

AN EVALUATION OF CLAY MINERALS AS SUPPORT MATERIALS IN ANAEROBIC DIGESTERS

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Abstract

The use of different clay minerals as support in anaerobic digestion has been studied. The support materials were evaluated in a batch microdigester and their effect in the digestion process was measured at the beginning of the process (startup) and at an intermediate point of the digestion process when the maximum differences between support materials were observed (working digester).

All the systems with support were more efficient than the control (support-free). The following order of purification was established:

STARTUP: Bentonite > talc > vermiculite > nontronite > montmorillonite > pyrophyllite > stevensite > sepiolite.

WORKING DIGESTER: Sepiolite > stevensite > talc > nontronite > bentonite > montmorillonite > vermiculite > pyrophyllite.

Bentonite, montmorillonite, talc and vermiculite were favourable for startup, as they rapidly released Ca^{2+} or Mg^{2+} to the medium.

The best COD removal efficiencies were obtained with sepiolite and stevensite which release Mg^{2+} progressively to the medium. The presence of Fe^{3+} , Co^{2+} and Ni^{2+} in the structure of the mineral stimulated anaerobic digestion.

Keywords: Supports, anaerobic digestion, clay minerals.

INTRODUCTION

The performance of a continuous anaerobic digester may be limited to a significant extent by the loss of biomass suspended in the processed effluent [1]. Such losses may be reduced by providing a solid support for bacterial attachment within the digester. Various particulate supports have been used in laboratory studies, including glass beads [2, 3], expanded polyurethane [4], sepiolite powder [4], polyvinyl chloride [5, 6], vermiculite powder [7], and feldspar particles [7]. Work involving the use of clay minerals as supports [8, 9] has demonstrated the superiority of sepiolite over supports such as polyvinyl chloride, polypropylene, and biolite.

Clays are particularly promising as support materials because their surface characteristics, porosity, and chemical composition favour both the initial attachment of microorganisms and the subsequent development of substantial bacterial populations. However, only some of the many existing clay minerals have been studied, often after processing to obtain modified forms. Thus, there is considerable scope for investigating the effectiveness of a variety of raw clays with differing chemical compositions and properties, such as internal and external specific surface, ion exchange capacity, solubility, and adsorption characteristics.

MATERIALS AND EXPERIMENTAL METHODS

The clay minerals used as supports were:

- Stevensite supplied by Tolsa, S. A. (Spain).
- Sepiolite from Vallecas (Spain). Supplied by Tolsa, S. A.
- Talc supplied by Malagueña de Talcos, Fuengirola (Spain).
- Vermiculite from Santa Olalla (Spain).
- Nontronite from Holen-Hagen. Source Clay Mineral Repository. Columbia. Missouri (USA).
Material approximately 20% rich in nontronite.
- Bentonite supplied by Minas de Gádor (Spain).

- Ca-Montmorillonite (STx-1), Source Clay Mineral Repository. Columbia. Missouri (USA).
- Pyrophyllite from Hillsboro, North Carolina (USA).

Bacterial biomass was obtained from an anaerobic reactor treating piggery wastewater.

Synthetic feed. The composition of the synthetic feed is shown in Table 1.

Table 1. Synthetic feed (composition per litre).

Sodium acetate	30 g
Sodium lactate	8 g
PO ₄ HK + PO ₄ HK ₂	5 g
Proteins	10 g
Vitamins	
C	150 mg
B ₁	30 mg
PP	40 mg
B ₂	5 mg
B ₆	6 mg
B ₁₂	7 mg
A	15,000 VI
D ₃	12,000 VI
E	15 VI
Biotin	0.18 mg
Folic acid	0.3 mg

Analysis

Chemical analysis of the supports was carried out by acid digestion in a Teflon-lined pressure vessel [10]. The concentrations of elements were measured by atomic absorption spectrometry and flame photometry.

The chemical oxygen demand (COD) and pH were measured by the APHA Standard Methods [11].

The purification efficiency was calculated as
$$\frac{(\text{COD})_{\text{initial}} - (\text{COD})_{\text{final}}}{(\text{COD})_{\text{initial}}} \times 100 \quad (\text{i})$$

Experimental procedure

The support materials were evaluated in a batch microdigester of 125 ml capacity specially designed (Figure 1) to allow sampling to be carried out while maintaining anaerobic conditions. This microdigester consisted of a screw-cap bottle with a valve which allowed the exit of evolved gases but not the entry of air.

Figure 1.

Microdigesters were loaded with the different support materials (10 cm³) and synthetic feed (55 cm³) and were inoculated with adapted bacterial biomass (10 cm³). The microdigesters were stirred on an orbital stirrer and thermostatted at 36 ± 1 °C. A support-free blank was prepared for comparison. The experiments were done in triplicate.

The decrease of organic matter content from the feed for each support material before inoculation with bacterial biomass was calculated using equation (i), after a contact time of 48 hours.

After inoculation with the bacterial biomass the effect of the support materials was studied by measurement of the purification efficiency at the beginning of the process (startup) and at an intermediate point of the digestion process when maximum differences between materials were observed (working digester). As the number and small size of the microdigesters causes some practical difficulties in measurement of gas yield, the startup and working digester stages were determined in previous experiments by regularly determining the COD of the different microdigesters. The time for each process was 15 and 30 days respectively. The microdigesters were sampled by piercing the caps with a syringe having a 10 cm needle. The piercing was immediately repaired with silicone.

Before and after the anaerobic digestion, the supports were studied by X-ray diffraction and scanning electron microscopy.

The scanning electron microscopy (SEM) was performed in an ISSI apparatus, model SS40. The observed bacteria were fixed in osmium tetroxide and glutaraldehyde in a buffer solution of sodium cacodilate followed by dehydration with acetone-water solutions of different concentrations.

X-ray diffraction patterns (XRD) were obtained using a Siemens diffractometer, model kristaloflex D-500, using Ni-filtered Cu K_α radiation. Samples taken from the digesters were prepared for X-ray analysis by placing them on a glass slide and drying at room temperature.

The CEC of the supports was determined by exchange with ammonium acetate at pH 7.

RESULTS AND DISCUSSION

The decrease of organic matter content (consumption) in the feed for each support material before inoculation with bacterial biomass is given in Table 2. The decrease of organic matter in the solution is probably due to processes of adsorption on the support material and to precipitation on the support materials by formation of organometallic complexes with cations (Ca^{2+} , Mg^{2+} , Fe^{3+} , Fe^{2+} , Al^{3+} , etc.) coming from clays, mainly as exchangeable cations. These mechanisms may be very important in determining the development of the anaerobic process due to the fact that the attraction of organic matter to the support material, by either adsorption or precipitation, creates a reserve of nutrients for the bacterial biomass.

Table 2. Values of consumption of organic matter (OM) from the feed for each support material.

Support	OM (%)
Control (support-free)	0
Stevensite	5.4
Sepiolite	1.0
Talc	1.0
Vermiculite	1.7
Nontronite	17.5
Bentonite	9.6
Montmorillonite	3.9
Pyrophyllite	2.7

Figure 2 gives the results of the treatment achieved for each system in the two stages studied: startup and working digester.

Figure 2.

The data obtained indicated that in the first stage, all the systems with support material were more efficient than the control (support-free). This is in agreement with the finding of Baier [12] that in aqueous medium, a microbial film forms over the surface of particles of the support material, increasing the bacterial biomass and culture activity and, so, the development of the process.

In the second stage, treatment efficiencies in the digesters with added support were also better than in the control. SEM examination showed a high microbial activity on all the supports used in this work.

Magnesium-rich supports

Stevensite.

This mineral is an expandible trioctahedral smectite. It contains exclusively Mg^{2+} in octahedral position. Its CEC is $0.45 \text{ mol}_c \text{ kg}^{-1}$.

XRD of stevensite (Figure 3a) indicated that the prevailing mineral was accompanied by illite ($10.08, 5.00 \text{ \AA}$ etc.). Some quartz ($4.27, 3.34, 1.81 \text{ \AA}$ etc.) and dolomite (2.89 \AA) were also present. In the diffraction peak at 15.16 \AA , stevensite showed a shoulder at 12.16 \AA . In XRD of the stevensite after treatment with synthetic feed, broad diffraction bands appeared in the diagrams above 19.40 \AA , with a second order above 9.65 \AA . The increase of the 15.0 \AA to 19.40 \AA indicates that a part of the feed added was integrated into the interlamellar space of the clay (Figure 3b).

Figure 3.

Treatment with bacteria produced a very marked modification in the XRD of the stevensite support (Figure 3c). A well-defined diffraction peak appeared at 10 \AA , probably because part of the stevensite became saturated with K, moving the original 15.16 \AA peak to 10 \AA and increasing the intensity of the illite peak at 10 \AA . A well-defined diffraction peak attributable to sepiolite appeared at 12.16 \AA , and there was a small broad diffraction peak around 16 \AA . This confirms the assumption that most, if not all, of the components were displaced from the interlamellar space and that the material was a mixture of stevensite and sepiolite.

In startup, this material (21.9%) was better than the control (15.5%) and slightly higher than sepiolite, but was worse than the other materials. At the stage of working digester, the efficiency was higher (80%) than those of the other materials.

This material behaved quite similarly to sepiolite (see later), in agreement with its composition being a mixture of stevensite and sepiolite.

The increase in purification efficiency must be related to the supply of magnesium to the medium from the clay [8], both as exchangeable cation, and from crystal structure due to the low stability of this mineral [13].

Sepiolite.

This is a fibrous mineral, trioctahedral with Mg^{2+} in octahedral position. Its CEC is $0.1 \text{ mol}_c \text{ kg}^{-1}$. Channels of $11.5 \times 5.3 \text{ \AA}$ run the whole length of the fibre.

XRD showed that the sample comprised this mineral with impurities of illite, dolomite and calcite.

Sepiolite behaved very poorly at startup, with a purification efficiency of only 19.7% (close to that of the control, 15.5%). In the working digester, sepiolite gave the highest purification efficiency (82.2%, as compared with 49% in the control) of all the materials tested.

The difficult startup must be related with the hydrophobic nature of sepiolite and the small consumption of the feed observed before inoculation (Table 2), making bacterial growth difficult on the support material. In addition, the very low exchange capacity of this material does not allow the release of exchangeable cations to the medium. Due to the mentioned above the startup is similar to the control (support-free).

Nevertheless, in the next stage various effects make the increase of bacterial activity possible. First of all, the hydrophobic nature of sepiolite results in a preferential interaction with filamentous bacteria, such as Methanotrix, which have a membrane which is also hydrophobic [15]. Bacilli and cocci develop around the fibrillar conglomerate. The SEM study showed a high bacterial activity.

The transfer of the cation Mg^{2+} to the medium at startup is small, as a result of the low exchange capacity ($0.10 \text{ mol}_e \text{ kg}^{-1}$) of sepiolite, but as time goes on, more cation is released from the crystal structure, due to the low stability of the mineral. The importance of this cation to the process has been suggested by Perez Rodriguez *et al.* [8]. Moreover the presence of small amounts of calcite and dolomite can result in a slow release of Ca^{2+} and Mg^{2+} to the solution, which also favours the digestion process.

It is remarkable that the content of iron is very small as compared with, that in other supports tested that start up well: bentonite (3.29%), talc (4.65%), etc. The beneficial effect of iron has been described [14].

Talc.

This is a trioctahedral non-expanding mineral of type 2:1. Mg^{2+} is the main cation in octahedral coordination. This mineral has a very low CEC and small surface area.

XRD of the talc support indicated that it contained basically this mineral (75%), accompanied by chlorite (15%). Dolomite and magnesite were also present as impurities.

XRD of the sample treated with synthetic feed did not show diffraction peaks corresponding to acetates and other salts, which were present in the other materials under study. This agrees well with the data on its interaction with the organic matter of the medium (Table 2), as the organic matter consumption was only 1%. Once the support material was subjected to the anaerobic process, it presented a diagram with similar characteristics to those of the original sample.

Talc showed good results at startup (31.9%) as compared with the control (15%). The value of purification in the working digester was very high (80%), being surpassed only by that of sepiolite (82.2%).

Table 3. Chemical analysis of the materials used as support (%). Stev: Stevensite, Sep: Sepiolite, Verm: Vermiculite, Non: Nontronite, Bent: Bentonite, Mont: Montmorillonite, Pyro: Pyrophyllite.

	Stev.	Sep.	Talc	Verm.	Non.	Bent.	Mont.	Pyro.
SiO ₂	56.71	62.23	45.03	41.87	90.14	65.02	70.10	66.42
Al ₂ O ₃	3.18	3.28	1.83	16.87	1.62	17.10	16.00	27.31
Fe ₂ O ₃	0.81	0.74	4.65	3.78	4.91	3.29	0.85	0.20
CaO	1.30	1.35	2.08	0.23	0.46	1.81	1.59	0.09
MgO	28.18	22.90	30.24	23.79	0.20	4.19	3.69	0.01
Na ₂ O	0.33	0.21	0.11	0.02	0.14	0.24	0.27	0.10
K ₂ O	0.65	0.85	-	0.03	0.66	0.23	0.08	0.24
MnO	-	0.03	0.05	0.16	-	0.06	0.01	-
Cr ₂ O ₃	T	-	0.40	-	-	-	-	-
Cu	T	T	-	0.01	40 ppm	-	-	-
Zn	80 ppm	T	55 ppm	-	-	72 ppm	-	-
Co	T	-	70 ppm	-	T	-	-	-
Ni	T	-	0.16	0.01	49 ppm	42 ppm	-	-
L.o.I.	8.84	8.38	15.86	12.98	0.87	7.66	7.51	5.41

T = Traces. L.o.I. = Loss on ignition.

The good results for the working digester stage could be associated with the cations existing in the material (Table 3), both in the structure of the talc and chlorite in octahedral positions (Mg, Fe, Mn, Cr, Ca, Ni, Co and Zn), and in the dolomite and magnesite. Some of these cations, Ni, Co and Fe (Table 3) would be transferred slowly to the medium and are very necessary for microbial activity. All these elements create an appropriate habitat for development of the bacterial biomass.

The SEM study of the talc after anaerobic digestion showed the presence of bacteria together with the mineral (Plate 1).

The vermiculite had a good startup (30.1%) as compared with the control (15.5%). Its efficiency in the working digester was lower than the other materials, reaching only 65.2% (49% in the control). This behaviour of vermiculite supports the results obtained by Perez-Rodriguez *et al.* [8], attributing the good startup to the existence of Mg^{2+} as exchangeable cation.

It might be inferred that the effect of magnesium at the working digester stage, decreases because it is released within a short time as exchange cation, affecting only the startup.

In order to check the importance of the magnesium in vermiculite, experiments were carried out with vermiculite saturated in K^+ , giving a COD removal efficiency lower than that of the Mg-

Figure 4.

XRD of the vermiculite (Figure 4a) was typical for the mineral. When feed was added, a series of diffraction peaks appeared, corresponding to mixed layers of vermiculite with Mg^{2+} in the interlamellar space and vermiculite with other ions in the interlamellar space (24.48, 12.23, 8.14 Å, etc.) (Figure 4b). Once the anaerobic process developed, the XRD corresponded to a mineral with d_{001} at 9.98 Å and its rational series (data not shown). These data suggested a displacement of interlamellar magnesium by potassium ions. This replacement of magnesium ions with potassium from the medium was deduced by Perez-Rodriguez *et al.* [8]. However, it should be pointed out that when other media containing ammonium ions instead of potassium, were used, a d_{001} diffraction at 10.32 Å and its rational series appeared (Figure 4c), in agreement with an exchange of the original magnesium for ammonium ions.

This is a triocahedral expanding mineral of type 2:1 with magnesium and some iron in octahedral coordination, and substitution of tetrahedral Si^{4+} by Al^{3+} . The CEC is 1.4 mol. kg^{-1} , and the exchangeable ion is Mg^{2+} .

Vermiculite.

Plate 1.

vermiculite. The values obtained were the following: startup 18% and 30% for K-vermiculite and Mg-vermiculite, respectively, working digester 50% and 65%.

Iron-rich support

Nontronite.

This is a dioctahedral smectite with iron in octahedral coordination and substitution of tetrahedral Si^{4+} by Al^{3+} . The CEC is about $1 \text{ mol}_e \text{ kg}^{-1}$.

XRD of the nontronite support indicated that it also contained a high proportion of quartz and feldspars. The high quartz content in this material was corroborated by the high percentage of SiO_2 shown by chemical analysis of the sample (Table 3). These experimental data indicate that this sample was approximately 20% nontronite.

On addition of the medium, XRD of this material showed, in addition to the peak of the original sample, the presence of acetates, other salts of the feed, and possibly magnesium ammonium phosphate.

When the digester was inoculated with bacterial biomass, and sampling was performed during the working stage of the digester, XRD of the material showed peaks similar to those of the original nontronite, with the other diffractions practically disappearing.

Nontronite gave a high efficiency at startup, almost double that of the control (28.3% against 15.5%) (Figure 2). The ability of the Fe^{3+} present in the nontronite to precipitate organic polymers gives this material the highest power of interaction with the organic matter (17.5%) (Table 2), and offers a great availability of the latter to the bacterial biomass. The beneficial influence of Fe^{3+} as the exchangeable cation of the clay has been described previously [15]. However, various materials give better results at startup than nontronite (Figure 2), possibly due to pH which is lower with nontronite (6.8) than with materials which start up better (bentonite 7.8; talc 7.3; vermiculite 7.1).

It may be considered that this nontronite has impurities which give it a broad spectrum of cations, apart from the already mentioned Fe^{3+} , though in small amounts. Chemical analysis of the material showed the presence of Mg and Na and traces of Ni, Cu and Co (Table 2).

These components make nontronite a microsystem rich in microelements essential for the development of the bacterial biomass, facilitating its growth and activity, and leading to values of efficiency up to 77.9%, compared to 49% in the control.

The SEM study of the nontronite after anaerobic digestion showed the presence of bacteria (bacilli) together with the mineral (Plate 2).

Plate 2.

Aluminium-rich supports

Bentonite.

This is a clay rock constituted by montmorillonite. It is a dioctahedral expanding mineral of type 2:1. The CEC is $0.92 \text{ mol}_c \text{ kg}^{-1}$.

XRD of the bentonite (Figure 5a) indicated that it contained principally montmorillonite, but other minerals appeared, such as illite (diffractions at 10.04, 4.98 Å, etc.), quartz (4.25, 3.33 Å, etc.), and feldspars (3.23, 3.19 Å, etc.). On treating this material with synthetic medium, diffractions appeared that can be attributed to these components, whereas the other peaks (Figure 5b) are due to acetates and other added organics.

Figure 5.

The medium caused modifications of the d_{001} diffraction of the mineral. This diffraction moved from 14.62 to 16.72 Å, indicating that some component of the feed has been incorporated into the interlamellar space.

On adding the bacterial biomass, XRD of the bentonite showed characteristics more similar to the original material (Figure 5c), almost without indication of the organic compounds of the feed. The d_{001} diffraction approximated that of the original, although the peak was broader and less intense, which seems to indicate a certain modification of the interlamellar space.

This behaviour suggests that a considerable part (10%) of the feed was adsorbed onto the

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bentonite, where it was consumed by the bacterial biomass forming the film. The interlamellar space may play a role, by both adsorption of organic compounds and cationic exchange.

Bentonite presented the highest percentage of purification at startup. It also offered good results in the following stage.

Organic matter content in the solution decreased considerably, as it was attracted by the bentonite. At the same time, the micro-organism adsorption capacity of this clay resulted in high concentrations of biomass.

The chemical analysis of this material is shown in Table 2. Calcium (1.81%) is present mainly as exchangeable cation. The cation Ca^{2+} may stimulate the formation of the microbial film, forming a bridge between the surface layer of the support material and microbial membranes, both of which carry a negative charge [16].

Montmorillonite.

The CEC of this mineral is $0.82 \text{ mol}_c \text{ kg}^{-1}$.

The XRD peaks of the d_{001} basal spacings indicated modifications, similar to those in bentonite, both on addition of feed and with the bacterial mass.

Montmorillonite gave values of purification in the working digester similar to those of bentonite (72%), but lower values for startup (26.9%). These differences may be attributed to the higher organic matter consumption of bentonite (Table 2).

Pyrophyllite.

This is a dioctahedral non-expanding mineral of type 2:1 with Al^{3+} in octahedral coordination. The charge density of the surface is practically zero, and so its CEC is very low. The specific surface area is $2 \text{ m}^2 \text{ g}^{-1}$.

The values of purification yielded by pyrophyllite were not constant in the triplicate experiments carried out, probably due to the heterogeneous particle size of the material used. In any case, the pyrophyllite presented the least favourable values for the working digester stage.

CONCLUSIONS

The data obtained indicate that in the first stage (startup) and in the second stage (working digester), all the systems with clay as support material were more efficient than the control.

It is concluded that in clay minerals having an accessible interlamellar space -and therefore a high internal surface area ($> 500 \text{ m}^2\text{g}^{-1}$)- such as bentonite, montmorillonite, vermiculite and stevensite. this plays an important role, as it is accessible to the medium added. However, in the case of vermiculite, when K^+ or NH_4^+ is presents in the medium as constituent of the feed, only cationic exchange between either cation and magnesium originally present takes place. These cations pass to the interlamellar space, causing a collapse of the layers, which then cannot participate any more in the process.

Although this interlamellar space plays an important role in the processes taking place in the digester, it is not the only element responsible for the degradation, since the highest efficiency was not achieved with bentonite, montmorillonite or vermiculite, which are those of greatest interlamellar surface. In the case of sepiolite, the surface of its channels may also play a role in the degradation process, but this alone cannot be considered responsible for the greater efficiency, since its specific surface ($250 \text{ m}^2 \text{ g}^{-1}$) is smaller than that of bentonite, montmorillonite or stevensite. Probably, the physicochemical properties of the surface also have an important influence, those of sepiolite being different from the others.

Bentonite, montmorillonite, talc and vermiculite are favourable for startup, as they rapidly release Ca^{2+} or Mg^{2+} to the medium, either by cation exchange or by dissolution of carbonates due to the initial pH of the system (6.3). Clay minerals which release Mg^{2+} gradually, such as sepiolite and stevensite, stimulate bacterial development to give improved COD removal efficiencies.

The presence of Fe^{3+} in the minerals may affect the efficiency of the digester if this cation can be released to the solution, because it could precipitate organic compounds if present at high concentration and could also stimulate bacterial activity. This may explain the high COD removal efficiencies obtained with nontronite. The beneficial effect of Fe^{3+} as the exchangeable cation of these clays has been described previously [15]. Talc, which has a high proportion of iron, gives one of the

highest yields of all the microdigesters used. It should be noted that these minerals contain cobalt and nickel, which can stimulate anaerobic digestion if liberated gradually to the medium.

The specific surface of talc is small ($\approx 10^2 \text{ m}^2 \text{ g}^{-1}$). However, its effectiveness in the purification process is very high, which suggests that its chemical composition favours degradation. The nontronite sample used in this study did not have a high specific surface area because only around 20% of it consisted of the mineral nontronite, which would have made the greatest contribution to the overall surface area. The chemical composition favours precipitation of great amounts of organic matter, responsible for the higher efficiency in purification.

Pyrophyllite with small specific surface, $\text{CEC} \approx 0$, with only aluminium and silicon in its structure, and high chemical stability, shows the lowest purification rate.

It is concluded that when clay minerals are used, the following factors can be considered as favouring a high rate of anaerobic digestion: internal and external specific surface, ion exchange capacity, stability, and chemical composition. Stability and chemical composition seem to have the greatest effect on the efficiency of treatment in the working digester.

From the data obtained, the following order of purification can be established:

STARTUP: Bentonite > talc > vermiculite > nontronite > montmorillonite > pyrophyllite > stevensite > sepiolite.

WORKING DIGESTER: Sepiolite > stevensite \geq talc > nontronite > bentonite > montmorillonite > vermiculite > pyrophyllite.

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FIGURE CAPTIONS

- Figure 1. Digester designed for this work.
- Figure 2. Purification efficiency (%) obtained in microdigester with different supports. ■ startup.
□ working digester.
- Figure 3. XRD of a) stevensite, b) stevensite plus synthetic feed, c) the mineral after being used as support in the digestion process.
- Figure 4. XRD of a) vermiculite, b) vermiculite plus synthetic feed, c) vermiculite after being used as support in the digestion process.
- Figure 5. XRD of a) bentonite, b) bentonite plus synthetic feed, c) the mineral after being used as support in the digestion process.
- Plate 1. Scanning electron micrograph of the talc after anaerobic digestion.
- Plate 2. Scanning electron micrograph of the nontronite after anaerobic digestion.

TABLE HEADERS

- Table 1. Synthetic feed (composition per litre).
- Table 2. Values of consumption of organic matter (OM) from the feed for each support material.
- Table 3. Chemical analysis of the materials used as support (%). Stev: Stevensite, Sep: Sepiolite, Verm: Vermiculite, Non: Nontronite, Bent: Bentonite, Mont: Montmorillonite, Pyro: Pyrophyllite.



MICRODIGESTER



VALVE

Figure 1

Wagman et al.

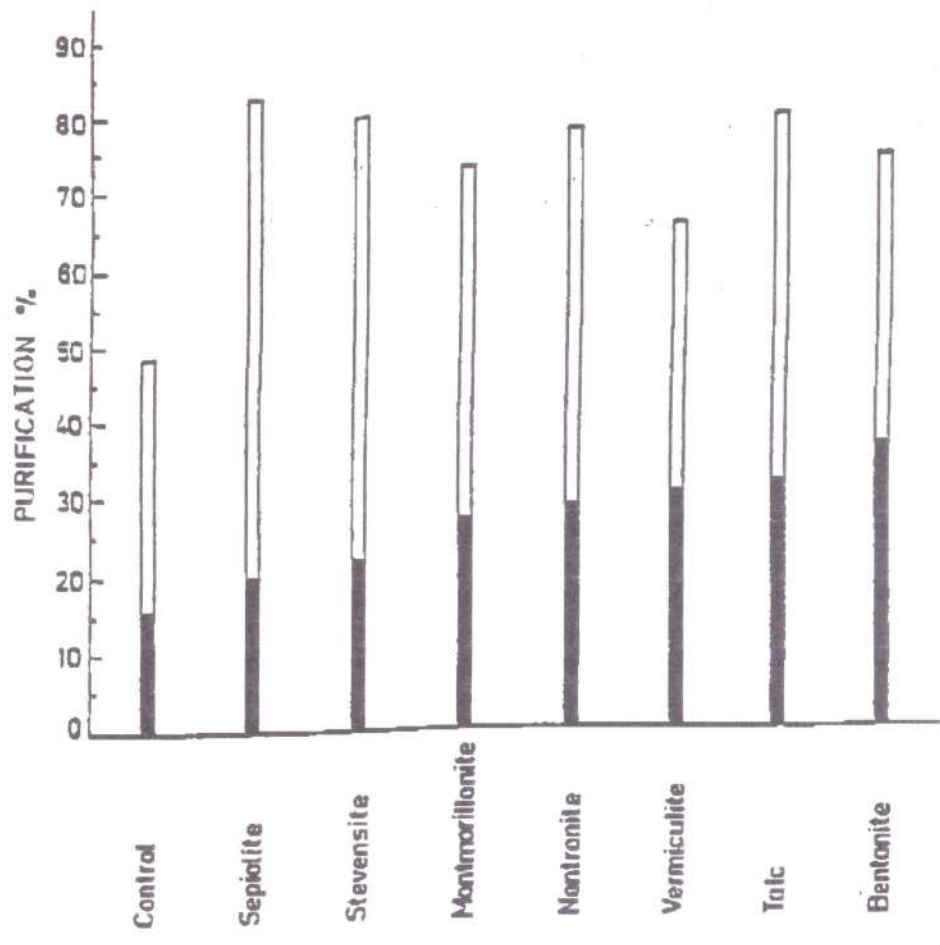


Figure 2
Maguadua et al.

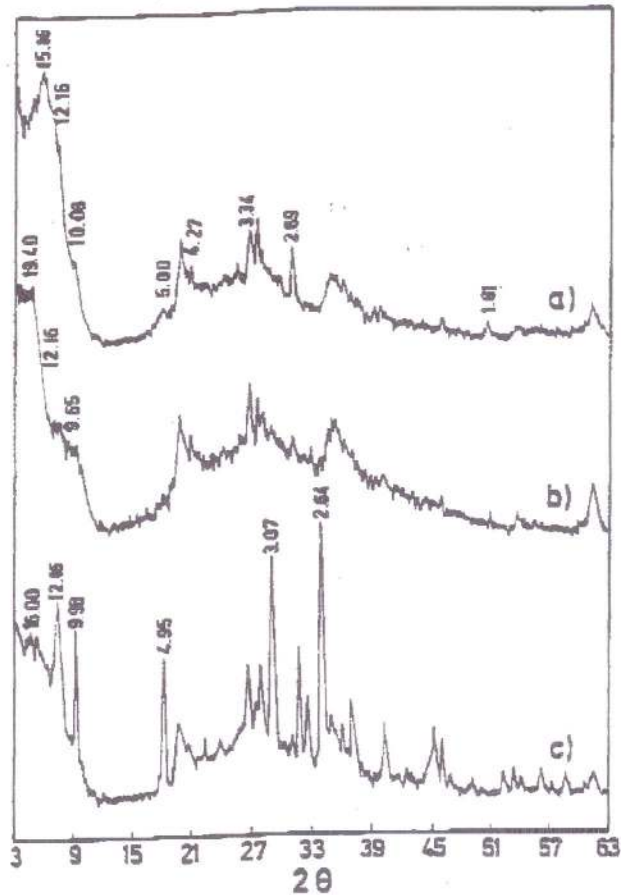


Figure 3
Magueta et al.

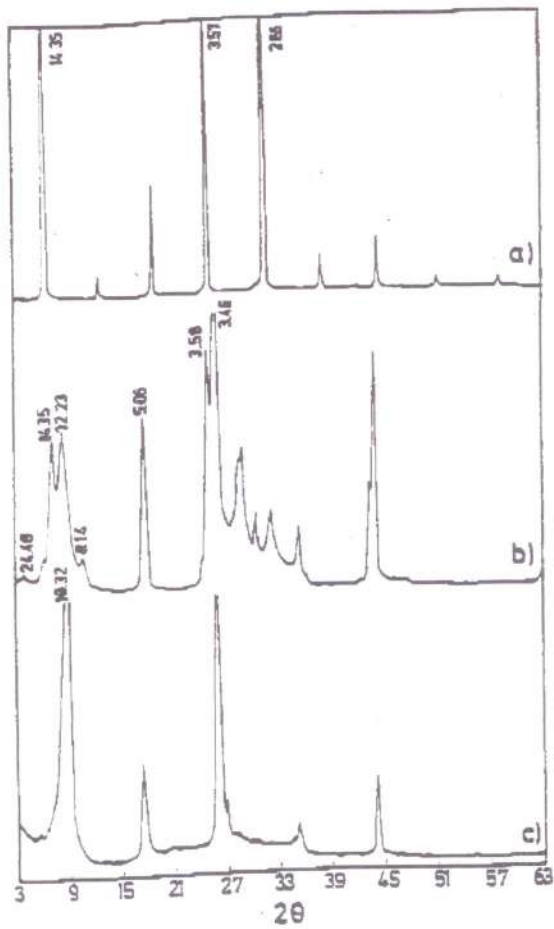


Figure 4
Uryveda et al.

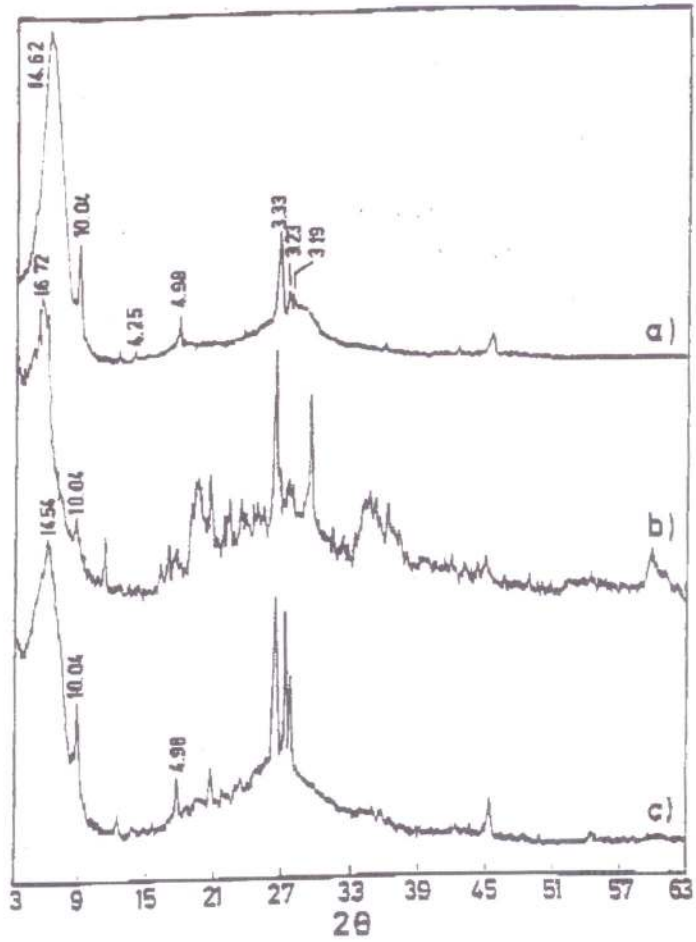


Figure 5
 Aligned et al.

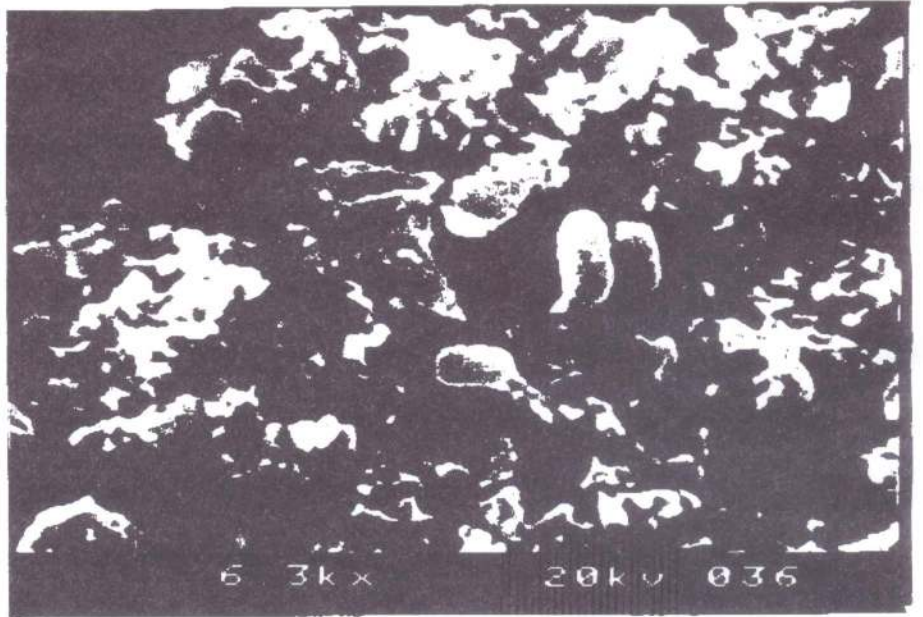


Plate 1



Plate 2