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#### Chapter

### An Introduction to Montmorillonite Purification

Hakan Ciftci

#### **Abstract**

Purification of montmorillonite is a process to remove non clay minerals (gangue) such as calcite, feldspar, quartz, opal (C-T), and mica from montmorillonite ore. This is performed to make montmorillonite suitable for use in sensitive applications such as pharmaceutical, cosmetic, food, and advanced materials for nanotechnology. Gangue minerals in raw montmorillonite ores can cause serious health problems when used in pharmaceutics, cosmetic, and food industries and reduce material quality in advanced materials production. Montmorillonite purification can be divided into two main classes as physical and chemical purification. Physical purification processes are based on particle size difference between the gangue and montmorillonite minerals. Purification processes based on gravity separation are ineffective since the specific weights of gangue and montmorillonite minerals are very close to each other. Physical purification process includes sedimentation, centrifugal separation, aero separation, and sieving techniques. Chemical purification of montmorillonite is based on dissolution and so extraction of carbonates, metal hydroxides, organic materials, and silica, respectively, using different leaching techniques.

**Keywords:** montmorillonite, bentonite, purification, beneficiation, enrichment, leaching

#### 1. Introduction

Montmorillonite, a type of smectite mineral, is an aqueous aluminum silicate. It has a layered crystalline structure with the general chemical formula of  $(Na,Ca)_{0.33}(Al,Mg)_2$   $(Si_4O_{10})(OH)_2$ \* $nH_2O$ . Rocks that mostly contain montmorillonite mineral are also called as bentonite. For this reason, sometimes the term bentonite is used instead of montmorillonite. Montmorillonite clay has some superior characteristics such as high surface area, high swelling capacity, good adsorbent ability, high cation exchange capacity, plasticity, high chemical stability, and good mechanical properties [1–4]. Due to these properties it exhibits, montmorillonite has many uses and research areas, some of which can be listed as pharmaceutical and cosmetic industry, adsorbents, catalysts, drilling mud, and filler in construction industries such as ceramics [2, 5–7].

Raw montmorillonite ores (bentonite) generally contain gangue minerals such as quartz, opal (C-T), mica, calcite, and feldspar, as well as montmorillonite minerals. While raw montmorillonite is mostly used as raw material for

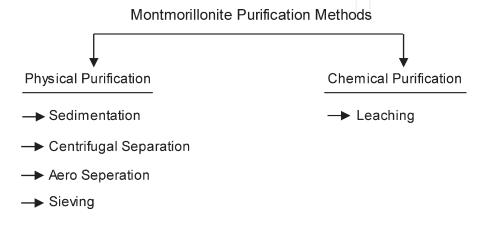
drilling mud, cement, and ceramic, it is used in purified form (montmorillonite) in pharmaceutical, cosmetic, food, and advanced materials industries [8]. For example, thanks to the strong adsorption and detoxification effect of montmorillonite on toxic substances, it is widely used in the treatment of esophagitis, gastritis, colitis, and similar diseases [9]. Purified montmorillonite are also used as raw materials for cosmetics due to their decontamination, detoxification, itching, and beautifying properties [3]. Along with these, montmorillonite is widely used as drug delivery system and food protective material, closely related to our life and health [10]. For such uses, it is necessary to separate montmorillonite minerals from gangue minerals (purification) to ensure health and material quality. For this purpose, different methods have been used in many studies on the purification of montmorillonite.

#### 2. Purification of montmorillonite

The specific weight of clay minerals and accompanying gangue minerals (quartz, feldspar, calcite, opal, mica, etc.) are very close to each other (2.4–2.7 g/cm³) [11]. For this reason, gravity separation processes based on specific weight difference in order to separate gangue minerals from clay minerals cannot give successful results. The particle size difference between montmorillonite and gangue minerals ensures several physical separation techniques, however. In addition, chemical purification of clay minerals can be summarized as decomposition of carbonates, dissolution of metal hydroxides, oxidation of organic substances, and dissolution of silica. All purification methods can be grouped into two main classes as physical, and chemical purification as shown in **Figure 1**.

#### 2.1 Physical purification

Physical purification methods are the most used techniques for the montmorillonite purification. The processes are easy and based on the difference in particle sizes of montmorillonite and gangue minerals. The particle size distribution of montmorillonite clay is between 0.1  $\mu m$  and 2  $\mu m$  and it has an average particle size of 0.5  $\mu m$  [12]. The particle size of most of the gangue minerals is larger in the raw form and generally ranges from 20  $\mu m$  to 1 cm, however. The physical purification methods according to particle size difference can be listed as sedimentation, centrifugal separation, aero separation, and sieving.



**Figure 1.**Purification methods of montmorillonite clay.

#### 2.1.1 Sedimentation

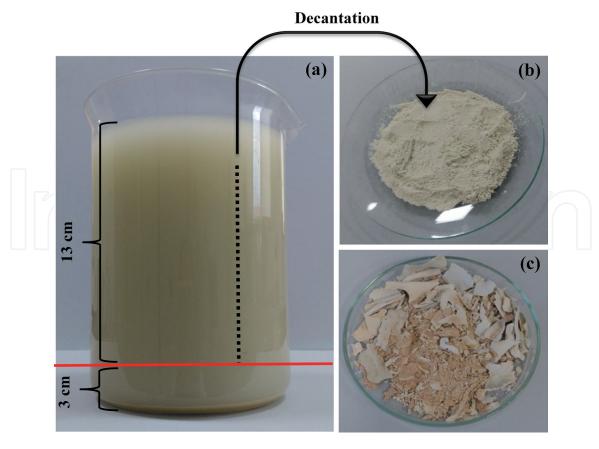
Clay minerals like montmorillonite are well dispersed in very small sizes in the aqueous media, while gangue minerals remain in coarse sizes. For this reason, the method generally used in montmorillonite purification is sedimentation (settling) in water, depending on the particle size difference. During the sedimentation process, clay minerals dispersed in water in much smaller particle sizes remain suspended, while gangue minerals in coarse sizes settle to the bottom. In this process, suspended clay minerals can be separated from other minerals by decantation. In order to prevent particle/particle interactions during the sedimentation process and thus increase the purification yield and recovery, the solid content in the water should be between 0.5% and 1.0%. Stokes sedimentation equation is generally used to estimate sedimentation time Eq. (1). For an example, a quartz particle with a diameter of 1  $\mu$ m settles from a height of 0.1 m in approximately 26 h and 25 min. As another example, the dispersion obtained with a sedimentation height of 20 cm and a sedimentation time of 52.5 h contains only particles under 1  $\mu$ m size [12].

$$t = \frac{18\eta h}{(\rho - \rho o)gd^2} \tag{1}$$

Here; t: sedimentation time (s),  $\eta$ : fluid viscosity (g/cm.s), h: sedimentation height (cm),  $\rho$ : solid specific weight (g/cm<sup>3</sup>),  $\rho$ 0: liquid specific weight (g/cm<sup>3</sup>), g: gravitational acceleration (9.81 m/s<sup>2</sup>), d: particle diameter (cm).

An example of laboratory scale sedimentation process for montmorillonite purification is given below, step by step [1].

- 1. The particle size of raw montmorillonite clay is first reduced to less than 5 mm using a jaw crusher and then a roller mill. Since montmorillonite is well dispersed in water and to keep the gangue minerals in coarse sizes, no extra crushing and/or grinding process is applied.
- 2. After the size reduction, 20 g of crushed raw montmorillonite sample is added to a beaker which contains 2 L of distilled water.
- 3. The clay water dispersion obtained is kept for 24 h and then mixed with a mechanical mixer at 1000 rpm for 30 min.
- 4. After the mixing, the sedimentation process is started and the dispersion is kept for 8 h to complete settle the coarse gangue mineral particles. In this process, much finer particles of montmorillonite are suspended in water.
- 5. The dispersion on the sediment is siphoned (decantation) up to 3 cm height of the sediment as shown in **Figure 2**.
- 6. In order to prevent the settled gangue minerals from mixing with the suspended clay minerals as a result of the turbulence effect, the siphoning process is continued from top to bottom slowly up to a height of 3 cm from the bottom.
- 7. Finally, the montmorillonite particles in the dispersion obtained after siphoning are separated by centrifugation or filtration and then dried at 35-50°C for 24 h.



**Figure 2.**An example of sedimentation process; (a) raw montmorillonite dispersion, (b) purified montmorillonite, (c) settled gangue minerals [1].

#### 2.1.2 Centrifugal separation

One of the physical purification methods performed for separating montmorillonite clay and gangue minerals according to the difference in particle size is centrifugal separation. Centrifuge is a technique in which centrifugal force is used to separate various components in a liquid from each other or from the liquid. In solid—liquid separation processes, centrifugation is performed by rotating a closed container containing liquid and solid particles radially at high speed. It works by causing denser and/or larger particles to move outward in the radial direction, while less dense and/or smaller objects shift and move towards the center. In solid—solid separation processes, an aqueous media containing two or more different solids moves by following two different ways under the effect of centrifugal force. As the water moves in both directions, heavy and/or coarse particles move on one way and less dense and/or small particles moves on the other way. For this technique hydrocyclone, Falcon gravity concentrator (FGC), Knelson gravity concentrator (KGC), and multi gravity separator (MGS) devices are generally used (Figure 3).

Hydrocyclone (**Figure 3a**) is one of the most used mineral processing equipment in the plants that can be used to separate different minerals from each other based on both their particle size and specific weight. In some cases it is also used as dewatering equipment. In montmorillonite purification processes, multi stage hydrocyclone systems should be used to ensure maximum yield and purification degree (**Figure 4**). Multi gravity separator (MGS) (**Figure 3b**) are generally used to beneficiate minerals which liberation particle sizes are under 500  $\mu$ m. MGS consists of an inclined drum that rotates around its own axis while shaken axially in a sinusoidal motion. Inside the drum is a scraper assembly that rotates in the same direction as the drum, but at a slightly faster speed. MGS also separates minerals based on particle size difference and therefore clay ores such as montmorillonite

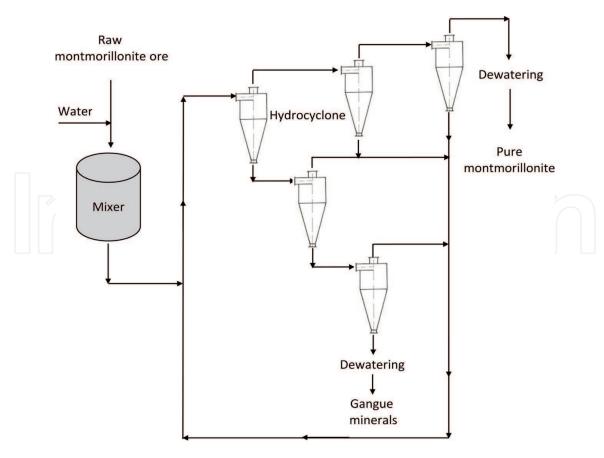


**Figure 3.**Photographs of laboratory scale (a) hydrocyclone, (b) multi gravity separator, (c) falcon gravity concentrator, (d) Knelson gravity concentrator.

can be purified using MGS. FGC (**Figure 3c**) and KGC (**Figure 3d**) are the similar devices and work as batch system. There is a slight structural difference between them and the entire bowl in the KGC is grooved while a part of the Falcon bowl is grooved. Maximum 5 wt.% solid ratio should be used when using all centrifugal separators to ensure maximum yield and purification degree.

#### 2.1.3 Aero separation

Aero separation is based on the different motion characteristics of mineral particles in various devices working with air flow media. Aero classifiers (separators) are divided into two main groups as static and dynamic separators, and classify mineral particles according to their size, shape, and specific weight. In aero cyclone and static separators, the ore is fed to the classifier at a certain speed and classification is performed under the effect of this speed. In dynamic separators the motion of particles is controlled by both air and a blade stator rotating at a certain speed. Dynamic separators are the most used type among aero separators because of its high efficiency and capacity. The figures of the some aero separators are given in **Figure 5**.

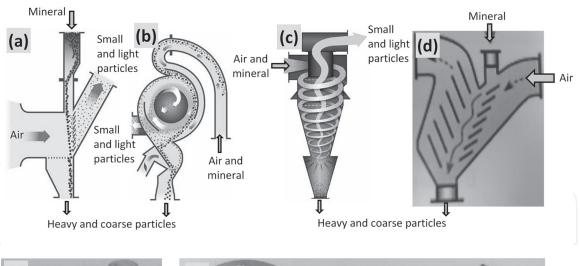


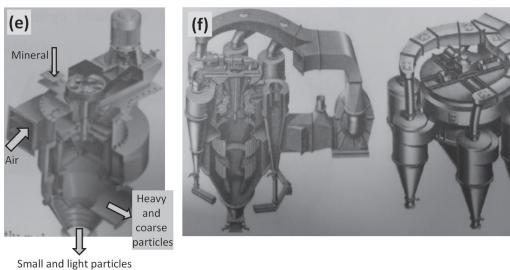
**Figure 4.**A simple flow sheet for montmorillonite purification using multi stage hydrocyclone process.

The working principles of aero separators are similar. For the classification process, the ground ore is fed into the separator along with the air and suspended. The mineral particles are moved under the gravity and centrifugal forces according to their specific weight, shape, and size. The combination of these forces determines the movement direction of the particles, and the particles are separated from each other. The particles move with the air if the particle size and weight are small enough. The value at which gravity and centrifugal force are in equilibrium is called the separation size or "cut point". In other words, the cut point of a separator defines that the particles having a size of cut point value moves with both coarse and small particles.

Grinding is the most important process in the montmorillonite purification using aero separators. Because gangue minerals become thinner to the particle size of clay minerals at the end of extreme grinding and this is an undesirable situation. For an efficient purification, there should be a significant particle size difference between montmorillonite and gangue minerals. To ensure this, grinding should always be controlled by particle size measurements. Apart from this, different grinding media such as glass and/or plastic based balls can be used instead of steel balls. The specific gravity of glass and plastic balls is less than steel balls, and this ensures that the softer clay minerals are largely dispersed, while the harder gangue minerals are not grinded too much and remain in coarse sizes.

In montmorillonite purification processes using aero separators multi stage processes should be used to obtain maximum yield and purification degree. **Figure 6** shows an example of simple flow sheet for montmorillonite purification process using multi stage dynamic separator. The number of separators in the process can be increased or decreased by prior experimental studies.





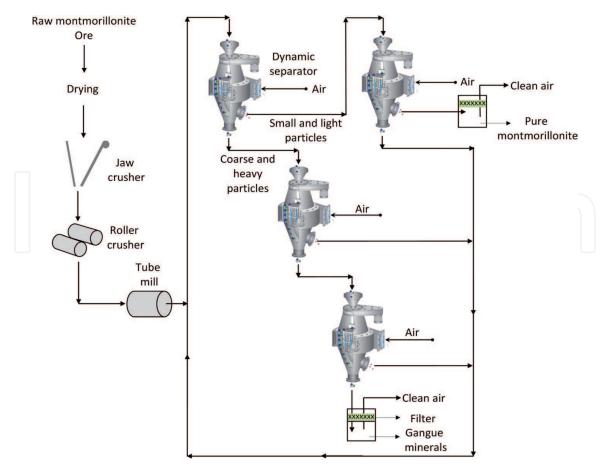
**Figure 5.**Aero separators, (a) gravitational static separator, (b) centrifugal static separator, (c) aero cyclone static separator, (d) v-type static separator, (e) dynamic separator, (f) dynamic and cyclonic separator [13, 14].

#### 2.1.4 Sieving

Sieving is the most used process part in mineral processing plants. Minerals are classified according to their particle sizes by various different sieves. Montmorillonite purification can be performed using both wet and dry sieving processes. Since the montmorillonite particles are very well dispersed in water (<2  $\mu m$ ), there is no need to pre-grind the raw ore in the wet sieving purification process. In this way, it is ensured that the gangue minerals remain in coarse sizes. However, if the dry sieving process is to be performed, it is necessary to do a controllable grinding before the sieving in order to disperse the agglomerated clay mineral particles. The yield and the purification degree of the montmorillonite purification process by sieving are in most cases lower than other methods because the sieving efficiency of the sieves in fine sizes decreases too much.

#### 2.2 Chemical purification (leaching)

Leaching is the process of extracting organic or inorganic substances from a solid by dissolving them in a liquid. It is generally used for the extraction of valuable minerals (especially gold and rare earths) from raw ores, and the process is classified as chemical beneficiation (enrichment) method. However, in some cases, it can also be used to remove waste (gangue) minerals from valuable ores. Chemical clay



**Figure 6.**A typical flow sheet for montmorillonite purification using multi stage dynamic separator.

purification is one of them and is based on decomposition of carbonates, dissolution of hydroxides, oxidation of organic materials, and dissolution of silica.

Carbonated minerals such as calcite dissolve easily in dilute hydrochloric (HCl) acid, and acetic acid (CH<sub>3</sub>COOH). For this reason, raw montmorillonite clay containing carbonated minerals can be purified from carbonates by first treating with dilute HCl or CH<sub>3</sub>COOH. During acid treatment, the pH value of the clay dispersion should be kept under constant control and the pH value should be prevented from falling below 4.5. Below this pH value, the clay structure can be damaged in a long time [15]. After acid treatment, the edges of the crystals are opened and the  $Al^{3+}$  and  $Mg^{2+}$  cations of the octahedral layers become soluble and at the same time the catalytic properties of the clay increase. Since an increase in the specific surface area of acid-treated clays is observed, the adsorption capacity of the clays also increases [16–18].

Iron, aluminum, and manganese (hydr)oxides can be removed from the clay ore by complexing multivalent cations with citrate. There are amorphous and crystal forms of free iron oxides in most of clay ores. Fe<sup>3+</sup> should be reduced to Fe<sup>2+</sup>, which when treated with sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) forms a stable citrate complex. The use of citrate with sodium dithionite not only helps iron extraction, but also removes some alumina coatings, thus helping to dissolve free silica cements stabilized with alumina coatings [19, 20]. **Table 1** shows several chemicals which were tested for dissolution of iron hydroxides. For all chemical combinations, the same procedure outlined below can be performed. Each reaction given in **Table 1** is carried out with stirring for 3 hours and repeated twice. The final solid product obtained is centrifuged and washed at least twice with 0.5 mol/L sodium chloride (NaCl) solution. Finally, samples are washed several times in distilled water to remove residual NaCl [21].

Method	Used chemicals
A	$Na_3C_6H_5O_7$ (sodium citrate, 29.4 g), NaOH (0.5 mol/L), $Na_2S_2O_4$ (sodium dithionite, 0.5 g), $pH\sim7$
В	$(NH_4)_2C_2O_4$ (ammonium oxalate, 0.25 mol/L), $H_2C_2O_4$ (oxalic acid, 0.1 mol/L), $pH\sim 3$
С	$(NH_4)_2C_2O_4$ (ammonium oxalate, 0.25 mol/L), $Na_2S_2O_4$ sodium dithionite (0.5 g)
D	HNO <sub>3</sub> (0.5 mol/L)

**Table 1.**Chemicals used for dissolution of iron hydroxides from montmorillonite [21].

Another recommended procedure for removing of iron hydroxides can be summarized as follow. First, 15 g of montmorillonite ore is dispersed in 250 mL water and then prepared dispersion is added in a 200 mL buffer solution consisting of 0.3 M sodium citrate, 1 M sodium hydrogen carbonate, and 1.2 M HCl. The mixture is then heated to 75°C and 4 g sodium dithionite is added. After 30 min mixing, solid liquid separation is applied and then the solid material is washed with 200 mL 0.05 M HCl. After washing, the reduction process is repeated and then the washing is performed with a mixture of 200 mL 0.5 M NaCl and 200 mL 0.5 M sodium acetate. Finally, the resulting solid product is added to 1000 mL solution (250 mL 30%  $\rm H_2O_2$  + 750 mL 0.5 M sodium acetate) and kept at 70°C for 30 min to ensure oxidation of the organic substances. Following the oxidation process, solid–liquid separation is performed and organic substances are removed by washing with 200 mL 0.5 M NaCl twice [15, 22].

Organic substances can be removed from clay ores by oxidizing using hydrogen peroxide ( $H_2O_2$ ), sodium hypochlorite (NaOCl), aqueous bromine (Br), and sodium peroxodisulphate ( $N_2S_2O_8$ ) in some buffer solutions such as sodium hydrogen carbonate and sodium tetraborate [23–28]. By using  $Na_4P_2O_7$  as a dispersing agent in the  $H_2O_2$  treatment, the amount of organic carbon removal can be increased [29]. Kaiser and Guggenberger [30] investigated a modified NaOCl treatment on many soil samples and found that from 77–95% of the initial organic carbon could be removed from soil. It has been suggested that the efficiency of removing organic matter by  $Na_2S_2O_8$  process is superior to  $H_2O_2$  and NaOCl [31].

The amorphous silica in the clay ore can be removed easily by dissolving in a boiling solution containing 5%wt. sodium carbonate ( $Na_2CO_3$ ). Since this reaction makes the leaching of hydroxides difficult, it should be used when all the chemical processes described above are completed [15].

#### 3. Evaluation of the purification methods

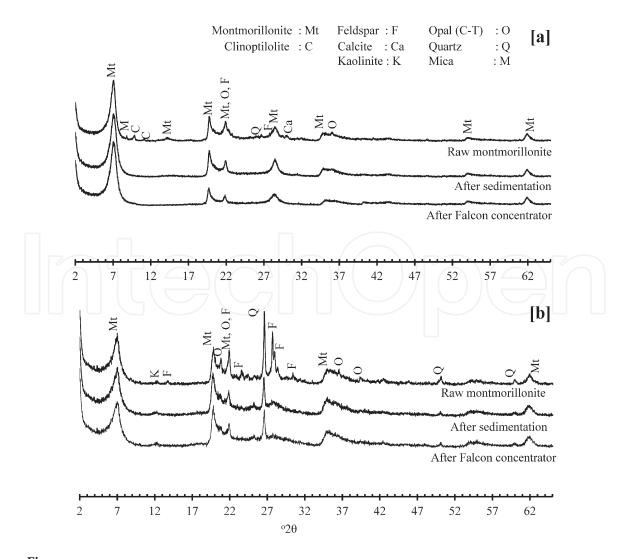
The efficiency of each purification technique can be assessed based on XRD, XRF, particle size, cation exchange capacity (CEC), swelling index (SI) analyzes before and after experiments. The montmorillonite content can be calculated using quantitative XRD data and rietveld analysis. The yield is obtained by calculating the percentage by weight of the product obtained after beneficiation to the fed product. Apart from these, recovery can be calculated from Eq. (2) [32].

$$R(\%) = \frac{M_c * CEC_c}{M_f * CEC_f}$$
 (2)

Here; R is the recovery (%),  $M_c$  and  $M_f$  are the mass of concentrate and feed (%),  $CEC_c$  and  $CEC_f$  are cation exchange capacities of concentrate and feed, respectively.

For an example, **Figure** 7 shows a sample of XRD patterns of two different type montmorillonite ores before and after purification by sedimentation and centrifugal separation techniques. The sedimentation process was performed exactly as described in the Section 2.1.1. FGC was used for centrifugal separation and the process used can be summarized as follow. Beneficiation trials were performed at 300 G centrifugal force and 1.5 L/min suspension feed rate. For this, 1.0% clay dispersion was prepared as described in the sedimentation process and then left for 10 minutes to allow the coarse particles to settle. The dispersion remaining on the collapsed particles was completely removed and fed to FGC once [1].

According to **Figure 7**, most of the gangue minerals were removed from raw montmorillonite-a by sedimentation and FGC. However, some of quartz minerals and little amounts of kaolinite remained in montmorillonite-b after both sedimentation and FGC processes. This can be explained by the fact that the quartz and kaolinite particles smaller than 5 µm are suspended in water and moves with montmorillonite particles. Small amounts (<3%) of such small particles that could not be detected by the XRD device may also have remained in the montmorillonite-a products. Considering the degree of purification, XRD data did not show any significant difference between sedimentation and FGC techniques for both clays. Apart from XRD analysis, cation exchange capacity (CEC), swelling index (SI), and yield were also calculated before and after purification processes. The results are summarized in the **Table 2** [1].



**Figure 7.**XRD patterns of two different type montmorillonite clays before and after beneficiation processes, (a) montmorillonite-a, (b) montmorillonite-b [1].

Sample	CEC (meq/100 g)	SI (mL)	Yield (%)
Montmorillonite-a (before purification)	80	25	_
Montmorillonite-a (after sedimentation)	95	27	67
Montmorillonite-a (after FGC)	92.5	27	81
Montmorillonite-b (before purification)	60	9	_
Montmorillonite-b (after sedimentation)	90	11	45
Montmorillonite-b (after FGC)	87.5	11	68

Table 2.

CEC, SI, and yields of montmorillonite samples before and after purification.

Although the montmorillonite contents in purified products were almost the same according to XRD patterns and the data in **Table 2**, much higher yields were obtained by FGC compared to the sedimentation technique. Therefore, it would be a better choice to use FGC to beneficiate montmorillonite clays in a shorter time and with higher yields.

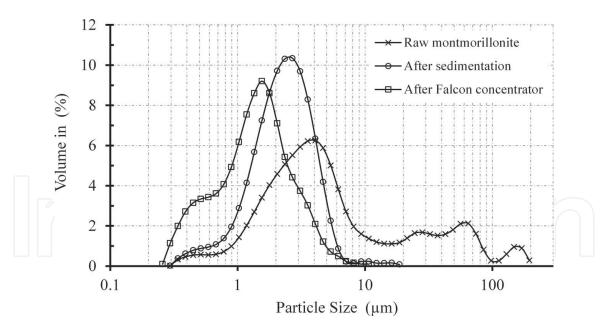
In another study which investigated the purification and modification of montmorillonite reported a combination of sedimentation, modification, flotation and FGC techniques. According to reported results, a product of purified and organically modified montmorillonite was obtained with 75% yielding, and 97% montmorillonite content calculated from quantitative XRD analysis [33].

In a study, purification of montmorillonite was investigated by centrifugal separators and it was reported that commercial centrifuge equipment such as Multi Gravity separator, Hydrocyclone, FGC, and KGC operating with a residence time of 10–15 seconds and G forces less than 300 G are not suitable for obtaining pure quality montmorillnoite. This is the case for montmorillonite ores containing very small sizes (<10  $\mu m$ ) gangue minerals. In addition, FGCs can be operated up to 300 G forces and 1–2 inch Mozley type hydrocyclones can be used up to 3500 G forces at 7–8 bar feed pressures [34].

Particle size distributions before and after beneficiation can also be evaluated to roughly see the degree of purification. **Figure 8** reveals that there are particles larger than 10  $\mu$ m in raw clay sample which can be attributed to gangue minerals. As expected, all purified clay samples shows narrower size distributions because of removed coarse gangue minerals [35]. Another research group was also reported close results on this issue and reported that the particle size distribution of montmorillonite purified by sedimentation is between 0.3–7.5  $\mu$ m [36].

Hydrocyclone is also most used beneficiation equipment for montmorillonite [37–39]. It has some advantages such as continuous system, high capacity, and working with higher solid ratio when compared to sedimentation, FGC, and KGC techniques. Multi stage hydrocyclone system should be used to ensure sufficient yield ratios (approximately 75%), however. The solid ratio is one of the most important parameter that should be around 5%. When higher solid ratios are used, separation is adversely affected due to problems such as particle-particle interactions and obstruction of the apex outlet due to high swelling of montmorillonite.

In a detailed study of multi-stage hydrocyclone application, two hydrocyclones with a large vortex finder diameter (14.3 mm) and then a smaller one (8.0 mm) were run in series with each other. As a result, purified montmorillonite with a cation exchange capacity (CEC) of 98 meq/100 g and 75% yield, which has the properties required for commercial grade drilling mud, water/solvent based bentonite, and sub material for nanocomposite technology, was obtained. In addition, waste with a CEC of 27–32 meq/100 g and 15% yield was obtained. The CEC of montmorillonite sample before beneficiation process was calculated to be 78 meq/100 g [39].



**Figure 8.**An example of particle size distributions of a montmorillonite clay sample before and after beneficiation processes [35].

Conventional decanter centrifuge devices apart from FGC, KGC, MGS, and hydrocyclones were also used to beneficiate montmorillonite ores. For an example, Gong et al. [8] investigated purification of montmorillonite using conventional centrifuge device. The process performed in this study combines grinding, dispersion, and centrifugal separation, respectively. Maximum 96.5% montmorillonite content with 71% yield was obtained by optimal parameters (grinding time 60 min, dispersant dosage 1%, centrifuge speed 700 rpm, and centrifuge time 2 min). Although products with high montmorillonite content and efficiency are obtained, the capacity of decanter centrifuges is very low compared to other techniques and therefore their usage areas on an industrial scale are limited. The centrifugation time for decanter centrifuge devices can be calculated using the following equation based on Stockes' law.

$$t = \lceil \eta \log_{10} (R/S) \rceil / \lceil 3.81N^2 r^2 \Delta S \rceil$$
 (3)

Here; t: centrifugation time (second),  $\eta$ : viscosity of the fluid (poise), S: distance from the suspension surface to the ax of rotor (cm), R: distance from the deposit surface to the ax of rotor (cm), N: rotation speed (rpm), r: maximum radius of the desired particles (cm),  $\Delta S$ : specific gravity difference between the particles and the liquid suspension (gcm<sup>-3</sup>).

Appropriate dispersion of clay minerals before purification is one of the most important stage of physical purification processes. The more successful the dispersion process, the more successful the purification rate and yield. Sodium hexametaphosphate ( $Na(PO_3)_6$ ) is generally used as a dispersant agent for clay minerals.  $Na(PO_3)_6$  is used at grinding or dispersion stages and is generally used in the range of 0.5–3% according to the clay weight. Zeta potential analysis can be used to determine exact amount of dispersant. In the measurements performed against the amount of dispersant, the amount of dispersant at the point where the zeta potential is fixed can be taken as the optimum value.

Most of the gangue minerals in the raw montmorillonite ores can be removed by physical purification methods. However, the particle sizes of gangue minerals are very important here. Some montmorillonite ores may contain very fine ( $<5\,\mu m$ ) gangue minerals. Such small particles occasionally settle between the clay layers and/or form small aggregates with clay particles. Consequently, the large particles settle in the dispersion, while the suspended fine gangue particles move with the clay minerals in aqueous or air media and their separation is not possible. In this case, chemical purification methods can be preferred either alone or in combination with physical methods in cases where products with high montmorillonite content (>%98) and yields are desired.

In a study chemical purification methods which listed in **Table 1** were used. The efficiency of the purification methods was assessed by elementary analysis and X-ray fluorescence analysis. C and D methods showed best results for two different montmorillonite ore that iron hydroxide amounts decreased from 11.34% to 2.21% and from 3.88% to 0.33%, respectively. As a result, it is reported that the (hydr) oxides were completely removed, and very small amount of remaining iron belongs to the montmorillonite structure. In addition, the clay structure was not affected severely at the end of leaching trials [21].

Menegatti et al. [24] investigated removal of organic matter from clay ores using disodium peroxodisulphate ( $N_2S_2O_8$ ). Sodium hydrogen carbonate ( $N_2HCO_3$ ) was used as buffer. It is reported that the use of  $N_3HCO_3$  as a buffer instead of  $N_3HCO_4$  and  $N_3B_4O_7$  was more efficient. The leaching technique was performed at  $80^{\circ}C$  for 60 min and the buffer/oxidant mass ratio was kept as 1:1. As a result, more than 98% of organic substances were removed from clay ores. The authors also stated that their new method was more effective than conventional oxidative procedures using hydrogen peroxide, sodium hypochlorite, and ozone.

#### 4. Conclusion

Purification of montmorillonite was investigated in two main classes as physical and chemical purification. There are generally physical purification methods in the literature because of simple and fast application process. However, in physical methods, the purification yield and purification degree (montmorillonite content) generally remain between 65 and 80% and 70–95%, respectively. This depends on the type of ore, method, and process used. Sedimentation, hydrocyclone, and Falcon gravity concentrator give better results compared to other physical enrichment methods working in aqueous environment when used at optimal parameters mentioned above. Dynamic aero separators can also show good results and they are good candidates for dry clay beneficiation methods. However, there is no literature knowledge that dynamic separators are used for clay purification. A detailed research study on clay beneficiation using dynamic separators will be a good study to show the clay enrichment efficiency with dry methods.

In physical purification methods multi stage processes for hydrocyclone, centrifugal separator, and aero separator increase the yield and purification degree. Some montmorillonite ores contain very thin ( $<5\,\mu m$ ) quartz and other mineral particles. These particles cannot be separated easily using sedimentation, centrifugal separators, and sieving techniques.

In this context, leaching (chemical purification) is useful technique for montmorillonite purification in cases highest yield (>90%) and montmorillonite content (>%95) is desired. In the chemical purification process, leaching operations should be performed in the following order; dissolution of carbonate minerals, dissolution of metal hydroxides, oxidation of organic substances, and finally silica dissolution. After each stage, the washing process should be done at a sufficient level.

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