2016a). However, some impurities, such as quartz, can be removed by granulometric methods (Thuc *et al.*, 2010). The decomposition of carbonates, dissolution of (hydr)oxides, and oxidation of organic materials are also employed to purify clay minerals (Bergaya *et al.*, 2006b). Ultrasound treatment also stabilizes smectite aqueous dispersions (Lapides & Yariv, 2004), followed by the separation of impurities using different methods (Thuc *et al.*, 2010). Another way to stabilize clay dispersions is by using dispersants such as sodium hexametaphosphate (NaHPM) to reduce edge-to-face interactions and deflocculate the clay particles (Levy *et al.*, 1991).

Different methods such as hydrocyclone (Boylu *et al.*, 2010), centrifugation (Chipera & Bish, 2001), and sedimentation are used to separate clays from other materials in bentonite dispersions. Purification can increase the cation exchange capacity (CEC) of bentonite (Özgen *et al.*, 2009), which is appropriate for further industrial use (Gong *et al.*, 2016a).

The surface treatment of clay minerals and clay modifications has attracted significant interest, and organoclays have found critical applications in many industries (Sohrabi-Kashani *et al.*, 2023).

Replacing inorganic interlayer cations of clays with organic cations can significantly improve clay properties. This results in organoclays that exhibit remarkable properties, especially in clay/polymer composite and water purification. An organic cation's intercalation transforms hydrophilic clays into hydrophobic materials, increases the basal spacing of clay layers, and can cause exfoliating clay layers (He *et al.*, 2014). The most commonly used organic cations for preparing organoclays are cationic surfactants (Rafiei & Ghomi, 2013), such as specific amines and quaternary ammonium salts (Motawie *et al.*, 2014) which can be adsorbed on clay surfaces. The long carbon chain causes increased interlayer space and enhances specific properties (Kooli *et al.*, 2009).

Merging acid activation and organic molecule intercalation provides a magnificent enhancement for clay mineral properties (Bergaya *et al.*, 2006a; Lagaly *et al.*, 2006; Kooli *et al.*, 2009).

Organoclays are now used in a wide range of applications, such as polymer nanocomposites (in automotive, packaging, aerospace, etc.) (Guo *et al.*, 2018), rheological modifiers in paints, inks, greases, and cosmetics (Patel *et al.*, 2006), adsorbents for wastewater pollutants (Amin *et al.*, 2014) and heavy metal ions removal (Yadav *et al.*, 2019), catalysts (Adams & McCabe, 2006) and drug delivery carriers (Mattausch, 2015). One of the most significant uses of organoclays is in polymer nanocomposites. Adding a low percentage of organoclays to polymers can enhance properties (Chan *et al.*, 2011), such as strength and thermal resistance, and reduce gas permeability and flammability. However, these improvements strongly depend on the structure and properties of organoclay and the polymer used in composites. (Xi *et al.*, 2007).

Low-density polyethylene (LDPE) is a cheap, tough, and flexible polymer widely used in many applications (Jordan *et al.*, 2016). LDPE/ clay composites can be superior to untreated LDPE or conventional composites. These composites can exhibit better thermal and mechanical properties (Olewnik *et al.*, 2010; Awad, 2021).

In this work, several bentonites of Iranian deposits were gathered and analyzed. After selecting the most suitable source of bentonite, the commercial purification process was applied. Subsequently, specific surfactants were used to obtain organoclay. X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray fluorescence (XRF) were carried out to analyze the synthesized organoclays. Finally, modified organoclay was used to prepare LDPE/ organoclay composite, and polymer properties were evaluated using thermogravimetric analysis (TGA) and tensile tests.

2. EXPERIMENTAL

2.1 Materials

In this study, eight different bentonites were collected from Iranian bentonite mines of different geographic locations (Table 1). NaHMP from Sina Chemistry Company was used as a dispersant. Deionized water and CTAB (CAS 57-09-0), octadecylamine (CAS 124-30-1), and hydrochloric acid (HCl, 35%) were purchased from Merck company, and LDPE was purchased from Sinashimi Hekmataneh Company. Additionally, cloisite15a (CL15) is an organoclay provided by Southern Clay Products and was used as a reference sample in this research.

2.2 Methods

2.2.1. Purification

Ahmadi et al.(2022) found out that the dispersion method is a more efficient way to purify raw bentonite, and the following procedure is carried out by the dispersion method (Ahmadi *et al.*, 2022). Two raw bentonites were chosen: IB, selected for its high purity and lower cristobalite value compared to other samples, and NBZ, selected to demonstrate the efficiency of the purification process by separating a variety of impurities from bentonite. 5g of raw crushed bentonite powder and 0.25g of NaHMP were dispersed in 200 ml of deionized water, and the mixture was stirred using an MR Hei-standard stirrer from Heidolph Company for 3 hours. Two methods were used to separate supernatant from sediment. In the first method, the dispersion was allowed to stand statically for seven minutes, and the supernatant was centrifuged twice using the centrifuge from Aryanpaya company. In the second method, the dispersion was allowed to stand statically for 12, 24, 36, and 48 hours, after which the supernatant was separated. The final dispersions were dried at 100°C for 24 hours by Memmert dryer. The purification procedure is shown in Fig. 1(a). The purified powder of NBZ was named NBZP and the purified powder of IB was named IBP (in centrifuge route), and IBSEDI (in sedimentation route). Purified samples codes are shown in Table 1.

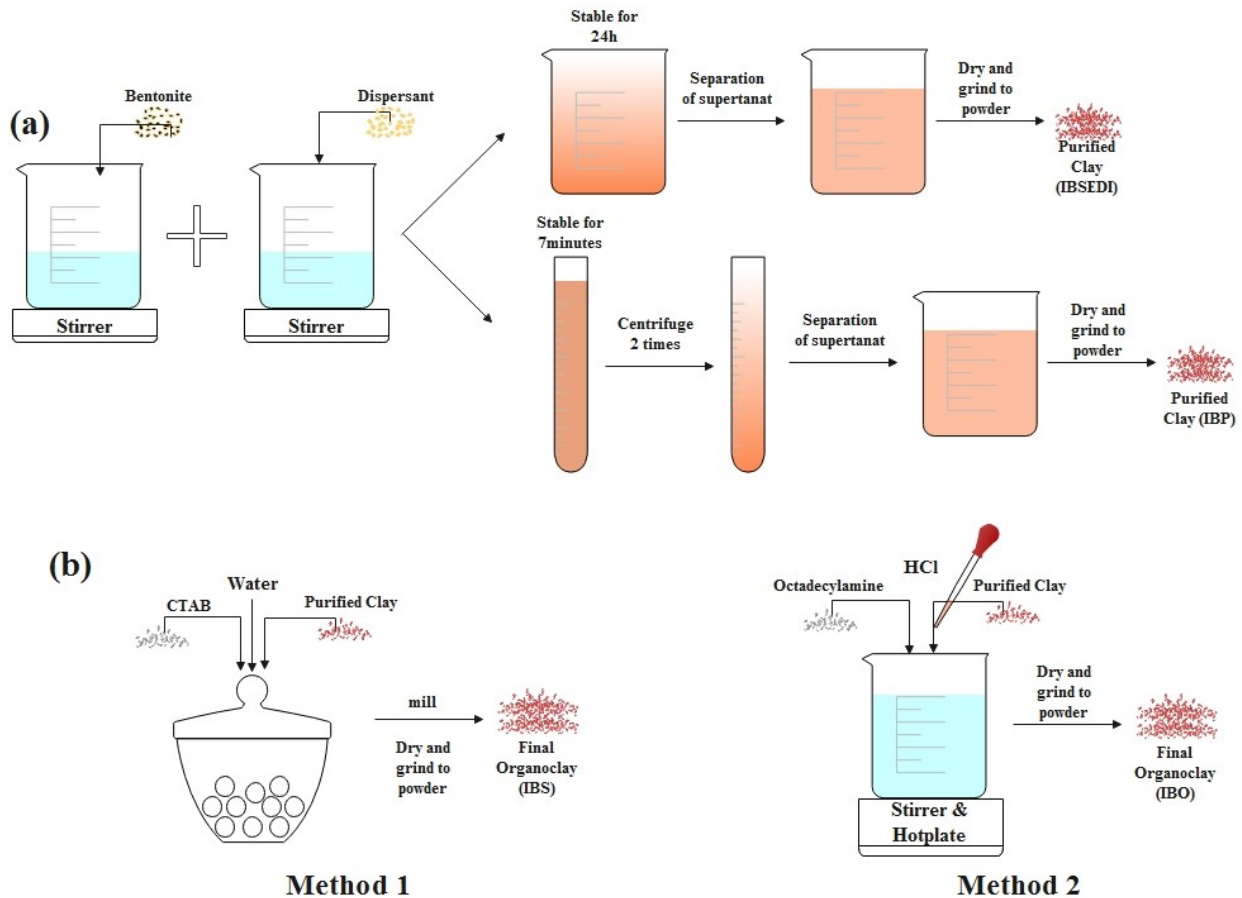


Fig. 1. Graphical procedure of (a) bentonite purification and (b) organoclay preparation

2.2.2 Organoclay preparation

2.2.2.1 Method 1

2.5g of as-purified bentonite and 0.87g of CTAB were sequentially added to 125 ml of deionized water to prepare the dispersion. The dispersion was milled using a planetary mill with zirconia balls for about two hours at 300 rpm and then dried at 100°C for 24 hours (Ahmadi *et al.*, 2022). The final powder of method 1 was named IBS.

2.2.2.2 Method 2

Four grams of optimized purified bentonite (IBSEDI) were added to 100 ml of deionized water and stirred for one hour at 60°C. Separately, another dispersion was prepared by mixing various amounts of Octadecylamine (0.5CEC, 1CEC, 2CEC, and 3CEC of optimized purified bentonite) with 0.92ml of HCl (35%) and 20ml of deionized water. Two dispersions were stirred for 24h at 60°C. The final dispersion was dried at 100°C for 24h. The procedure of the second method is shown in Fig. 1(b). The final powder of method 2 was named IBO. Organoclay sample codes are shown in Table 1.

2.2.3 Composite preparation

Composite samples weighing 45g, consisting of LDPE and organoclay additive at concentrations of 0%, 1%, 2%, 3%, 4%, and 5%wt, were prepared using a W50-EHT internal mixer operating at 180°C for 10 minutes at 75rpm. Subsequently, the samples were hot-pressed at 200°C for 8 minutes to produce rectangular sheets (for SEM and TG analyses) and dog-bone-shaped samples (for the tensile test). Tensile tests were conducted three times, and average values were used for result analysis. Composite sample codes are shown in Table 1.

Table 1

Name codes of raw bentonites and their geographic locations, purified samples with their purification method and duration, organoclay samples with their surfactants, and composite samples with their amount of additives

Raw Bentonite Code	Geographic Location	Purified Sample Code	Purification Method	Time Duration	Prepared Organoclay Code	Surfactant	Amount of Surfactant	Composite Sample Code	% of Additive (IBO2)
IB	Ferdows	IBP	Centrifugation	2 minutes	IBS	CTAB	0.87 g	PE	0
NBC	Khorasan	NBZP	Centrifugation	2 minutes	IBO0.5	Octadecylamine	0.5 CEC	P1	1
NBZ	Birjand	IBSEDI12	Sedimentation	12 hours	IBO1	Octadecylamine	1 CEC	P2	2
NBSS	Sirjan	IBSEDI24	Sedimentation	24 hours	IBO2	Octadecylamine	2 CEC	P3	3
NBSK	Sirjan	IBSEDI36	Sedimentation	36 hours	IBO3	Octadecylamine	3 CEC	P4	4
NBF	Ferdows	IBSEDI48	Sedimentation	48 hours				P5	5
NBE	Isfahan								
NBSH	Shahrood								

2.3 Characterization techniques

The chemical composition of the samples was analyzed by the XRF instrument (PW1480, Philips, Netherlands). Particle size distribution was determined using a particle size analyzer, and specific surface area was evaluated using the Mastersizer 2000 instrument (Malvern, UK). Phase analysis of the milled and sieved powder (200 mesh) was performed by XRD (Advanced D8, Bruker, US). The instrument was equipped with a Cu target ($\lambda=0.154$ nm) and operated in the 2θ range of $0.8-8^\circ$ (low angle) and $5-80^\circ$ (normal mode), with a scan rate of $0.04^\circ 2\theta/s$. Morphological analysis was conducted using SEM (Vega Tescan-Lmu, Tescan analytics, France), energy dispersive spectroscopy (EDS) (XFlash 6-10, Bruker, US), and FESEM (Mira 3 LMU) for selected samples. The surface of the samples was coated with a thin layer of gold utilizing a vacuum evaporation method. Composite samples were cooled in liquid nitrogen, broken, and then the microstructure of their cross-sections was examined using FESEM (MIRA3TESCAN-XMU).

TG analysis was conducted under a nitrogen atmosphere with a temperature range from 25°C to 600°C at a heating rate of $10^\circ\text{C}/\text{min}$ using the TG 209F3 NETZSCH machine. Tensile tests were conducted using the Santam STM-50 tensile machine at room temperature. The crosshead speed was $50\text{mm}/\text{min}$, and samples were dog-bone-shaped with 16.8cm length and 3cm width.

The CEC of raw and purified bentonite (IB and IBSEDI samples) was measured based on the following procedure (Ahmadi *et al.*, 2022). Five grams of raw and purified bentonite powder were added to 33 ml of sodium acetate of 1 N separately, and the dispersion was shaken for about five minutes. Then, the mixture was centrifuged at 2500 rpm for five minutes (three times) using an sr1 centrifuge from Arminad company, Iran, to separate the sedimented particles. Subsequently, 33 ml of ethanol was added to settle the particles, shaken for five minutes, and centrifuged at 2500 rpm for five minutes (three times). The electrical resistivity of alcohol was measured by a

conductometer (HI98312, HANNA Instruments, Romania). If the value was lower than 40 $\mu\text{mho/cm}$, the washing was completed, and in the case of a higher value, the washing was continued. All the sodium acetates and soluble salts were removed as alcoholates. After the washing stage, 33 ml of ammonium acetate was added to the washed clay. The dispersion was shaken and centrifuged at 2500 rpm, each for five minutes, while the supernatant was separated and poured into a balloon of 100 cm^3 (repeated twice). Finally, 1 N ammonium acetate was added to the filled balloon to exchange ammonium ions with all adsorbed Na^+ ions. The amount of released sodium was determined by a flame photometer (PFP-7, Jenway company, UK). The CEC was calculated according to the following equation, where V, A, C, and W are the final volume (ml), sodium condensation (mg/l), coefficient of dilution, and mass of the sample powder (g), respectively.

$$\text{CEC (eq/g)} = \text{CEC (meq/100g)}/10 = V^{\text{cc}} \times A \text{ (mg)}/1000^{\text{cc}} \times 1 \text{ meqNa}/23 \text{ mg} \times C \times 100 \text{ g}/W$$

3. Results and discussion

3.1 Cation exchange capacity (CEC)

The cation exchange capacity (CEC) is crucial data for determining the amount of surface modifier and ensuring the quality of organoclay preparation in subsequent steps. The CEC values for IB and IBSEDI are 6.944 eq/g and 12.128 eq/g, respectively. The increase in CEC value after purification indicates successful purification. This increase suggests an elevated proportion of montmorillonite in the sample, resulting in higher cation exchange capacity (Pereira *et al.*, 2018). The CEC value serves as a guide for determining the appropriate amount of surfactant required for synthesizing organoclay. Based on the behavior, type, and cation exchange capacity of the clay, a

specific amount of surfactant is required to ensure that the organoclay reaches its saturation value and the interlayer cation sites of the clay are adequately filled with the surfactant. Surfactants can penetrate between particles and may compromise certain properties, such as thermal properties if used excessively ((He *et al.*, 2014)). As CEC value increases, more surfactant enters between layers, and the distance between layers increases (Rihayat *et al.*, 2018).

3.2. Phase characterization

3.2.1. Raw Bentonite

The phases present in raw bentonites are depicted in Fig. 2. As anticipated, many phases exist in raw bentonites besides the montmorillonite phase (Boylu *et al.*, 2010; Modabberi *et al.*, 2019). Various impurities in mineral bentonites can cause problems in the organoclay preparation and application ((Modabberi *et al.*, 2015; Gong *et al.*, 2016)).

Different clay phase peaks in the IB sample show that two different smectites named montmorillonite (Reference code: 000120204) and beidellite (Reference code: 000470197) exist in the sample. Other impurities are also shown in Fig. 2. For further studies, samples IB and NBZ were selected. IB was chosen due to its high purity and lower cristobalite value compared to other samples, and NBZ was selected to prove the purification process's efficiency by separating a variety of impurities from bentonite.

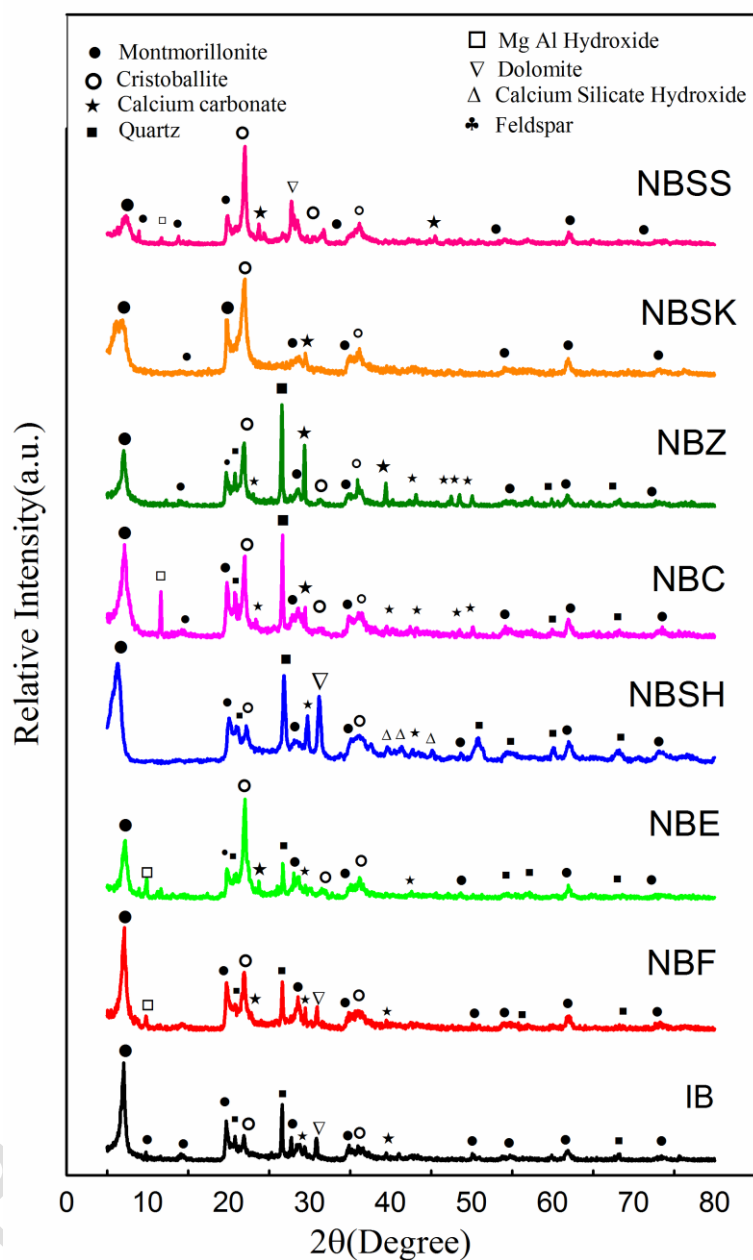


Fig. 2. X-ray diffraction patterns of Raw Bentonites.

3.2.1. Purified Bentonite

Existing phases in NBZ bentonite, before and after the purification process, are shown in Fig. 3

(a). A comparison between NBZ and NBZP reveals that quartz, calcium carbonate, and feldspar are predominantly separated from the bentonite, while the cristoballite content is relatively reduced

in the purified sample. Due to its dispersing properties, NaHMP prevents sedimentation by loading the clay plates and making the purification process progress faster (Gong *et al.*, 2016b).

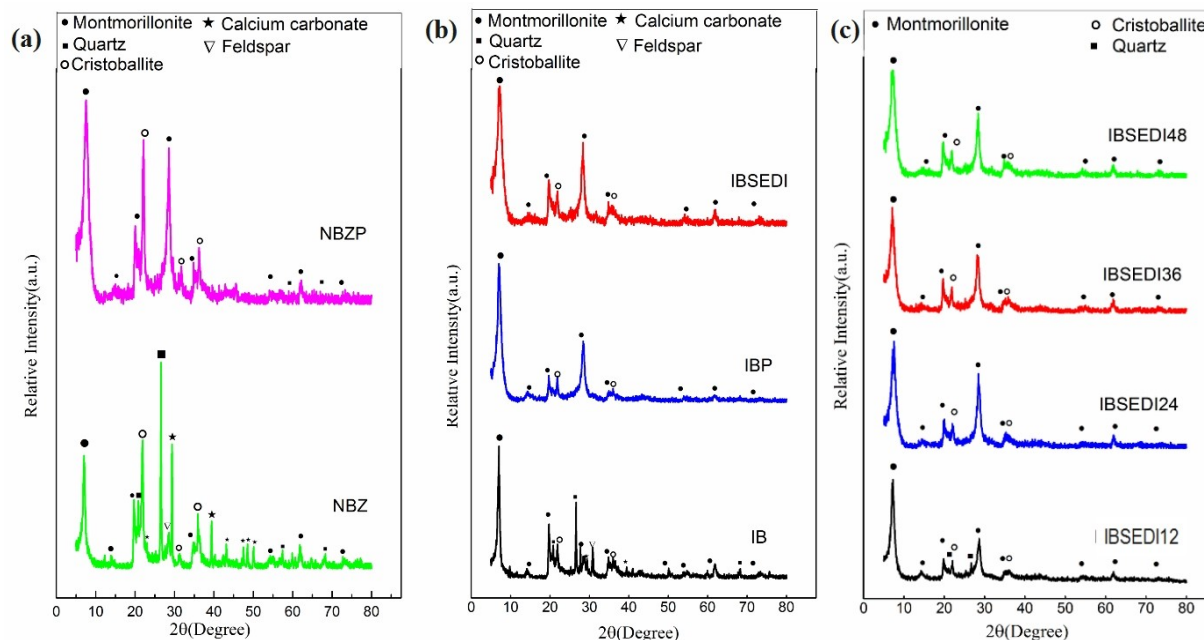


Fig. 3. X-ray diffraction patterns of (a) Raw (NBZ) and purified (NBZP), (b) Raw (IB) and purified (IBP, IBSEDI) bentonites, and (c) X-ray diffraction patterns for different times of impurities settling in IBSEDI samples

Fig. 3 (b) illustrates the comparison between two diverse methods. IBP represents the centrifuged sample, while IBSEDI represents the sedimented sample prepared after 24 hours of sedimentation. As shown in Fig. 3 (b), the existing phases in these two samples are largely similar. Due to the simplicity of the sedimentation method, it has been selected for further discussion. The intensity of a peak at 28° has increased in IBP and IBSEDI compared to IB due to the relative increase of clay phase content compared to the impurities characteristics peaks. This peak corresponds to the characteristic peak of the clay (004) planes and is expected to disappear after clay exfoliation in organoclay samples.

The peak at 7.13° in IB, is shifted to higher angles in IBSEDI. This peak shift is attributed to the substitution of Ca^{2+} and Mg^{2+} by Na^+ and the smaller size of Na^+ cations compared to Ca^{2+} and Mg^{2+} , which can cause a decreased distance between the layers ((Oueslati *et al.*, 2007)).

To determine the optimized time for impurities sedimentation, the bentonite dispersions that was stable for 48, 36, 24, and 12 hours were studied. X-ray diffraction patterns (Fig. 3(c)) indicated that 24 hours of sedimentation is the optimized time for separating impurities because, in IBSEDI12, the relative value of impurities peaks are higher, while there is no significant change by passing the time to 48 hours, comparing the IBSEDI24, IBSEDI36, and IBSEDI48 samples. Consequently, IBSEDI24 has been selected as IBSEDI (optimized purified bentonite) for further investigations.

3.2.3. Organoclays

Two methods were evaluated based on XRD patterns to determine the optimal method for preparing organoclay. In Fig. 4 (a) and (b) (normal and low-angle XRD patterns, respectively), IBS and IBO represent the organoclays prepared by ball-milling of the CTAB/clay dispersion (first method of organoclay preparation, section 2.2.2.1) and stirring of the octadecylamine/clay dispersion (second method of organoclay preparation, section 2.2.2.2), respectively. Additionally, cloisite15a (CL15) is an organoclay provided by southern clay products, served as a reference sample in this research. A comparison of low-angle XRDs indicates that IBO has a broader interlayer space. The exfoliation processing was improved by facilitating the entrance of octadecylamine molecules into the interlayer distance of montmorillonite sheets and more effective interaction with the internal surface of sheets. Thus, a relative increase in clay sheet interlayer compared to the CTAB-modified sample is caused by the relative in-situ leaching of

clay edges and surfaces by mild acid accompanying octadecylamine. Therefore, due to the better exfoliation of IBO, it has been selected for further studies.

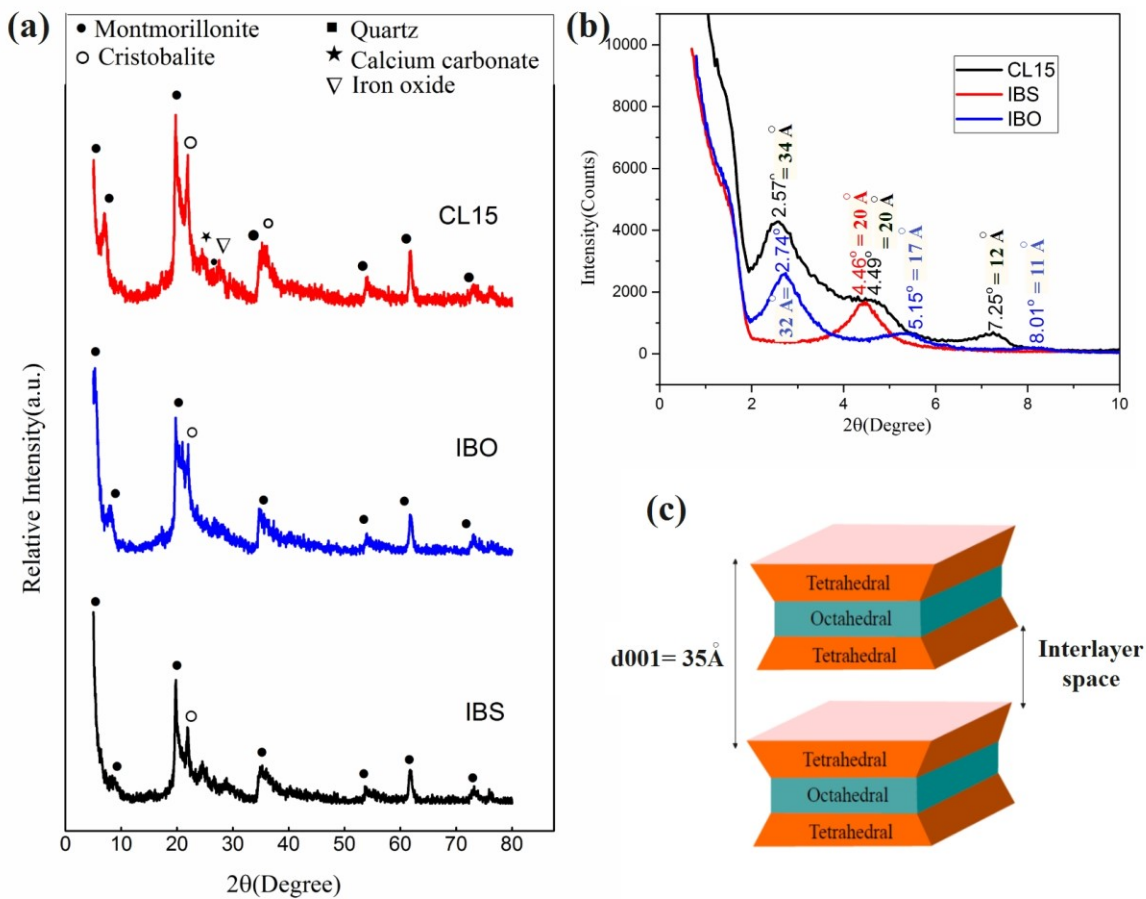


Fig. 4. (a) X-ray diffraction patterns of IBS, IBO, and CL15, (b) Low-angle X-ray diffraction patterns of IBS, IBO, and CL15, (c) Interlayer space and d_{001} of montmorillonite layers of raw bentonite.

Different samples were prepared using surfactant concentrations of 0.5CEC, 1CEC, 2CEC, and 3CEC to optimize the amount of surfactant in organoclay and named IBO0.5, IBO1, IBO2, and IBO3, respectively. In Fig.5 (a) and (b), the XRD patterns of these samples are shown. The difference in peak intensity in the samples is due to the different particle sizes and degrees of exfoliation in the samples (Zhu *et al.*, 2019). The IBO2 sample is saturated by surfactant, and a further amount of surfactant can decrease exfoliation quality as observed in the IBO3 sample.

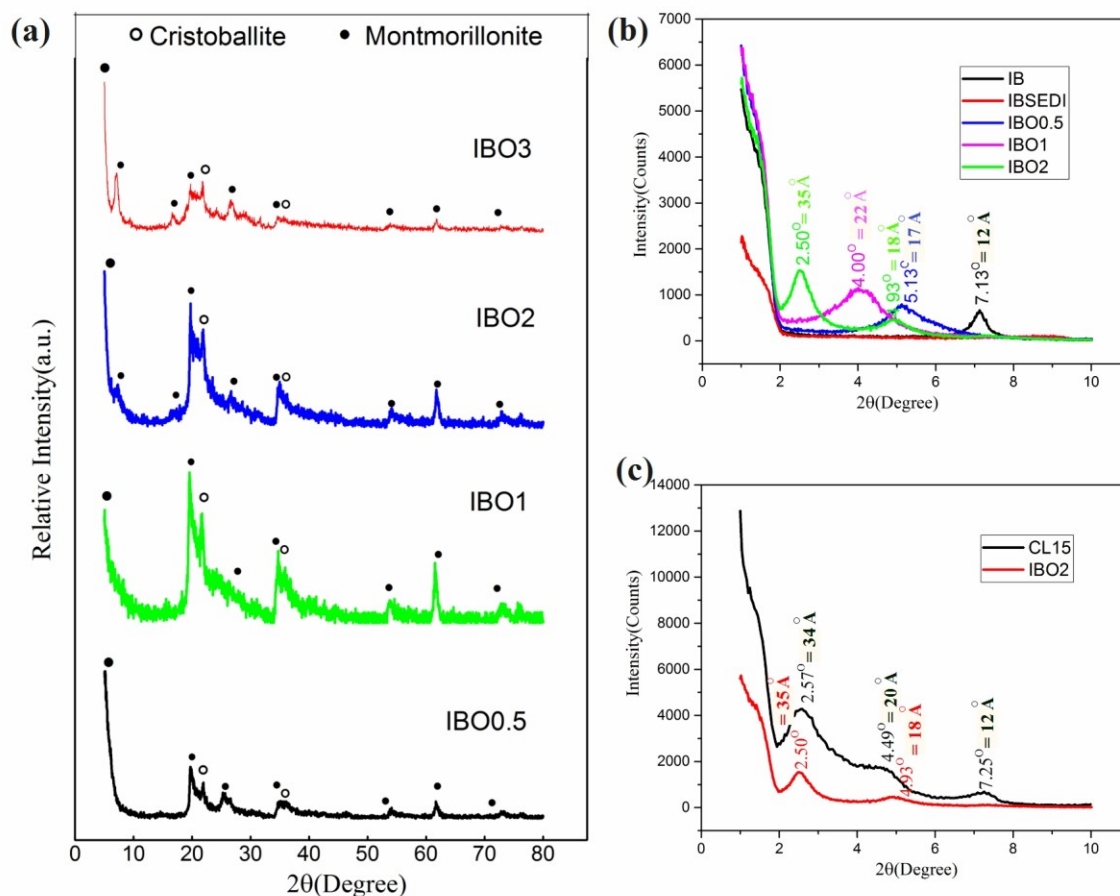


Fig. 5. (a) X-ray diffraction patterns of IBO0.5, IBO1, IBO2, and IBO3, (b) Low-angle X-ray diffraction patterns of IB, IBSEDI, IBO0.5, IBO1, IBO2, and CL15 (c) Low-angle X-ray diffraction patterns of CL15 and IBO2

The peak at 7.13° in IB, which shifted to higher angles in IBSEDI, exhibited an inverse shift to 5.13° , 4° and $(2.5^\circ$ and $4.93^\circ)$ in IBO0.5, IBO1, and IBO2, respectively. In fact, in sample IBO2, all the sheets have not been exfoliated similarly, and the peaks mostly shifted and can be detected at about 2.5° and 4.93° . Using the Bragg equation: $2d_{001}\sin\theta=\lambda$, where d_{001} is the interplanar distance of (001) reflection plane, θ is the diffraction angle, and λ is the wavelength, d_{001} of IB is

12Å, and d_{001} of IBO0.5, IBO1 and IBO2 are 17Å, 22Å and (35Å and 18Å), respectively (Choi *et al.*, 2005; Epp, 2016).

Based on the analysis of XRD patterns, it can be concluded that IBO2 is the optimized sample due to the high efficiency of exfoliation and shifting peaks to lower angles. Fig. 5(c) compares the low-angle XRD pattern of IBO2 and CL15. The similarity between these two samples confirms the successful preparation of organoclay.

3.3 Morphological analysis

To study the morphology of the samples, SEM was employed. Fig. 6(a) and (b) show SEM micrographs of NBZ and NBZP, and Fig. 6(c) and (d) represent their EDS analysis. EDS analysis reveals that by the purification process, the Al/Si ratio increases from 0.03 in NBZ to 0.15 in NBZP, which indicates an increase in the relative amount of clay in samples compared to raw materials containing impurities such as quartz. This increase confirms the relatively successful purification process (Zhang *et al.*, 2014).

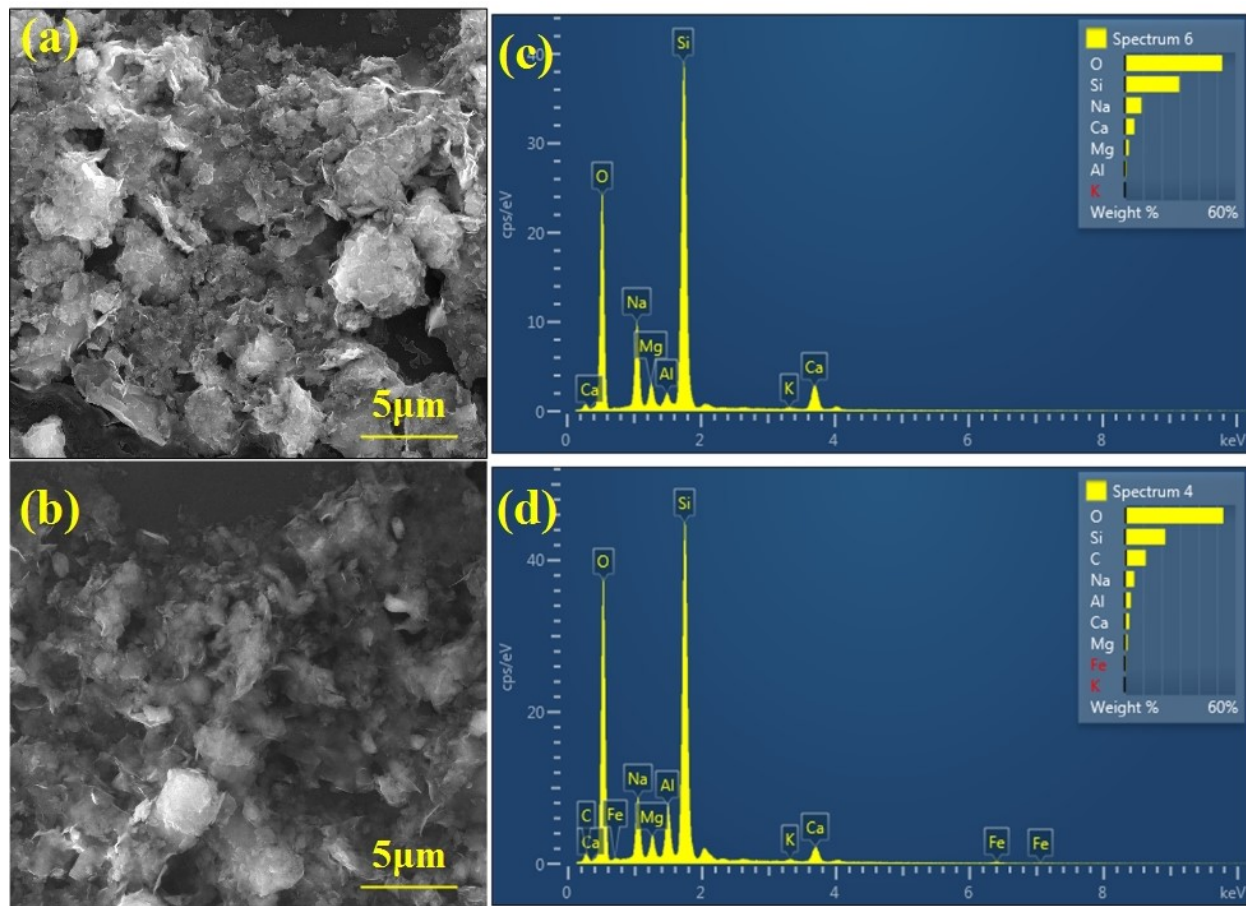


Fig. 6. SEM images of (a) NBZ and (b) NBZP (magnitude 10Kx), and EDS analysis of (c) NBZ and (d) NBZP. The reduction in Si/Al aspect ratio of (d) compared to (b) is the result of silica impurities removal during the purification step.

SEM images of IB and IBP are shown in Fig. 7(a, b). A relative increase in plate-like morphology is evident after the purification process. The observed relative increase in plate-like morphology after the purification process suggests that the purification has effectively removed impurities and non-clay minerals from the sample, leaving behind a higher proportion of clay minerals with a plate-like structure. This change is significant because clay minerals, such as montmorillonite,

typically exhibit a plate-like morphology and are desirable for various applications due to their unique properties, such as high surface area and cation exchange capacity.

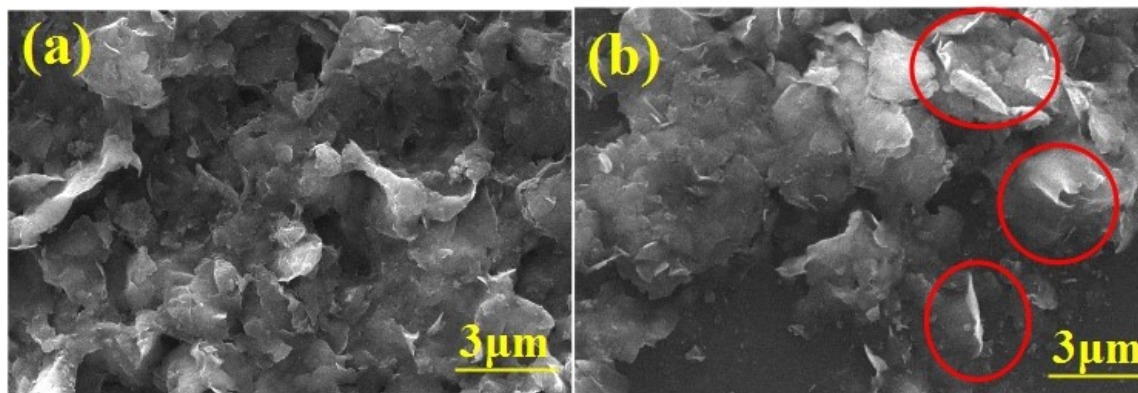


Fig.7. SEM images of a) IB and c) IBP (magnitude 10Kx)

SEM images of IBO0.5, IBO1, and IBO2 at magnifications of 10Kx and 30Kx are shown in Fig. 8(a-f). Morphological changes indicate successful organoclay preparation in organoclay samples. To confirm this, SEM images of CL15 are shown in Fig. 8(g-h). The structural similarity between IBO samples and CL15 and the presence of plate-like clay structures in the samples indicate the high quality of prepared organoclays.

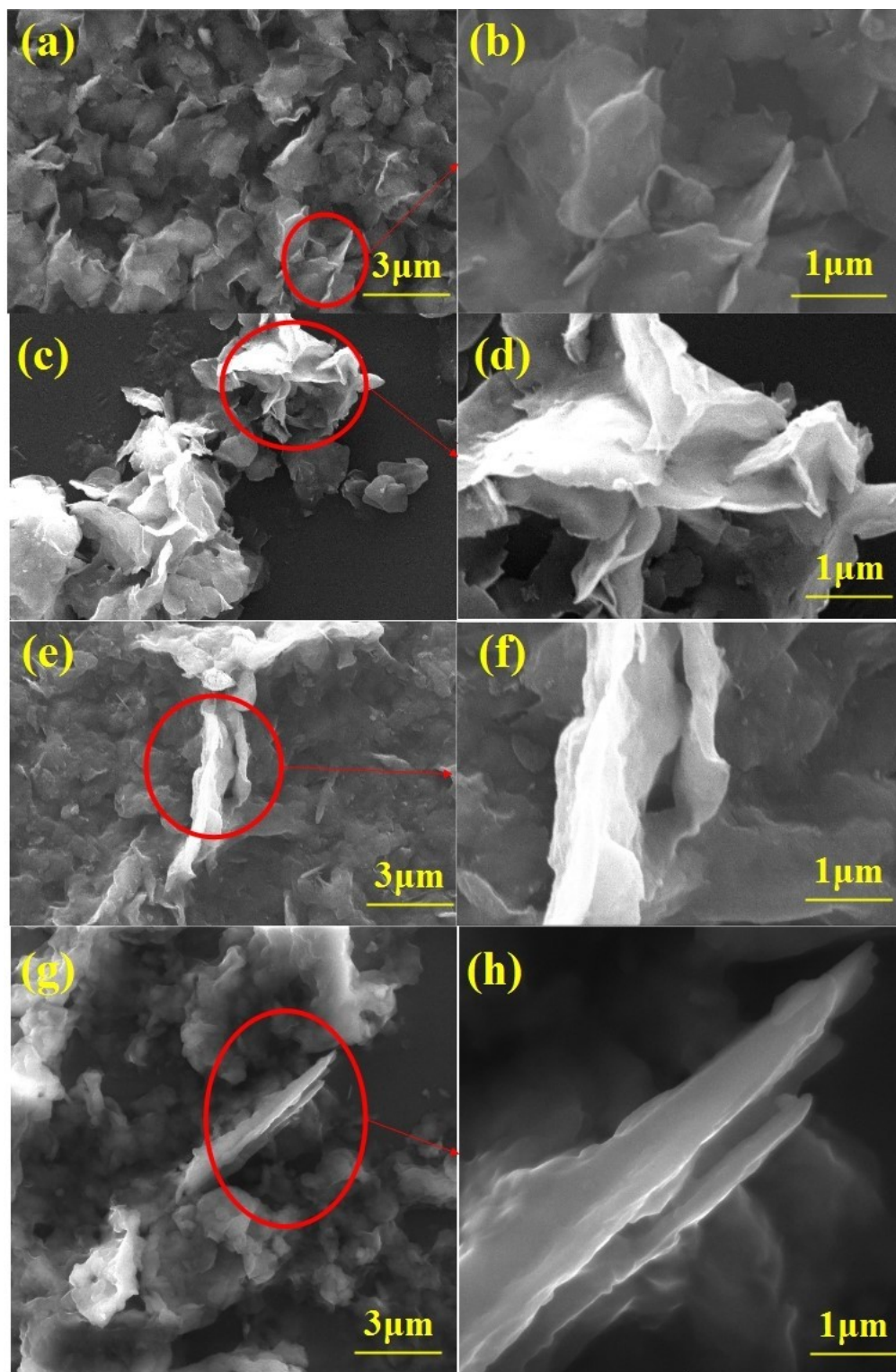


Fig. 8. SEM images of (a-b) IBO0.5, (c-d) IBO1, (e-f) IBO2, (g-h) CL15 (magnification of 10Kx and 30Kx)

FESEM images of PE and P1-5 composites at magnifications of 5Kx are shown in Fig. 9(a-f). Complete dispersion of exfoliated clay platelets in the polymer matrix has occurred. To achieve improved properties of composites, dispersion of additives within the matrix is necessary. (Eckel *et al.*, 2004; Jang *et al.*, 2005; Hadi *et al.*, 2018). From P5 to P1, the organoclay content is reduced, so the SEM images show less clay platelets. Fig. 9(g) and (h) are FESEM images of P5 at a magnification of 15Kx and 75Kx, respectively.

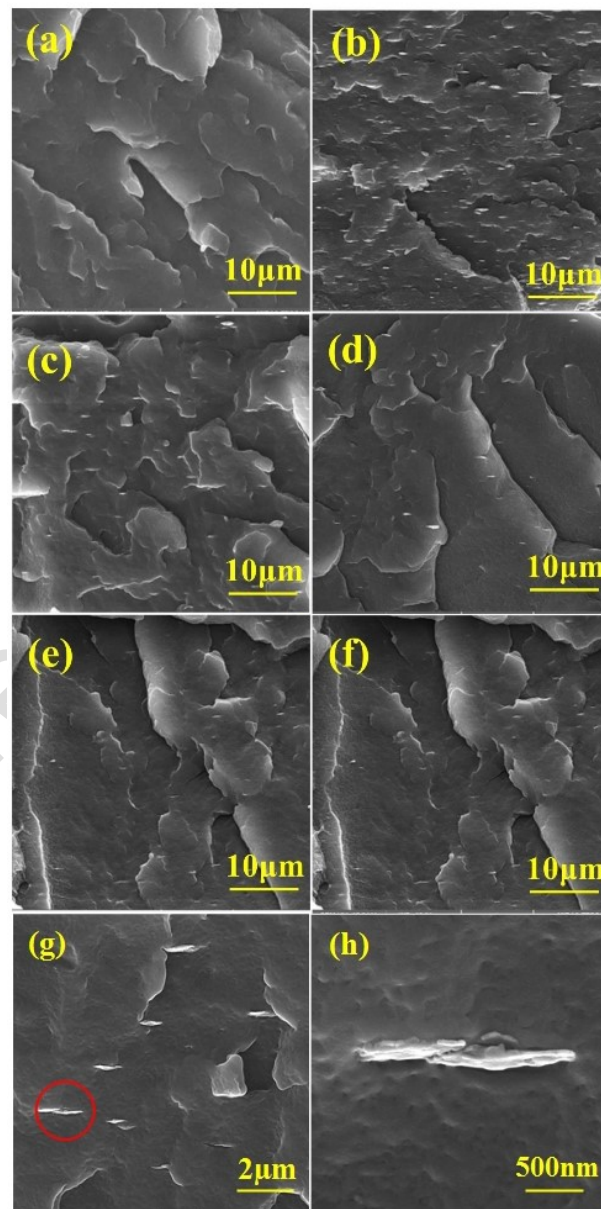


Fig.9. FESEM images of (a) PE, (b) P5, (c) P4, (d) P3, (e) P2, (f) P1 (magnitude 5Kx), (g) P5 at a magnification of 15Kx and, (h) P5 at a magnification of 75Kx

3.4 Chemical analysis

Table 2 presents the chemical analysis of four samples: IB, IBSEDI, IBO1, and IBO2. Comparison between IB and IBSEDI reveals that the addition of sodium hexametaphosphate to the bentonite dispersion for purification results in the replacement of interlayer cations such as calcium by sodium cations, which dissolve from the sodium hexametaphosphate in water. Furthermore, by performing the purification process, the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ has decreased, which indicates the relative increase of clay amount in bentonite (Thuc *et al.*, 2010). Replacing the interlayer sodium with octadecylamine organic molecules and removing sodium cations through washing dramatically reduces the sodium content in the samples (Xi *et al.*, 2007; He *et al.*, 2014).

Table 2
Chemical composition of IB, IBSEDI, IBO1 and IBO2

TiO ₂	Cl	P ₂ O ₅	SO ₃	K ₂ O	Fe ₂ O ₃	CaO	MgO	Na ₂ O	Al ₂ O ₃	SiO ₂ (wt%)	Sample
0.60	0.46	0.17	1.03	0.64	4.26	3.73	3.79	4.42	10.37	69.93	IB
0.43	Very low	5.88	0.75	0.39	5.17	1.35	3.64	8.55	15.62	58.21	IBSEDI
0.60	1.48	2.29	0.38	0.42	4.94	0.07	3.14	0.64	11.98	74.03	IBO1
0.65	6.81	3.30	0.63	0.46	6.12	0.11	3.00	0.68	15.65	62.58	IBO2

3.5 Thermal analysis of composites

Incorporating clay into a polymer matrix can enhance thermal stability. Clay layers act as thermal insulators. Clay layers act as thermal insulators by impeding the transfer of heat through the composite material. The arrangement of clay platelets within the polymer matrix creates a barrier that reduces the movement of heat energy, thereby enhancing the material's resistance to thermal conductivity. In addition, clays help char formation so that polymer decomposition can occur at higher temperatures (Mattausch, 2015). The thermal resistance of the composite can be influenced by the thermal stability of the surfactant used in modified organoclay. Xiong et al.(2004) tested two different modified montmorillonite and found out that montmorillonite modified by an aromatic modifier has higher thermal resistance compared to montmorillonite modified by a quaternary alkyl ammonium salt (Xiong *et al.*, 2004; Pavlidou & Papaspyrides, 2008).

Fig. 10(a) shows the TG analysis of PE (pure LDPE) and P5 (the sample containing 5%wt of organoclay) in a nitrogen atmosphere from 25°C to 600°C at a heating rate of 10°C/min. The detailed temperatures of Fig. 10(a) are shown in Table 3. T_i represents the temperature at which 10% of the sample is decomposed, while $T_{50\%}$ represents the midpoint of degradation. Another important parameter in TG analysis is the fraction of non-volatile material at 600°C in samples, known as char (Olewnik *et al.*, 2010). Compared to PE, T_i and $T_{50\%}$ in P5 (sample with 5%wt of organoclay) were 17°C and 13°C higher, respectively. The residue of P5 in 600°C is 43.4%, representing higher thermal stability of the composite and the successful char formation.

Table 3

TG tests results of PE and P5 samples

Sample	T _i (°C)	T _{50%} (°C)	Residue at 600°C (%)
PE	428	466	≈ 0
P5	445	479	43.4

3.6 Mechanical analysis of composites

Degree of dispersion is one of the most critical factors affecting composites' mechanical properties. If clay and matrix polymer have proper bonding, clay can bear the applied load due to its higher modulus and stiffness than the polymer matrix. Organomodified clays can usually increase the tensile strength and Young's modulus of polymer matrix (Chan *et al.*, 2011; Mattausch, 2015)

Fig. 10(b,c) shows tensile test results, indicating that the tensile strength improves up to its saturation point by adding organoclay to LDPE. **The addition of organoclay to LDPE results in an improvement in tensile strength until reaching saturation.** The tests were repeated three times for each sample, and average values of tensile strength, elongation at break, modulus, their corresponding errors are provided in Table 4. The tensile strength of PE increased from 8.67 MPa to 9.03 MPa in sample P4, and with the addition of more organoclay, sample P5 failed, and tensile strength decreased to 7.93 MPa. It can be concluded that there is a saturation point for mechanical properties, **beyond which further additives** can destroy polymer properties due to the increased stress concentration points (Jordan *et al.*, 2016; Awad, 2021; Sohrabi-Kashani *et al.*, 2022). **Additionally**, by adding organoclay to the LDPE matrix, the Young's modulus of the sample increased from 510 MPa in PE to 548 MPa in P2, and Elongation at break rose from 437% in PE to 682% in P2.

Table 4

Tensile test results of PE and Composite samples

Sample	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
PE	8.67 (± 0.12)	437 (± 10)	510 (± 4)
P1	8.59 (± 0.10)	281 (± 8)	490 (± 3)
P2	8.81 (± 0.15)	682 (± 16)	548 (± 5)
P3	8.93 (± 0.13)	650 (± 14)	531 (± 3)
P4	9.03 (± 0.17)	525 (± 11)	516 (± 6)
P5	7.93 (± 0.10)	676 (± 17)	527 (± 4)

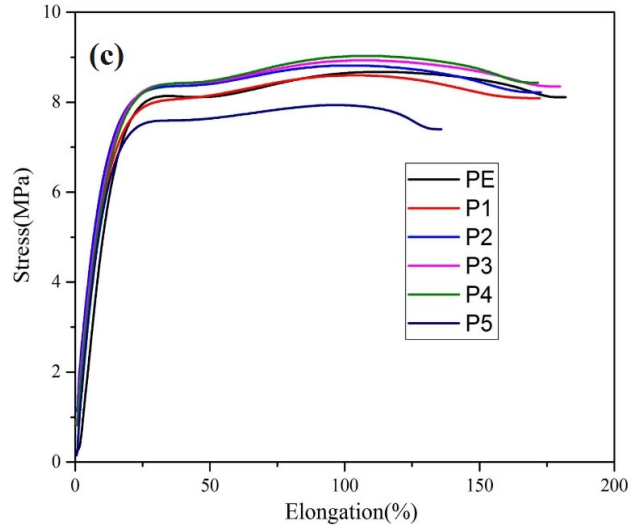
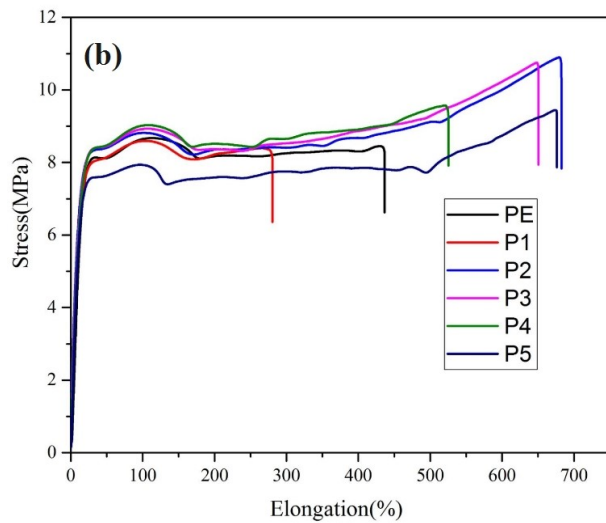
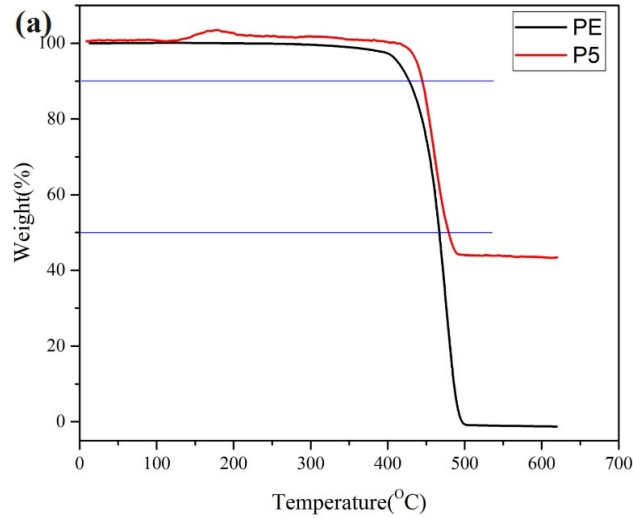


Fig. 10. (a) TG analysis for Polyethylene and P5 composite, (b) Tensile test results for PE and composite samples to **breakpoint** and, (c) Tensile test results for PE and composite samples to **deformation** point

4. Conclusion

In this study, Iranian bentonite was purified and modified to **prepare polymer/organoclay** composites. In the purification process, **by the sedimentation method**, impurities like quartz, calcium carbonate, and feldspar were removed (<4%wt), **and the cristobalite amount was reduced**. **The organoclay was prepared by the purified bentonite and octadecylamine surfactant and test results indicate that by using the optimum ratio of surfactant and bentonite, the interlayer space** **widen from 12Å in raw bentonite to 35Å in sample containing 2CEC of octadecylamine**. The polymer/organoclay composites were prepared using the hot mixing method, and the results show that the additive was fully dispersed in the matrix, and both the thermal and mechanical properties of composites were improved compared to the pure LDPE. **In the sample containing 5%wt of organoclay, T_i (the temperature at which 10% of the sample is decomposed) and $T_{50\%}$ (the midpoint of degradation) were 17°C and 13°C higher than in the polyethylene, respectively. The tensile strength of LDPE increased from 8.67 MPa to 9.03 MPa in the sample with 5%wt of organoclay.** Therefore, the various polymer-based and especially LDPE-based composites can be modified and **improved more by using less purified and optimized Iranian bentonites compared to raw bentonite.**

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Adams, J.M. & McCabe, R.W. (2006) Chapter 10.2 Clay Minerals as Catalysts. *Developments in Clay Science*, **1**, 541–581.

Ahmadi, F., Ghanbari, H., Moghaddam, F.S. & Naghizadeh, R. (2022) Optimized purification procedure for Iranian calcium bentonite for producing montmorillonite nanosheets. *Clay Minerals*, **57**, 120–130. Mineralogical Society.

- Amin, M.F.M., Heijman, S.G.J. & Rietveld, L.C. (2014) Nanoclay for Micropollutant Removal in Wastewater-Effective Alternative? *Advanced Materials Research*, **1024**, 11–14.
- Awad, S.A. (2021) Mechanical and thermal characterisations of low-density polyethylene/nanoclay composites. *Polymers and Polymer Composites*, **29**, 1325–1332.
- Bahranowski, K., Gawęł, A., Klimek, A., Michalik-Zym, A., Napruszewska, B.D., Nattich-Rak, M., Rogowska, M. & Serwicka, E.M. (2017) Influence of purification method of Na-montmorillonite on textural properties of clay mineral composites with TiO₂ nanoparticles. *Applied Clay Science*, **140**, 75–80.
- Bergaya, F., Theng, B.K.G. & Lagaly, G. (2006a) Chapter 7 Modified Clays and Clay Minerals. *Developments in Clay Science*, **1**, 261.
- Bergaya, F., Lagaly, G. & Al, Et. (2006b) Handbook of clay. *Handbook of Clay Science*, 8–10.
- Boylu, F., Çinku, K., Esenli, F. & Çelik, M.S. (2010) The separation efficiency of Na-bentonite by hydrocyclone and characterization of hydrocyclone products. *International Journal of Mineral Processing*, **94**, 196–202. Elsevier B.V.
- Chan, M., Lau, K., Wong, T., Ho, M. & Hui, D. (2011) Composites : Part B Mechanism of reinforcement in a nanoclay / polymer composite. *Composites Part B*, **42**, 1708–1712. Elsevier Ltd.
- Chipera, S.J. & Bish, D.L. (2001) Baseline studies of the clay minerals society source clays: Powder X-ray diffraction analyses. *Clays and Clay Minerals*, **49**, 398–409.
- Choi, Y.S., Xu, M. & Chung, I.J. (2005) Synthesis of exfoliated acrylonitrile-butadiene-styrene copolymer (ABS) clay nanocomposites: Role of clay as a colloidal stabilizer. *Polymer*, **46**, 531–538.
- Eckel, D.F., Balogh, M.P., Fasulo, P.D. & Rodgers, W.R. (2004) Assessing organo-clay dispersion in polymer nanocomposites. *Journal of Applied Polymer Science*, **93**, 1110–1117.
- Epp, J. (2016) *X-Ray Diffraction (XRD) Techniques for Materials Characterization*. P. in: *Materials Characterization Using Nondestructive Evaluation (NDE) Methods*. Elsevier Ltd, 81–124 pp.
- Forbes, E. & Chryss, A. (2017) Surface and Colloid Science, and Rheology. Pp. 81–110 in: *Fundamentals of Clays*.
- Galán, E. (2006) Chapter 14 Genesis of Clay Minerals. *Developments in Clay Science*, **1**, 1129–1162.
- Golubeva, O.Yu., Ul'yanova, N.Yu., Kostyreva, T.G., Drozdova, I.A. & Mokeev, M. V. (2013) Synthetic nanoclays with the structure of montmorillonite: Preparation, structure, and physico-chemical properties. *Glass Physics and Chemistry*, **39**, 533–539.
- Gong, Z., Liao, L., Lv, G. & Wang, X. (2016a) A simple method for physical purification of bentonite. *Applied Clay Science*, **119**, 294–300.
- Gong, Z., Liao, L., Lv, G. & Wang, X. (2016b) A simple method for physical purification of bentonite. *Applied Clay Science*, **119**, 294–300.

- Guo, F., Aryana, S., Han, Y. & Jiao, Y. (2018) applied sciences A Review of the Synthesis and Applications of Polymer – Nanoclay Composites. 1–29.
- Hadi, A.J., Abdulkadir, H.K., Hadi, G.J., Yusoh, K. Bin & Hasany, S.F. (2018) Mechanical and thermal properties of the waste low and high density polyethylene-nanoclay composites. *Oriental Journal of Chemistry*, **34**, 1069–1077.
- He, H., Ma, L., Zhu, J., Frost, R.L., Theng, B.K.G. & Bergaya, F. (2014) Synthesis of organoclays: A critical review and some unresolved issues. *Applied Clay Science*, **100**, 22–28. Elsevier B.V.
- Jang, B.N., Wang, D. & Wilkie, C.A. (2005) Relationship between the solubility parameter of polymers and the clay dispersion in polymer/clay nanocomposites and the role of the surfactant. *Macromolecules*, **38**, 6533–6543.
- Jordan, J.L., Casem, D.T., Bradley, J.M., Dwivedi, A.K., Brown, E.N. & Jordan, C.W. (2016) Mechanical Properties of Low Density Polyethylene. *Journal of Dynamic Behavior of Materials*, **2**, 411–420. Springer International Publishing.
- Kooli, F., Liu, Y., Alshahateet, S.F., Messali, M. & Bergaya, F. (2009) Reaction of acid activated montmorillonites with hexadecyl trimethylammonium bromide solution. *Applied Clay Science*, **43**, 357–363. Elsevier B.V.
- Lagaly, G., Ogawa, M. & Dékány, I. (2006) Chapter 7.3 Clay Mineral Organic Interactions. *Developments in Clay Science*, **1**, 309–377.
- Lapides, I. & Yariv, S. (2004) The effect of ultrasound treatment on the particle-size of Wyoming bentonite in aqueous suspensions. *Journal of Materials Science*, **39**, 5209–5212.
- Levy, G.J., Srianmrg, I., Alperovitch, N. & Merwe, A.J.V.A.N.D.E.R. (1991) Effect of Na-Hexametaphosphate on the hydraulic conductivity of kaolinite-sand mixtures. **39**, 131–136.
- Mattausch, H. (2015) *Properties and applications of nanoclay composites*. P. in: *Polymer Nanoclay Composites*. Elsevier Inc., 127–155 pp.
- Modabberi, S., Namayandeh, A., López-Galindo, A., Viseras, C., Setti, M. & Ranjbaran, M. (2015) Characterization of Iranian bentonites to be used as pharmaceutical materials. *Applied Clay Science*, **116–117**, 193–201. Elsevier B.V.
- Modabberi, S., Namayandeh, A., Setti, M. & López-Galindo, A. (2019) Genesis of the Eastern Iranian bentonite deposits. *Applied Clay Science*, **168**, 56–67. Elsevier.
- Motawie, A.M., Madany, M.M., El-Dakrory, A.Z., Osman, H.M., Ismail, E.A., Badr, M.M., El-Komy, D.A. & Abulyazied, D.E. (2014) Physico-chemical characteristics of nano-organo bentonite prepared using different organo-modifiers. *Egyptian Journal of Petroleum*, **23**, 331–338. Egyptian Petroleum Research Institute.
- Olewnik, E., Garman, K. & Czerwiński, W. (2010) Thermal properties of new composites based on nanoclay, polyethylene and polypropylene. *Journal of Thermal Analysis and Calorimetry*, **101**, 323–329.

- Oueslati, W., Karmous, M.S., Ben Rhaiem, H., Lanson, B. & Ben Haj Amara, A. (2007) Effect of interlayer cation and relative humidity on the hydration properties of a dioctahedral smectite. *Zeitschrift fur Kristallographie, Supplement*, **2**, 417–422.
- Özgen, S., Yildiz, A., Çalışkan, A. & Sabah, E. (2009) Modeling and optimization of hydrocyclone processing of low grade bentonites. *Applied Clay Science*, **46**, 305–313.
- Pacufa, A., Bielańska, E., Gawel, A., Bahranowski, K. & Serwicka, E.M. (2006) Textural effects in powdered montmorillonite induced by freeze-drying and ultrasound pretreatment. *Applied Clay Science*, **32**, 64–72.
- Patel, H.A., Somani, R.S., Bajaj, H.C. & Jasra, R. V. (2006) Nanoclays for polymer nanocomposites, paints, inks, greases and cosmetics formulations, drug delivery vehicle and waste water treatment. *Bulletin of Materials Science*, **29**, 133–145.
- Pavlidou, S. & Papaspyrides, C.D. (2008) A review on polymer-layered silicate nanocomposites. *Progress in Polymer Science (Oxford)*, **33**, 1119–1198.
- Pereira, I.D.S., Silva, V.C., Duarte Neto, J.F., Neves, G.A., Ferreira, H.C. & Menezes, R.R. (2018) Influence of the purification of bentonite clay from new deposits in the state of Paraíba-Brazil for use in water-based drilling fluids. *Ceramica*, **64**, 538–546.
- Rafiei, B. & Ghomi, F.A. (2013) Preparation and characterization of the Cloisite Na⁺ modified with cationic surfactants Caspian sea View project Organoclay synthesis View project. *Journal of Crystallography and Mineralogy*, **21**, 25–32.
- Rihayat, T., Salim, S., Arlina, A., Fona, Z., Jalal, R., Alam, P.N., Zaimahwati, Z., Sami, M., Syarif, J. & Juhan, N. (2018) Determination of CEC value (Cation Exchange Capacity) of Bentonites from North Aceh and Bener Meriah, Aceh Province, Indonesia using three methods. P. in: *IOP Conference Series: Materials Science and Engineering*. Institute of Physics Publishing.
- ROSS, C.S. & HENDRICKS, S.B. (1943) Minerals of the montmorillonite group their origin and relation to soils and clays. *Geological survey professional paper 205-b*, **23–79**, 23–79.
- Sohrabi-Kashani, L., Yekta, B.E., Rezaie, H.R. & Zolriasatein, A. (2022) Synergistic effect of micro- and nano-TiO₂ on hydrophobic, mechanical, and electrical properties of hybrid polyurethane composites. *Journal of Materials Science: Materials in Electronics*, **33**, 14488–14507.
- Sohrabi-Kashani, L., Zolriasatein, A. & Eftekhari Yekta, B. (2023) Effect of silica nanoparticles modified with different concentrations of stearic acid on microstructure, mechanical & electrical properties of RTV-2 silicone rubber nanocomposite. *Asian Journal of Nanosciences and Materials*, **1**, 16–32.
- Thuc, C.N.H., Grillet, A.C., Reinert, L., Ohashi, F., Thuc, H.H. & Duclaux, L. (2010) Separation and purification of montmorillonite and polyethylene oxide modified montmorillonite from Vietnamese bentonites. *Applied Clay Science*, **49**, 229–238.
- Uddin, F. (2008) Clays, nanoclays, and montmorillonite minerals. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, **39**, 2804–2814.

Xi, Y., Frost, R.L. & He, H. (2007) Modification of the surfaces of Wyoming montmorillonite by the cationic surfactants alkyl trimethyl, dialkyl dimethyl, and trialkyl methyl ammonium bromides. *Journal of Colloid and Interface Science*, **305**, 150–158.

Xiong, J., Liu, Y., Yang, X. & Wang, X. (2004) Thermal and mechanical properties of polyurethane/montmorillonite nanocomposites based on a novel reactive modifier. *Polymer Degradation and Stability*, **86**, 549–555.

Yadav, V.B., Gadi, R. & Kalra, S. (2019) Clay based nanocomposites for removal of heavy metals from water: A review. *Journal of Environmental Management*, **232**, 803–817. Elsevier.

Zhang, B.B., Miao, M.Y., Bai, J., Yuan, G.J., Jia, Y.Y., Han, Z.X., Zhao, Z.G. & Su, H.Q. (2014) Researches on purification and sodium-modification of Ca-bentonite by tri-roller grinder. *Advanced Materials Research*, **962–965**, 809–813.

Zhou, C.H. & Keeling, J. (2013) Fundamental and applied research on clay minerals: From climate and environment to nanotechnology. *Applied Clay Science*, **74**, 3–9. Elsevier B.V.

Zhu, T.T., Zhou, C.H., Kabwe, F.B., Wu, Q.Q., Li, C.S. & Zhang, J.R. (2019) Exfoliation of montmorillonite and related properties of clay/polymer nanocomposites. *Applied Clay Science*, **169**, 48–66.

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