

## NEW MICROEMULSION COCONUT OIL AND BENTONITE BASED SYNTHESSES

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**ABSTRACT:** One microemulsion system based on coconut oil was prepared and used for a bentonite clay treatment. All materials were characterized by X-ray diffraction, infrared spectroscopy and thermogravimetric analysis and scanning electron microscopy. It was observed that the incorporation of coconut oil in the clay occurs and it does not lead to structure modification. Adsorption tests using methylene blue as a probe molecule were done and the materials prepared show higher adsorption capacity.

**KEYWORDS:** *bentonite, microemulsion, adsorption, metilene blue*

### 1. INTRODUCCION

Natural materials as bentonite clay are potential adsorbents (Shimada, 2012) yet not very selective. A new group called “especial clay” was created aiming the chemical property improvement on these materials (Bertella, 2011). This group embraces the chemical modified smectites, activated by acids or organic surfactant, aiming for increasing the selective character and the adsorption power (Damasceno, et al 2011)

The organic surfactants (sense active) are a two region, polar (head) and non-polar (tail) molecule compound, which are long known as liquid-liquid interfacial tension reducing agents and, therefore, facilitate the miscibility between immiscible liquids (Oliveira, 2004). The surface-active agents can form microemulsions that are characterized as spherical aggregations with diameters smaller than 14.15Å. The microemulsions are, in general, defined as two stable thermodynamic immiscible liquids systems (usually water and oil), isotropic and transparent that are localized on the water/oil interface (Oliveira, et al 2004). They can also present themselves in a circular, flattened or other two-layer format (Nakajima, ET AL 1997; Meier, 1996). The microemulsions are very efficient in metallic ions recovery process (Khraisheh, 2005), textile dye (Borba, 2011) and laboratory scale oil

(Tanthakit, 2010), using the liquid-liquid extraction. Using microemulsions impregnated in the diatomite, Dantas et al (2001) obtained great results on the heavy metals removal from industrial irradiates.

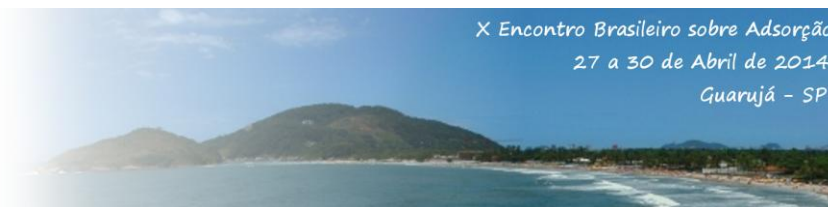
Considering that, this work has objected to join microemulsion and bentonite properties, displacing traditional surfactants of already proven efficiency (Pergher, 2005) for a natural surfactant of coconut oil base, in a microemulsion system.

### 2. EXPERIMENTAL

Bentonite from Santa Luzia’s – PB, Brazil field was used as adsorbent. The coconut oil was purchased in the city of Natal’s – RN local market. The paraffin and butanol fuel used are VETEC brand.

The microemulsion was prepared adding butyl alcohol (joint surfactant), saponified coconut oil (surfactant) and paraffin (oil phase). The joint surfactant/surfactant ratio was 0.5, 1 and 2. The diagrams were done adding the joint surfactant, the surfactant and water. Agitation was promoted to dissolve the surfactant aiming the best joint surfactant/surfactant (C/T) ratio evaluation.

The microemulsion formation chosen diagram was the 1:1 ratio with the conclusion of forming a bigger microemulsion region using less surfactant (figure 1).



The prepared microemulsion was added to the clay under agitation with mass corresponding to 50 % clay. The resulting material was dried at 70°C (158° F) for 8 hours.

The adsorbents were characterized by different complementary technics as scanning electron microscopy, X-ray diffraction, infrared spectroscopy and thermogravimetric analysis.

The scanning electron microscopy was done on a Philips electronic microscope model XL30 ESEM. The material analysis preparation procedure consisted of a solid portion deposition over a carbon tape that was fixed on to the sample holder. Next, a fine gold layer was deposited to give the sample conductivity.

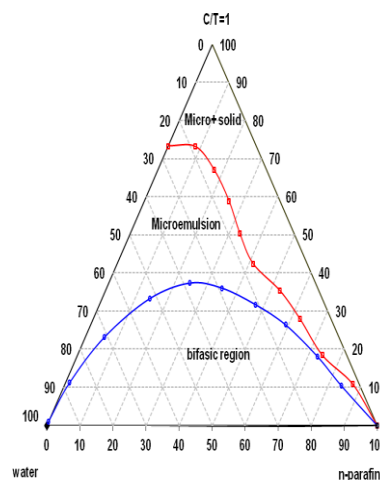
The X-ray diffraction analysis was done on a diffractometer model XDR-700 (Shimadzu) using a Ni filter, 30mA current and Cu- $\alpha$  ( $\lambda = 1,54 \text{ \AA}$ ).

It was used a Bomem spectrometer model MB 102 to analyze the infrared region spectroscopy with Fourier transformation, using potassium bromide (KBr) as dispersive agent.

### 3. RESULTS

The joint surfactant and surfactant (C/T=1) chosen diagram was 1:1 ratio (Figure 1) in order to obtain higher process balance. It is thought that every surfactant/joint surfactant (saponified coconut oil) is present on the microemulsion phase, although close to the biphasic region and the microemulsion with solids, a microemulsion's two phases balance can occur, resulting in this case, in surfactant presence between both phases. Starting on Figure 1 the more suitable diagram point that uses the least joint surfactant/surfactant and paraffin and is, at the same time, further from other phase's regions was chosen. This point had 50% C/T, 40% water and 10% paraffin.

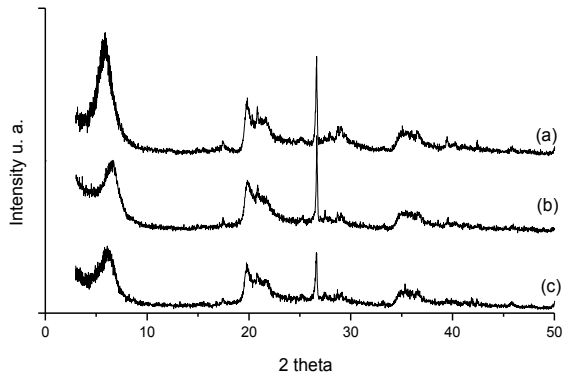
The bentonite clay diffractogram with montmorillonite clay minerals characteristic reflection of 001 in  $2\theta = 6.51^\circ$  and the quartz reflection of  $2\theta = 26.5^\circ$  is presented on Figure 2. After microemulsion treatment a 001 reflection displacement of  $2\theta = 6.51$  to  $6.7^\circ$  is observed, what means a basal spacing decrease of  $15\text{\AA}$  a  $13.37\text{\AA}$ .



**Figure 1.** Microemulsified system diagram formation on ratio C/T: 1.

This basal spacing decrease after microemulsified clay treatment indicates that the microemulsified system is interacting with clay surface and interlayered region. During the drying process occurs a decrease of the amount of alcohol and water (10%) in the microemulsified system by increasing the amount of oil and surfactant. This causes a reduction in the size of oil droplets, as well as the electrical conductivity of the environment and the electrostatic repulsion by the tendency to become less polar (Nakajima, 1997; Araújo, 2006). It increases the tendency of microemulsion to remove water contained in the interlayered section of the clay to try to stabilize the system (Dantas, 2001). It is expected that the microemulsified adsorbent submission to the aqueous phase will aggregate the surfactant molecules returning them to the initial stage.

Introducing the natural and microemulsified bentonite diffractogram, modified with microemulsion after pulverization with 25% butyl alcohol mass and 10% water mass on the dissector sample. The chosen mass corresponded to the TG loss with drying at 33°C (91.4°F) until sample was completely dry. It was observed that the treated clay's basal spacing increased practically equivalent to the clay in its natural state, however with less organized structure. In the natural material there was no modification. This may be an indication that the microemulsion in the clay structure interacted with the alcohol and the water pulverized and that the decrease in the sample spacing in Figure 2b may

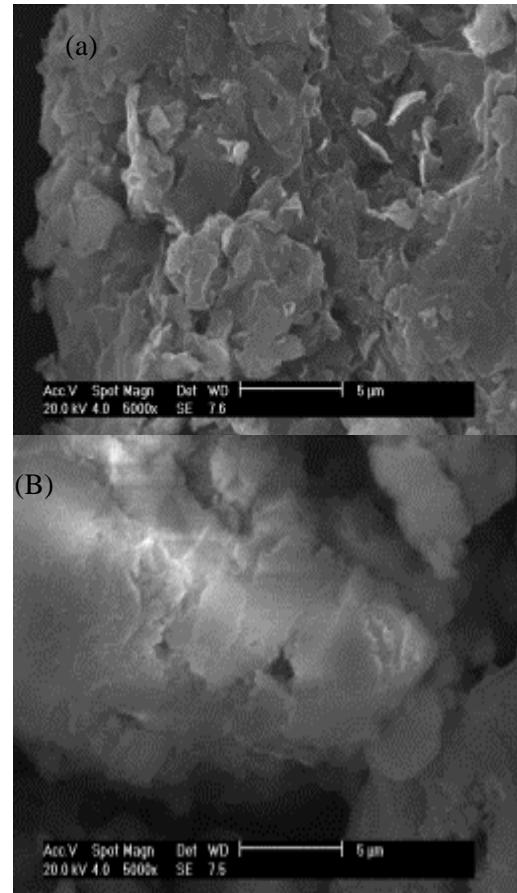


have been caused by the drying process at 70° C (158° F) for 8 hours.

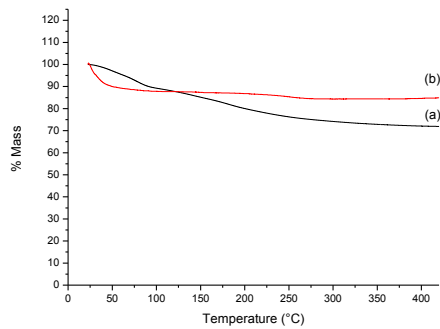
**Figure 2.** Natural bentonite X-ray diffractogram (a), superficially treated with microemulsion (b) treated with 25% pulverized butyl alcohol, 10% of mass (c).

Figure 3 presents scanning electron microscopy analysis results, where it is observed that bentonite clay layer morphology is kept after treatment, indicating that microemulsion is well distributed on the interlayered clay surface.

The thermogravimetric analysis (Figure 4) shows bentonite mass loss around 11.56% up to 100°C (212°F) due to adsorbed water interspersed between blades and interlayered cation coordination water. In high temperatures a loss of 5% regarding the structural hydroxide is seen. After microemulsion treatment, bentonite shows an initial loss up to 125% similar to natural bentonite. In high temperatures there is a 15 % loss due to water once the alcohol evaporates during drying. This result indicates that microemulsified coconut oil is incorporated to the clay.

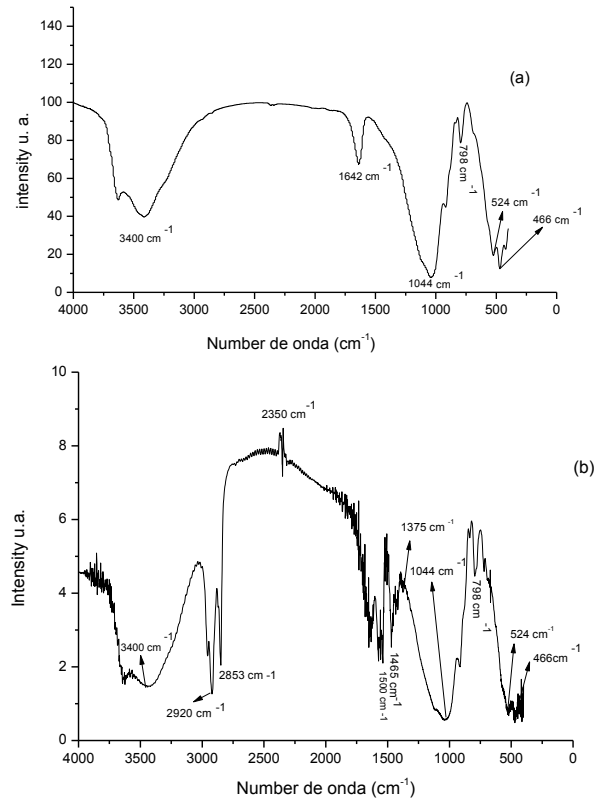


**Figure 3.** Natural bentonite micrographs (5.000 x increase) (a) and superficially treated WITH microemulsion (b).



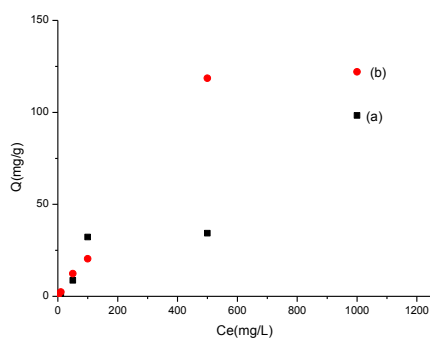
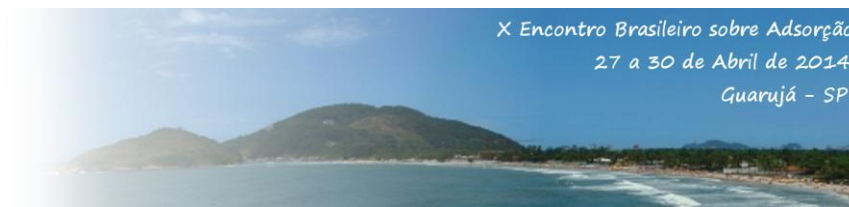
**Figure 4.** Natural bentonite thermogravimetric analysis (a) and microemulsified treated sample (b).

It was observed in the bentonite infrared spectrum, before and after treatment, OH stretching vibrations in  $3400\text{ cm}^{-1}$ , with correspondent variations at  $466\text{ cm}^{-1}$  referent to the chemical bond deformity Si-O-Si, and at  $524\text{ cm}^{-1}$  referent to the chemical bond vibration Si-O-Al, where the silicon belongs to the tetrahedral site and the aluminum belongs to the octahedral site. Outside the vibration plan in  $798\text{ cm}^{-1}$ , the quartz Si-O chemical bond stretching occurs. Si-O axial chemical bonds outside the plan are presented in  $1044\text{ cm}^{-1}$ . It is also observed a  $1642\text{ cm}^{-1}$  variation, which is due to the water (H-O-H) angular deformation, hydration (adsorbed water clay) (Fukushima, 1978; Wang, 2007). On the treated samples, variations  $2920, 2853\text{ cm}^{-1}$  are correspondent to the CH group vibrations. The chemical bonds  $1375\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$ , referent to the isobutyl and  $\text{CH}_2$  aggregation vibrations, respectively, indicate coconut oil incorporation. Absorptions in  $2350\text{ cm}^{-1}$  (figure 5b) are referent to the asymmetric axial deformation and to the  $\text{CO}_2$  respectively (Wang, 2007). Inside the microemulsion spectrum (figure 5b) it was proved by the chemical bonds that the microemulsion is fixed to the clay.



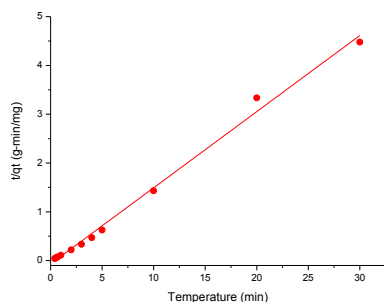
**Figure 5.** Natural bentonite infrared spectrum (a) and superficially treated microemulsion (b).

Figure 6 showed that the rate of removal of methylene blue increases significantly with the microemulsion in the clay treatment (Figure 6b) with removal percentage up to 100%. The microemulsion system stability is promoted by the clay that also helps polar and non-polar sites formations, as well as micelle formation that facilitate the adsorption process, making this adsorbent a potential material on effluents treatment. The study is not adapted to the Langmuir, Freundlich isotherm models.



**Figure 6.** Methylene blue adsorption curve using natural bentonite (a) and handled superficially with microemulsion (b).

The adsorption maximal capacity on the kinetic study was reached in 30 minutes. The kinetic study concentrations were calculated from  $t / qt$  vs  $t$  linear portions and are shown on Figure 7. The study is adapted to the second order pseudo model at  $R=0.997$  to the microemulsion treated bentonite (Figure 7). The second order pseudo value with constant rate of  $K_2 = 0.04$  is the maximal adsorption capacity at 9.99.



**Figure 7.** Methylene blue second order pseudo model kinetics using microemulsion superficially treated bentonite.

## 4. CONCLUSIONS

The structure and morphology of the material has not been modified after the surface treatment. DRX, GO and TG proved that it is possible the microemulsion incorporation to the material. These hydrophobic materials showed to be effective as methylene blue adsorbents, obtaining better adsorption capacity than the natural bentonite, indicating that the modification

with microemulsion increases the material ability to adsorb organic compounds.

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