Application of Nanotechnology in Oil and Gas Industry: Synthesis and Characterization of Vermiculite-Based Nano-adsorbent and its Application in Produced Water Treatment

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Vermiculite-based nano-adsorbent was successfully prepared via solution casting method from vermiculite that was first exfoliated by thermal shock followed by ultrasonic treatment. X-ray diffraction investigations showed that the combined effect of sonication and organo-modification led to extensive delamination of the vermiculite sheets. BET surface area measurements indicated flake thicknesses below 100 nm. Scanning electron microscopy images revealed that the organo-modification process of the vermiculite particles took place since the organo-modified sample presented a compact layer in its structure. Wastewater treatment performance evaluation of the synthesized vermiculite showed that the physicochemical and bacteriological properties improved significantly.It demonstrated that the material is efficient for wastewater treatment.

1. Introduction

The oil and gas (O&G) industries play an important role in the world economy. In terms of the final energy consumption matrix, the sector largely exceeds the global energy demand in greater proportions when compared to the other energy sectors. This scenario will not change in the short and medium terms, even though in the present context of changing the energy paradigm focused on renewable energy sources. According to the International Energy Outlook, (2016), fossil fuels still account for 78 % of energy use in 2040. Nevertheless, like most industrial production activities, O&G production process generates produced water (PW) as the main residue. PW is the technical name given to the water that exists in subsurface formations and generated as a waste by-product of O&G industry. PW is the largest waste stream associated with O&G extraction (Miller et al., 2020). Given the complexity of its composition, normally consisting of microorganisms, organic and inorganic compounds, PW has a great potential to pollute the environment and it is also responsible for inducing corrosion and scale problems in production and transport infrastructures (McLaughlin et al., 2020). All these aspects and since water pollution has become a major problem in recent years (Muradova et al., 2016), makes the management of PW one of the most debated topics at a global level. The alternatives usually adopted for the final destination are rejection, reinjection in the original well or reuse. In both cases, there is a need for specific treatment in order to comply with legal obligations, avoid negative impacts on the environment and production facilities. Various types of treatment technologies are used for wastewater treatment. Among them nanotechnology has appeared as one of the leading new innovative technologies with a great potential for treating wastewater more effectively and efficiently than other methods. More and more nanomaterials have been used for the removal of a wide range of pollutants from wastewaters (Lu et al., 2016b). However, studies on vermiculite-based nano-adsorbent for wastewater treatment are still scarce.

Vermiculite (VMT) is a low-cost and commonly available natural clay belonging to the group of phyllosilicates. Like most natural clays, the adsorptive capacity of natural VMT is limited. This capacity can be improved by modifying its surface, a modification that can be achieved via exfoliation by thermal shock at a temperature of approximately 900 °C. Further delamination of VMT flakes can be effected by sonication using high power

ultrasound (Ali et al., 2014). The present work explored all these exfoliation abilities presented by VMT to synthesize a VMT-based nano-adsorbent and to evaluate its applicability for PW treatment. Since PW is also made up of organic compounds, in this case, the adsorbent material must have the capability to remove these compounds. This can be achieved through a modification route with organic cations containing hydrocarbon chains, forming what is called organovermiculite. This ability was also explored in the present work. However, instead of the conventional organo-modification method carried out via ion exchange reaction using alkylammonium surfactants, the study explored another method, the surfactant-free organo-modification or solution casting method (Macheca et al., 2014). The solution casting method is the intercalation of polymer chains in the clay galleries. The method uses polyamides with protonated amine end groups as clay surface modifiers. The underlying principle for the success of the method is based on the following ideas: In some polyamides, the polymer chains themselves can provide the required organo-modification when amine functional groups are present e.g. at the chain ends. Dimer fatty acid-based polyamides (used in this study) are of this type of polyamides. Dimer fatty acid-based polyamides are amorphous polymers and are a special class of biopolymers derived from plant oils. They are soluble in lower carboxylic acids. When dissolved in these acidic solvents, the amine functional groups at the ends of some chains become protonated. It should be possible for these cationic molecules to ion exchange with the intercalated cations present in the clay galleries. This means that surface modification of the clay should be possible via solution intercalation of the polymer chains per se provided that suitable exchangeable ions are present in the clay. Figure 1 provides a schematic outline of the conceptual approach that was followed.

One of the advantages of the technique is that it also allows organo-modification of the external surfaces of nano-sized clay sheets suspended in an acidic solution. This may facilitate clay dispersion and to prevent agglomeration of nanoparticles when they are ultimately in solution. The technique still has the merit of using degradable polymers; this means that the waste materials resulting from the water treatment plant will have less impact on the environment. The study also sought to explore all these advantages offered by the technique to produce the desired adsorbent. The primary objective of the investigation was to explore the combined effect of thermal exfoliation, ultra-sonication and organo-modification to synthesize a VMT-based nano-adsorbent and to evaluate its applicability for PW treatment. The first part of the study focused on the synthesis and characterization of the organo-modified VMT sample. The wastewater treatment performance of the synthesized product was then carried out using adsorption and membrane filtration system. In this stage of the study, the focus was given to the effect of the wastewater treatment process on the physic-chemical and bacteriological parameters without looking at the mechanisms behind the adsorption and filtration phenomena.

2. Materials and methods

2.1 Materials

Mg-VMT grade superfine (1 mm) from Palabora Complex Mining (South Africa) was obtained from Mandoval Vermiculite. Chemically, Palabora VMT is a trioctahedral VMT intermediate between mica and VMT. XRF measurements indicated the following chemical composition: 42.55 wt.% SiO_2, 10.06 wt.% Al_2O_3, 9.49 wt.% Fe_2O_3, 4.61 wt.% CaO, 6.21 wt.% K_2O, 24.39 wt.% MgO, 1.16 wt.% TiO_2, 1.13 wt.% P_2O_5, and 8.70 wt.% LOI. All used chemicals were obtained from Merck Chemicals (South Africa) and used as received. The polyamide of choice was dimer fatty acid-based polyamide (co-polyamide - Euremelt 2138 grade). This was supplied by Huntsman Advanced Materials.

2.2 Methods

The VMT-based nano-adsorbent was prepared via a "solution casting method" from a VMT that was first exfoliated by thermal shock followed by ultrasonic treatment in the liquid medium. The experimental setup that was used is illustrated in Figure 1. The neat VMT (NVMT) was first subjected to an NH_4^+ ions modification process. The choice fell on NH_4^+ ions as, after exchanging, they can be removed by volatilisation as ammonia gas. It was proposed to first prepare NH_4^+-loaded clays by exhaustive ion exchange. Then to contact such NH_4^+-loaded clays dispersed in acetic acid with polymer solutions in the same solvent. The NH_4^+-exchanged VMT (AVMT) was prepared as follows: about 200 g of the VMT slurry was suspended in 500 mL of a 1 M solution of NH_4Cl at a pH = 5. The suspension was stirred for 2 h at room temperature and centrifuged for 1 h. The supernatant was decanted and replaced with fresh NH_4Cl solution. This procedure was repeated 4 times. The AVMT was washed with a large volume of de-ionized water until all Cl^- was removed (checked with $AgNO_3$ solution). After the NH_4^+ modification process, the flakes were dried in an air circulating oven at 60 °C for 48 h. Thermal exfoliation of VMT was achieved by exposing the material for 5 min to a temperature of 700 °C in a convection oven. The thermally exfoliated VMT flakes were then delaminated using a high-power ultrasound. This was carried out at 20 kHz and 375 W using an ultrasound probe (Sonics & Materials Inc., Model Vibracell VC375, 12.15 mm probe diameter). Typically, 2 g of clay were suspended in 300 mL of

deionized water and sonicated for 2 h. The slurry was allowed to settle for 2 h. Thereafter the supernatant was decanted. Water was added to the residue and the sonication proceeded for another 2 h. This process was repeated for a third time at which stage the remaining residue was discarded. The sonicated VMT flakes were recovered by filtration and dried in an air circulating oven set at 60 °C for 48 h. The resulting sample was milled to a powder and designated as unmodified VMT (UVMT). Part of UVMT flakes were then dispersed in acetic acid at desired solids content and used for the clay surface modification process. The remaining UVMT was kept for further analysis.
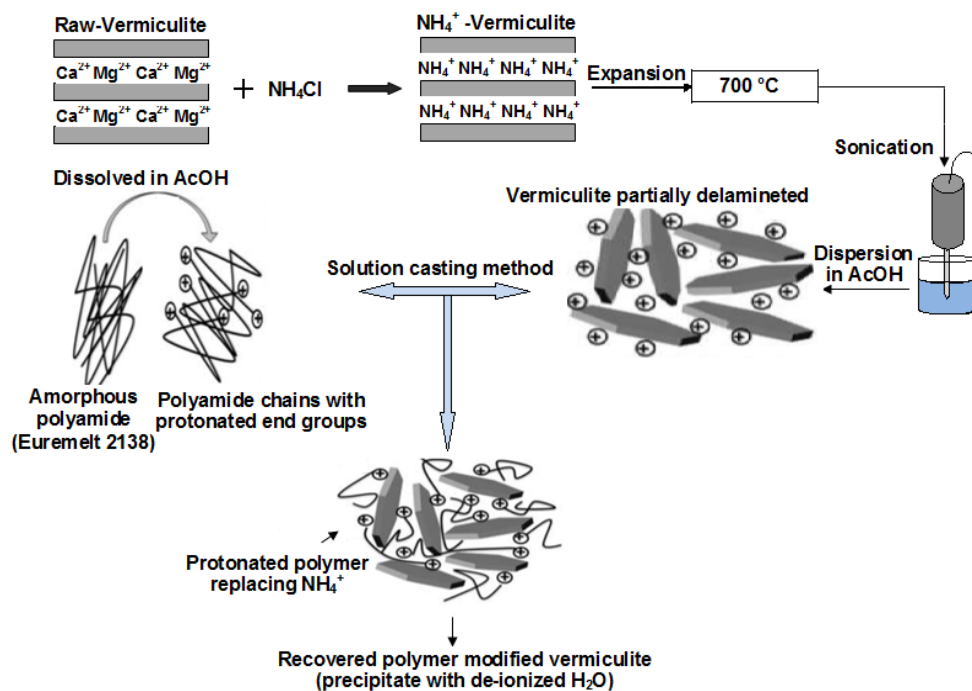

Figure 1: Schematic representation of the route to polymer-VMT modification via a solution casting method

A typical preparation procedure for the clay surface modification process was as follows: A weighed amount of the polymer was separately dissolved in acetic acid, corresponding to 16.67 wt.% of co-PA solution. The polymer solution was then mixed with the UVMT dispersion of acetic acid at a solids content of 13.7 wt.% using a kitchen mixer. In a 5 L stainless steel container, a predetermined amount of 13.7 wt.% clay dispersion of acetic acid was first stirred at room temperature for 10 min. Then, the 16.67 wt.% of co-PA solution was added drop by drop. After completion, mixing was continued for 50 min. After this period (while stirring) distilled water was added in order to precipitate the mixture. The precipitate was then separated from the solution by decantation and immersed in a large amount of distilled water for 6 days until the complete removal of acetic acid. The distilled water was replaced with a fresh one on a daily basis. The resulting material was dried at RT for 5 days and then milled to a powder and designated as organo-modified VMT (OVMT).

The PW was collected in a sterilized 500 mL sample bottle from one of the natural gas production platforms in Mozambique and taken to the laboratory in a cooler box containing ice cubes wrapped in a cellophane bag to lowdown the temperature of the water samples and to inhibit bacteria growth in the PW as most bacteria grow best between 20 to 30 ºC. Preservation of the sample was done in accordance with Norwegian O&G recommended guidelines for sampling and analysis of PW (2018). The wastewater treatment procedure was carried out using the membrane filtration process from water previously treated by adsorption with the organo-modified VMT sample (OVMT). Typically, a desired amount of clay (in wt.%) was added to the PW, keeping the PW/OVMT mixture for 3 min at a constant speed and temperature. After this time, the mixture was allowed to rest for 30 min and finally filtered using a vacuum pump.

2.3 Sample characterization and analysis

X-ray diffraction was conducted on a PANalytical X'Pert Pro powder diffractometer with a X'Celerator detector and variable divergence and receiving slits with Fe-filtered Co Ka radiation (k = 0.17901 nm) in the 2θ range of 2 to 60 ° at a scan rate of 1.0 °/min. The specific surface area was determined using nitrogen and the BET method at liquid nitrogen temperatures with a Micrometrics Tristar II BET instrument. Before measurements,

samples were degassed under vacuum at 100 °C for 24 h. A Zeiss Ultra 55 FESEM Field emission scanning electron microscope was used to study the morphology of the clay samples at 1 kV. The clay samples were coated with carbon using an EMITECH K950X sputter coater before analysis.

The wastewater treatment performance of synthesized products was carried out using practical analytical methods. This included analytical methods to determine some chemical species such as Chloride (Cl^-) SMEWW 4500-Cl^- D, Nitrites (NO_2^-) NP EN 26777:1996, Nitrates (NO_3^-) SMEWW 4500-NO_3^- B, and Ammoniac (NH_3) SMEWW 4500-NH_3 C. Other test conducted included: Conductivity NP EN 21888:1996, Total Hardness SMEWW 2340-C, Total Suspended Solid (TSS) L10-PT-MA-16 and Turbidity L25-PT-MA-12. Bacteriological analysis was also carried out. This included Total Coliforms L25-PT-MA-01, Faecal Coliforms L25-PT-MA-01 and Escherichia Coli L25-PT-MA-01.

3. Results and discussion

3.1 X-ray diffraction (XRD)

Figure 2 shows the XRD patterns of neat VMT (Figure 2a) and AVMT, UVMT and OVMT (Figure 2a). Neat VTM features multiple reflections, suggesting a mixed layer structure of VMT phase (1.43 nm reflection) and mica (biotite/phlogopite) with a 1.00 nm reflection. The 1.43 nm reflection is consistent with a VMT phase with two water layers in the galleries forming hydration shells around the exchangeable cations. The "hydrobiotite" features reflections at 2.441 nm and 1.221 nm corresponding to the lattice planes (001) and (002). The main peak, with an extensive line broadening, was found to be located at higher angles, suggesting a random distribution of the VMT and biotite layers. A broadening of the "hydrobiotite" reflection, as well as the disappearance of some of them, was observed in AVMT sample as well as in the diffractograms of both UVMT and OVMT. The broadening is attributed to the delamination of VMT sheets together with particle size reductions induced by sonication process.
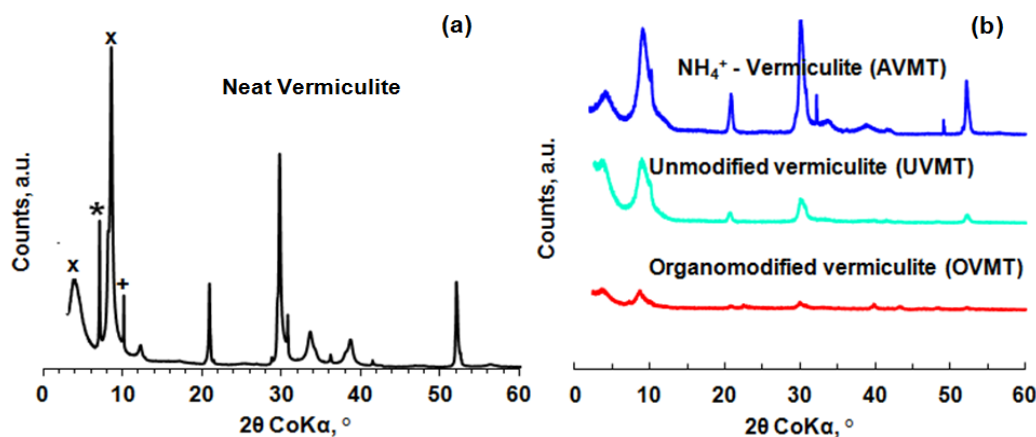

Figure 2: XRD patterns of (a) neat vermiculite and (b) AVMT, UVMT and OVMT. Key: *= VMT; **x** "hydrobiotite"; and **+** mica (biotite/phlogopite)

3.2 Scanning electron microscopy (SEM)

Figure 3 shows the morphology of the clay samples thorough SEM micrographs. Figure 3a and 3b show edge-view SEM micrographs of NVMT and AVMT flakes. Figure 3c and 3d show the slit-shaped gaps between the VMT platelets as a result of expansion caused by a 700 °C temperature shock. In the high-resolution micrographs (Figure 3d), it is visible that the separation of the stacks is imperfect and the thicknesses of the flake lamellae formed are in the micrometre range. SEM micrographs of the UVMT and OVMT samples are shown in Figure 3e and 3f. The two samples revealed an exfoliated structure with similar morphologies. However, the surface of the OVMT sample presented a compact layer in its structure, suggesting that the polymer surface modification of the VMT particles occurred. This means that the protonated amine functional groups at the ends of the polymer chains have attached the NPs surface. As expected, the ultrasound treatment led to a significant decrease in particle size.
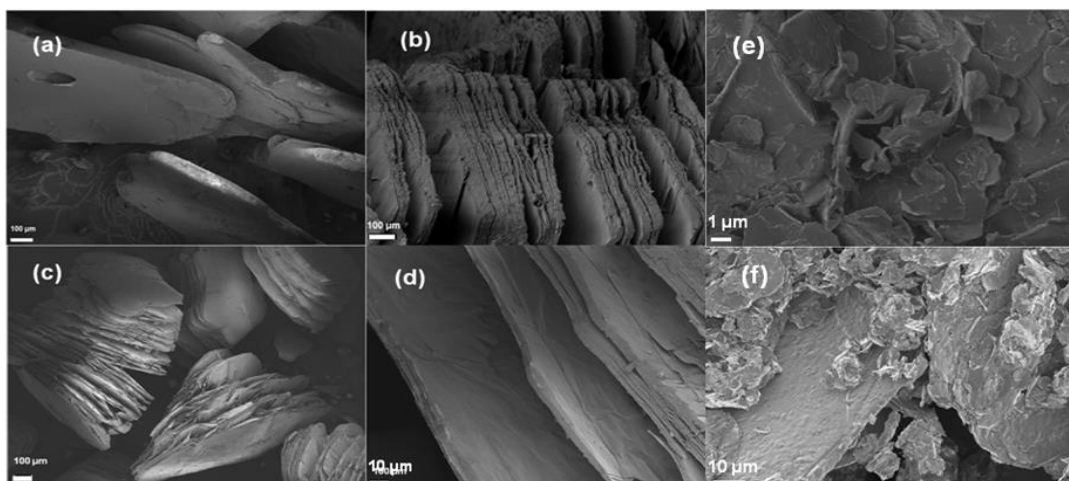
Figure 3: SEM micrographs of VMT samples: (a) NVMT (b) AVMT; (c) TEVMT at 100 μm; (d) TEVMT at 10 μm; (e) UVMT; and (f) (OVMT)

3.3. BET surface area and average flake thickness

The BET surface area and average flake thickness of the AVMT, UVMT and OVMT samples are shown in Figure 4. As can be seen from the figure, the sonication produced a remarkable increase in the specific surface area (Figure 4a). The BET specific surface area of the AVMT was 1.58 m^2 g^{-1}. This was increased to 11.5 and 9.65 m^2 g^{-1} in the UVMT and OVMT samples. The lower BET specific surface area exhibited by OVMT sample when compared with UVMT is explained by the presence of the coating layer.
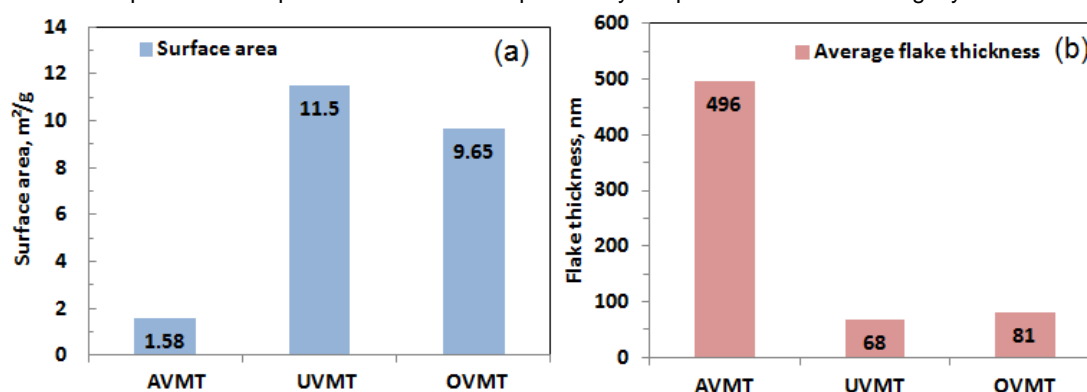

Figure 4: BET surface areas and average flake thickness of VMT samples

The nanostructure nature of the UVMT and OVMT can be confirmed by estimating the average thickness of the VMT flakes from the BET specific surface area using Eq(1):

$$t = \frac{2}{A_{BET} \cdot \rho}$$

(1)

where, t is the average flake thickness in m, ρ is the density of the VMT flakes, in kg m^{-3}; and ABET is the BET specific surface area in m^2 kg^{-1}. In the Eq(1) the edge surface area of the flakes is neglected. Applying this equation to the UVMT and OVMT samples and assuming ρ = 2.55 g cm^{-3} yielded average flake thicknesses of about 68 and 81 nm (Figure 4b), suggesting that for both VMT samples the flakes may include nano-scale particles as at least one dimension was less than 100 nm.

3.4. Physico-chemical and bacteriological analysis

Table 1 shows the results of the selected physicochemical parameters obtained from a laboratory analysis of the treated water. The wastewater treatment with OVMT led to a significant reduction in parameters such as Turbidity by 92 % (50 to 4.0 NTU), Total hardness by 87 (1,220 to 160 mg/L $CaCO_3$), Total dissolved solids by

51 % (970 to 480 mg/L), Total suspended solids by 82 % (140 to 25 mg/L), Conductivity by 87 % (5867 to 783 µs/cm), Nitrates by 42 % (60 to 25 mg/L). Three selected bacteriological parameters (not shown here) were equally analyzed namely Total and Faecal Coliforms and Escherichia Coli. The treatment with OVMT resulted in the significant reduction of the bacteriological content of the analyzed parameters from > 2.4x10^{6}, 1.1x10^{6} and 1.1x10^{6} to <3 CFU/100 mL, for the Total and Faecal Coliforms and Escherichia Coli.

Table 1: Selected physicochemical parameters of the analysis of untreated and treated water

Parameter	Feedwater	Water treated with OVMT	*NEDLN
Turbidity, NTU	50 ± 0.50	4.0 ± 0.04	>15
Total hardness, mg/L $CaCO_3$	1,220 ± 4.95	160 ± 0.14	-
Ammoniac, mg/L NH_4	32.1 ± 0.12	25 ± 0.07	-
Chlorines, mg/L Cl	3,315 ± 4.24	426 ± 0.14	600
Total dissolved solids (TDS), mg/L	970 ± 4.04	480 ± 0.28	5,000
Nitrates, mg/L	60 ± 1.41	35 ± 0.35	-
Total suspended solids (TSS), mg/L	140 ± 2.83	25 ± 0.14	>50
Electrical conductivity, µs/cm	5,867 ± 0.71	783 ± 0.07	No limit

*NEDLN is Nigerian Effluent Discharged Limits for Neashore (Isehunwa and Onovae, 2011).

4. Conclusions

XRD investigations showed that the combined effect of thermal exfoliation, sonication and organo-modification led to extensive delamination of the VMT sheets. BET surface area measurements revealed flake thicknesses below 100 nm. The modification process of the VMT particles through solution casting method has taken place since the modified sample (OVMT) presented a compact layer in its structure, suggesting that the protonated amine functional groups at the ends of the polymer chains have attached the surface of the nanoparticles. Wastewater treatment performance evaluation of synthesized product showed that the physicochemical and bacteriological properties improved significantly, showing clearly that this material has enormous potential and can be successfully applied as an adsorbent material for produced water treatment.

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