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Review article

Application of natural zeolites in anaerobic digestion processes: A review

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ABSTRACT

This paper reviews the most relevant uses and applications of zeolites in anaerobic digestion processes. The feasibility of using natural zeolites as support media for the immobilization of microorganisms in different high-rate reactor configurations (fixed bed, fluidized bed, etc.) is also reviewed. Zeolite, with its favorable characteristics for microorganism adhesion, has also been widely used as an ion exchanger for the removal of ammonium in anaerobic digestion due to the presence of Na^{+}, Ca^{2+} and Mg^{2+} cations in its crystalline structure. This property is also useful for improving the anaerobic process performances in the treatment of wastewaters with high concentrations of nitrogen compounds, such as cattle, pig and chicken wastes, as it prevents process inhibition. The influence of zeolite particle size and doses in batch mesophilic and thermophilic processes when referring to synthetic or different wastewaters is also reviewed. Finally, the role of zeolite in granulation processes, in anaerobic oxidation processes (Anammox) for promoting the retention of the biomass involved (given its low growth rate), and in hybrid and sequencing reactors such as the moving bed biofilm reactors (MBBR) are also discussed.

1. Introduction

Natural zeolites (Greek word meaning *boiling stones*) are generally found in rocks near active or extinct volcanoes, which means that zeolite deposits exist in many parts of the world. These deposits were originally discovered in Sweden by Cronsted in 1776 (Colella and Gualteri, 2007; de Gennaro et al., 2005, 2007).

For many years now, zeolites have been recognized for their attractive physical and chemical properties. They are of great interest to the scientific community, mainly because they exist in large mineable deposits (Bret et al., 2003; Christidis, 2006; Marantos et al., 2007), they possess valuable properties as previously mentioned, and because of their potential application in different areas of industry, agricultural technology and pollution control (Kesraoui-Ouki et al., 1994; Papaioannou et al., 2005).

Natural zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations, consisting of three-dimensional frameworks of SiO_4^{4-} and AlO_4^{5-} tetrahedra linked through shared oxygen atoms (Gerrard et al., 2004; Gottardi, 1989; Yeritsyan et al., 2008). They are porous materials characterized by their ability to 1) lose and gain water reversibly, 2) adsorb molecules of appropriate cross-sectional diameter (adsorption property or acting as molecule sieves) and 3) exchange their constituent cations without a major change in their structure (ion-exchange property) (Andrade et al., 2008; Christidis et al., 2003; Henry et al., 2008; Moirou et al., 2000; Salvestrini et al., 2010; Wang et al., 2008a,b). The exploitation of these properties underlies the use of zeolites in a wide range of industrial, agricultural and contamination prevention applications such as adsorption and separation, ion-exchange, ammonia removal in the treatment of municipal and other industrial wastewaters, the removal of caesium and strontium from radioactive wastes, the removal of heavy metals from industrial wastewaters as well as in animal feed additives, deodorizing animal installations, chemical and biochemical reaction catalizers, and in cultures of marine micro-algae, etc. (Burgess et al., 2004; Curtui, 2000; Karakurt et al., 2010; Karamanlis et al., 2008; Liang and Ni, 2009; McGilloway et al., 2003; Milán et al., 2001a,b,c; Ryakhovsya and Gainatulina, 2009; Shi et al., 2009; Velichkina, 2009).

The structure and physical properties of natural zeolite [channel and pore cavities, minimum diameter of pores in the range of 3 to 10 Å, average surface area of 24.9 m^2/g, low bulk density, high exchange (CEC) and adsorption capacities] make it ideal for use in biological purification wastewater processes (Carretero and Pozo, 2009; Christidis, 1998; Marty et al., 2010; Park et al., 2010; Rybicka and Calmano, 1988; Wong and Yeung, 2007). Consequently, the use of natural zeolite in different wastewater biological treatment processes has increased significantly

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over the past few years (Fernández et al., 2008a,b; Widiastuti et al., 2008).

The anaerobic treatment of medium and high-strength wastewaters with a high biodegradable content has a number of advantages (Fernández et al., 2008b); quite a high degree of purification with high organic load feeds can be achieved, low nutrient requirements are sufficient, small quantities of excess sludge are usually produced and, finally, a renewable combustible biogas is generated. The production of biogas enables the process to generate or recover energy instead of just saving it; this can significantly reduce operational costs compared with the high energy-consuming aerobic process.

However, one of the greatest problems in the anaerobic processing of wastewaters is the loss of biomass in systems with high hydraulic loading rates. To solve this problem, reactors have been designed with supports which fix the biomass and result in high loading densities and low hydraulic retention times (Fernández et al., 2007a,b; Nikolaeva et al., 2009; Umaña et al., 2008). With the increase of population density on the given support, there is a greater change of cross-feeding, co-metabolism and interspecies hydrogen and proton transfer, which may further stimulate the growth of microcolonies. Among the bioreactors most commonly used for this purpose are fluidized and fixed bed reactors, where bacteria colonize a support medium, thereby increasing the surface available for bacterial growth (Fernández et al., 2007a; Nikolaeva et al., 2009). In various studies, these reactor configurations have shown to be feasible for the treatment of different industrial wastewaters. The use of a porous support such as zeolite enables the anaerobic reactor to retain high biomass concentrations and thereby operate at significantly reduced hydraulic retention times (Milán et al., 2010a).

Keeping the above observations in mind, the objective of the present paper is to review the most relevant uses and applications of zeolites in anaerobic digestion processes. The feasibility of using natural zeolite as support media for the immobilization of microorganisms in different reactor configurations (fixed bed, fluidized bed, etc.) will also be reviewed. In addition, zeolite with its favorable characteristics for microorganism adhesion, has been widely used as an ion exchanger for ammonia removal in anaerobic digestion due to the presence of Na^+, Ca^{2+} and Mg^{2+} cations in its crystalline structure. This property is also useful for improving the anaerobic process performances in the treatment of wastewaters with high concentrations of nitrogen compounds, such as cattle, pig and chicken wastes, as it prevents process inhibition. At the same time, zeolite has shown a great capacity for metal adsorption and this property can be useful for removing toxic materials that can inhibit to the microorganisms responsible for the anaerobic digestion processes.

2. General characteristics and properties of natural zeolite

The following empirical formula represents the chemical structure of zeolites in a general context, where "x" is always equal to or greater than 2 and "M" is the cation of valence "n": $M_{2/n}O \cdot Al_2O_4 \cdot xSiO_2 \cdot yH_2O$

The variety of natural zeolite types results from differences in the way in which the SiO_4 and AlO_4 tetrahedra may link in space in one, two, or three dimensions and from the other ion types that are substituted within the channels. The tetrahedra of oxygens are arranged in four, five, six, etc. member rings, commonly called Secondary Building Units (SBU), which combine to form the channels and cavities of the various zeolites (Kesraoui-Ouki et al., 1994). There are about 50 different types of natural zeolites with different mineralogical compositions depending on their structure and Si/Al ratio (Baker et al., 2009; Giannetto et al., 2000; Gruszkiewicz et al., 2005; Yang et al., 2009). Some examples of the most typical zeolites used are shown in Table 1.

The nature of the void spaces and the interconnecting channels in dehydrated zeolites is an important element in determining physical and chemical properties. The channels in natural zeolites contain water that makes up 10%–25% of their weight. The adsorbed water may be driven off by heating under vacuum at several hundred degrees Celsius. The percentage of water removed from a zeolite by this procedure is a first measure of its adsorptive capacity, since the void volume left by the water molecules will be available for the adsorption of other molecules (Kesraoui-Ouki et al., 1994). In the case of competition over available sites for adsorption, the polarity of adsorbate molecules and their electrostatic interaction with the framework charge will determine which one is favored. Zeolites can be modified by ion-exchange to enable the separation of a variety of mixtures by selective adsorption. The adsorbed species may be removed by a decrease in pressure, an increase in temperature, displacement by another adsorbate, or a combination of all three (Kesraoui-Ouki et al., 1994). For obtaining the modified zeolites, stock samples of natural zeolites were treated with solutions of appropriate salts of cations (NaCl, $CaCl_2$, KCl or $MgCl_2$) at about 90 °C in a stirred vessel for about 2 h. This treatment was repeated twice to force the zeolites into the relevant homoionic forms as far as possible. Finally, the samples treated in this way were washed with de-ionized water and subsequently dried at 50 °C (Milán et al., 2001b).

Table 1
The Si:Al ratios for different types of natural zeolites.

Zeolite type	Si:Al ratio ranges
Analcite	1.00–3.00
Clinoptilolite	2.92–5.04
Chabazite	1.43–4.18
Edingtonite	1.00–2.00
Erionite	3.05–3.99
Faujasite	1.00–3.00
Ferrierite	3.79–6.14
Heulandite	2.85–4.31
Laumontite	1.95–2.25
Mordenite	4.19–5.79
Natrolite	1.5
Phillipsite	1.45–2.87
Stibilite	2.50–5.00
Wairakite	2.0

Assuming that the zeolite is in equilibrium with the aqueous phase it is in contact with, three main properties are important in ion-exchange applications: exchange kinetics, ion exchange capacity and cation selectivity. Ion-exchange kinetics concerns the time required for the counter-ion to travel to the exchange site and displace a cation in the structure. The capacity refers to the number of milliequivalents (meq) of a given cation per gram of zeolite that the zeolite can retain on its fully loaded exchange sites. This is a function of its silica-to-alumina mole ratio, and its cationic form. Cation selectivity refers to the preference order of a zeolite for cations, based on the energetics of the distance between anionic sites, cationic radii, and cationic hydration energies. Cation-exchange capacities are typically of the order of 2 meq per gram of zeolite.

Finally, another important property of natural zeolites is their effectiveness as a catalyst support due to their large surface area, the local high electric field density of the charge on the aluminosilicate framework, and the presence of acid sites on the framework (Kesraoui-Ouki et al., 1994).

3. Batch anaerobic processes

Although the anaerobic digestion processes in batch mode are not frequently applied at full-scale they are useful at laboratory-scale because they can be performed quickly with simple and inexpensive equipment, and are helpful in assessing the extent to which a material can be digested, providing relevant information related to the methane yield coefficient and kinetics of the process.

Clay minerals such as zeolites and other surface-active materials have been reported to influence microbial and enzymatic transformation of a variety of substances, including ammonium, sulfur, carbohydrates, proteinaceous materials and phenolic compounds (Borja and Banks, 1994; Borja et al., 1993a,b; Milán et al., 2003). In addition, according to previous results (Duran-Barrantes et al., 2008; Kotsopoulos et al., 2008; Milán et al., 2001a,b; Milán et al., 2003; Montalvo et al., 2005; Weiβ et al., 2010, 2011) zeolite has been found to be a successful microbial support in batch mesophilic anaerobic digestion of different substrates, because of the following characteristics:

1. Its high capacity for immobilization of microorganisms.
2. Its capacity for improving the ammonia/ammonium ion equilibrium.
3. The possibility of reducing the ammonia and ammonium ion in solution.

The colonization of activated zeolites (i.e. clinoptilolites) as carriers for microorganisms involved in batch anaerobic digestion processes was recently investigated (Weiβ et al., 2011). Zeolite particle sizes of 1.0–2.5 mm were introduced to anaerobic laboratory batch-cultures (500 mL) during biogas production from grass silage. Incubation over 5–84 days led the colonization of zeolite surface (Fig. 1). Morphological insights were obtained by using scanning electron microscopy (SEM). Single strand conformation polymorphism (SSCP) analysis based on amplification of bacterial and archaeal 16S rRNA fragments demonstrated structurally distinct populations preferring zeolite as operational environment (Weiβ et al., 2011).

The effect of natural zeolites on the anaerobic degradation of synthetic substrates such as acetate and methanol was evaluated by the determination of specific methane productivity (SMP) in batch mini-digesters of 50 mL (Milán et al., 2003). A kinetic characterization with data of accumulated methane gas volume was also reported. The addition of zeolites determined an increase in the apparent kinetic constant of the process achieving values twice as high as those observed in a control reactor. The addition of this clayey support brought about an increase in the microbial growth not only for the methanogens but also for the hydrolytic bacteria. A greater effect of modified natural zeolites on SMP was observed, increasing it by 8.5 times with magnesium zeolite, by 4.4 times with cobalt zeolite and 2.8 times with nickel zeolite (Milán et al., 2003).

In the same way, the addition of Mg^{2+} modified zeolite at a concentration of 0.1 g/g of volatile suspended solids (VSS) increased the specific methanogenic activity (SMA) and the apparent kinetic constant, k_0, showing SMA and k_0 values 15 and 2 times higher than those observed for control reactors during the batch methanogenesis of acetate and methanol, respectively (Milán et al., 2001b). In addition, the population of hydrolytic, acetogenic and methanogenic microorganisms increased 100, 10 and 100 times, respectively, compared to the results observed in the controls.

More recently, operating in batch mode with a mixture of volatile fatty acids (VFA) (acetic:propionic:butyric = 70:20:10) as a carbon source and based on the analyses of anaerobic biofilms, it was demonstrated that the heavy metal incorporated into the natural zeolites (nickel, cobalt or magnesium) showed a great influence on the predominance of species (Milán et al., 2010b) operating at similar doses of 0.05 g/g VSS. For example, the presence of nickel and cobalt favored *Methanosaeta*, while magnesium zeolite stimulated the presence of *Methanosarcina* and sulfate-reducing bacteria (SRB). Again, it was observed that the SMA was higher in digesters with modified natural zeolites when compared to control digesters.

The influence of particle size in the range from 0.07 to 1 mm and zeolite doses in the range from 0.05 to 0.40 g zeolite/g of inoculum (VSS) on the anaerobic digestion of synthetic wastewater was also studied at laboratory-scale in batch experiments (Montalvo et al., 2005). The influence of both factors (particle size and doses) on the kinetics of methane production was also studied. The anaerobic process was favored by the addition of zeolite at doses of between 0.05 and 0.30 g/g VSS, the optimum value being 0.10 g/g VSS. Values of the

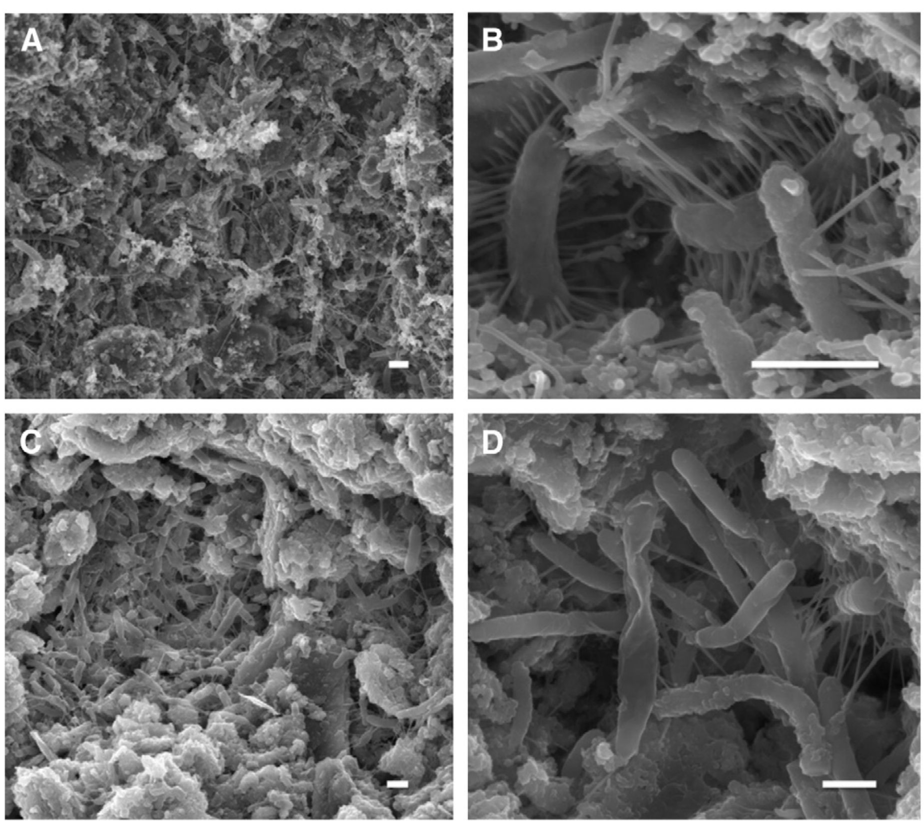

Fig. 1. SEM images (SE, in-lens detector) of colonized zeolite particles (<2.5 mm in diameter) after a 5 day batch-wise cultivation on a model substrate for grass silage at 45 °C. A) *CPD dried zeolite with area-wide biofilm formation. B) *CPD dried zeolite, cells forming fibrous structures. C) Lyophilised zeolite with biofilm formation mainly in a pit. D) Lyophilised zeolite, microorganisms colonizing a pit. (Bar length: 1 μm) (Weiβ et al., 2011). *CPD: critical point drying (drying method used for the zeolite).

kinetic constants were determined to be dependent on the zeolite doses, achieving a maximum value (0.22 $days^{-1}$) at a dose of 0.10 g zeolite/g VSS and a minimum value (0.14 $days^{-1}$) at a dose of 0.40 g zeolite/g VSS. In addition, during this study both the capacity for microorganism immobilization and for reducing the concentration of toxic nitrogen (NH_3) by the zeolite was relevant (Montalvo et al., 2005).

Anaerobic processes are efficient in reducing the concentration of organic matter in piggery waste and cow manure. The use of the methane gas obtained during the process could significantly reduce the cost of waste treatment (Milán et al., 2001a, 2003). The effect of different natural zeolite concentrations on the anaerobic digestion of piggery waste was studied in batch mode (Milán et al., 2001a). Zeolite doses in the range of 0.2–10 g/L of wastewater were used in experiments carried out at temperatures between 27 °C and 30 °C. It was found that the anaerobic process was favored by the addition of natural zeolite at doses between 2 and 4 g/L and increasingly inhibited at doses beyond 6 g/L. The apparent kinetic constant of the process increased with the amount of zeolite up to a concentration of 4 g/L. To be specific, the kinetic constant increased between 80% and 100% compared to the control. At a higher zeolite dose, the kinetic constant decreased, achieving a minimum value of 0.01 $days^{-1}$ for a zeolite dose of 10 g/L which is 17% lower than that observed for the control. The significant reduction in methane production and in the kinetic constant of the process at doses higher than 8 g/L may be explained by different factors. The increase of total solid concentration due to the addition of zeolite at the same time provokes a reduction of the free available water, affecting the transport of nutrients and metabolites in the vicinity of the zeolite particles and the microorganisms associated. Therefore, large amounts of zeolite could increase the apparent viscosity of the medium, thereby hindering mass transfer between the substrate and microorganisms responsible for the process and decelerating the process (Bowman, 2003; Cintoli et al., 1995; Milán et al., 2001a; Venlovsky et al., 1999).

On the other hand, the kinetics of the anaerobic digestion of cow manure has also been studied using a batch reactor with biomass immobilized on natural zeolite and the results compared with a control digester at mesophilic temperature (Borja et al., 1993a,b). It was observed that the apparent kinetic constant of the process and the mean rate of methane production decreased considerably, with substrate concentration in the control digester showing a major inhibition process due to the accumulation of ammonia nitrogen (NH_4^+ plus free NH_3). However, in the zeolite digester, the kinetic constant was virtually invariable in the COD range studied (1.4–9.8 g/L) due to the ionic exchange between the support and substrate. In addition, the methane yield coefficient was 5 times higher than in the control digester for high substrate concentrations (9.8–10.3 g/L). This same behavior has been reported more recently in the batch anaerobic digestion of swine wastewater at a temperature of 25 °C (Duran-Barrantes et al., 2008). The reactor with zeolite support always showed the minimum mean concentrations of NH_4^+–N and volatile fatty acids (VFA) in the effluents when compared with the effluents of reactors containing saponite, sepiolite and esmectite.

The effect of adding different types of natural and synthetic zeolites (mordenite, clinoptilolite, zeolite 3A and zeolite 4A) and other additives (manganese oxides such as hollandite and birnessite) on batch anaerobic digesters treating ammonium rich organic sludge (4500 mg N/L) has been also studied (Tada et al., 2005). It was observed that the addition of zeolites resulted in significant ammonium (NH_4^+) removals from the organic sludge. Natural mordenite also enhanced methane production by 1.7 times as compared with the other materials. Chemical analyses of the sludge after the digestion process revealed that the Ca^{2+} ions released from natural mordenite by a Ca^{2+}/NH_4^+ exchange, enhanced the methane production of the organic waste at a high NH_4^+ concentration. Natural mordenite had a synergistic effect on the Ca^{2+} supply as well as on the NH_4^+ removal during anaerobic digestion, which is effective for the mitigation of NH_4^+ inhibition against methane production.

The efficiency and mechanism of sediment capping with an active barrier system (ABS) using zeolite to simultaneously prevent phosphorus (P) and ammonium (NH_4^+) release from eutrophic lake sediments under anaerobic conditions was also investigated through a series of batch and sediment incubation experiments (Lin et al., 2011). These experiments proved that the zeolite as a component of the ABS has a dual function: (1) preventing the release of NH_4^+ from the sediments and (2) supplying Ca^{2+} through a Ca^{2+}/NH_4^+ exchange to improve the ability of the capping material to immobilize P release from the sediments.

The addition of zeolite also counteracted to some extent the inhibitory effect of ammonia during the batch thermophilic anaerobic digestion of cattle manure (Borja et al., 1996). As the free ammonia fraction increases with temperature and pH, it would be expected that the ammonia level tolerated at high pH and thermophilic temperatures would be low. Biogas reactors operating with cattle waste in batch mode often have a high pH (about 8) and, especially at thermophilic temperatures, the free ammonia concentration will be up to ten times higher than the free ammonia concentrations reported as inhibitory. Therefore, the addition of zeolite in these experiments had a stimulatory effect on the anaerobic process leading to a decrease in the lag phase and an increase in the methane production in ammonia inhibited reactors (Borja et al., 1996).

The effect of adding natural zeolite on the batch thermophilic anaerobic decomposition of pig wastes was also researched at zeolite doses of 0, 4, 8 and 12 g of zeolite/L of waste at 55 °C (Kotsopoulos et al., 2008). In this case, methane production was significantly higher in treatments with natural zeolite at doses of 8 and 12 g/L of waste, compared to those without zeolite. Furthermore, in treatments with natural zeolite, the reduction of volatile solids and biological oxygen demand (BOD_5) was statistically significant. The results appear to be caused by the zeolite adsorping the ammonia, thus having an effect not only on the toxicity of ammonia and on the C/N proportion but also on the regulation of acidity (pH) of the pig wastes.

Biogas production from hemicellulose-rich substrates was enhanced by the addition of hemicellulolytic bacteria immobilized on trace metal activated zeolite in batch cultures (Weiβ et al., 2010). Xylanase activity increased continuously during subsequent enrichment cycles by up to 162%. An increase in methane production by 53% compared to controls without the addition of microorganisms immobilized on zeolite was observed. Specific enrichment of hemicellulolytic bacteria during the process was confirmed by using single strand conformation polymorphism (SSCP) analysis based on the amplification of the eubacterial 16S rRNA fragments. Microorganisms belonging to the Bacteroides sp. and *Azospira oryzae* (Dechlorosoma sp.) groups could be identified as well as a wide spectrum of diverse species within the Clostridiales order (Firmicutes). Similarly, populations naturally colonizing zeolite (e.g. *Ruminofilibacter xylanolyticum* identified by SSCP analysis based on amplification of bacterial and archaeal 16S rRNA fragments) also showed pronounced hydrolytic enzyme activity (xylanase) in batch biogas production from grass silage (Weiβ et al., 2011).

Finally, a study of the microbial population immobilized on zeolite in batch experiments carried out with anaerobic sludges with various physical structures (granular and flocculent) derived from different sources revealed the presence of microorganisms following the order: *Methanococcaceae* > *Methanosarcina* > *Methanosaeta* (Milán et al., 2010a) by using 16S rRNA-based molecular techniques.

4. Fixed-bed anaerobic reactors

In conventional digesters such as batch, complete mixed, and plug-flow reactors, the hydraulic retention times (HRT) approach the values of the retention times of microorganisms or solid retention times (SRT). Therefore, in order to prevent the washout of the anaerobic microorganisms, high volumes of a reactor are required with respect to the volume of waste to be processed. With the aim of reducing the reactor volumes, different alternatives for microorganism retention such as sludge recycling or immobilization have been developed. Anaerobic fixed-bed reactors are based on the principle of the immobilization of microorganisms on a support, reducing the HRT. Compared with other high-rate anaerobic reactors, the fixed-bed digester has several favorable characteristics (Castilla et al., 2009; Nikolaeva et al., 2009; Umaña et al., 2008). This reactor configuration is more suitable for handling high pollution-load wastewaters because it has a high substrate removal efficiency. This type of digester is less sensitive to shock loads and operates at lower HRTs, thus requiring smaller volumes. Construction, operation and maintenance costs are lower. Its effluents contain few suspended solids, eliminating the need for the separation of solids or recycling and the biological system recovers more quickly to the conditions present before the digester operation was stopped. These characteristics render the fixed-bed digester extremely useful for the treatment of high-strength wastewaters.

Natural zeolite has been used for immobilizing anaerobic microorganisms in fixed-bed digesters treating cattle and piggery wastes as well as for simultaneously reducing the inhibitory effect of the ammonia produced during the anaerobic decomposition of proteins, aminoacids and urea (Nikolaeva et al., 2009; Umaña et al., 2008).

A laboratory-scale anaerobic fixed-bed reactor packed with a combination of zeolite and tire rubber treating screened dairy manure at HRTs in the range of 1.1–5.5 days was evaluated and compared to another similar reactor packed with only tire rubber (Umaña et al., 2008). It was observed that methane yield was a function of the HRT and of the type of support used, and was 12.5% and 40% higher in the reactor with zeolite and rubber support than in the reactor with only rubber for HRTs of 5.5 and 1.0 days, respectively. No clogging was observed in the reactor with zeolite during the operational period. The results obtained demonstrated that this type of reactor is capable of operating with dairy manure at a HRT 5 times lower than that used in a conventional reactor (Umaña et al., 2008). In addition, a first-order kinetic model was adequate for assessing the effect of HRT on the organic matter removal efficiency and methane production in the above-mentioned reactors. It was found that the kinetic constant for methane production was 29.4% higher in the reactor with zeolite than in the digester without this support material (Nikolaeva et al., 2009).

Fixed-bed reactors with zeolite support have also shown to be effective in the anaerobic treatment of low-strength wastewater such as a mixture of municipal wastewater and organic garbage leachate (COD: 700 mg/L) at HRTs of 12 and 36 h (Castilla et al., 2009). COD removal efficiencies of 83% were achieved at an organic loading rate (OLR) of 0.42 g COD/(L day) with 83% of total suspended solids being retained in the reactor.

5. Fluidized-bed reactors

Among the most commonly used bioreactor configurations for increasing the microbial population density are fluidized bed reactors, where bacteria colonize particles of a support medium, thereby increasing the surface available for bacterial growth (Borja et al., 1994; Fernández et al., 2007a,b; Kuba et al., 1990; Montalvo et al., 2008). The fluidized bed reactor is a digester configuration which has been demonstrated in various studies to be feasible for the treatment of both low and high strength industrial wastewaters (Fernández et al., 2001; García-Encina and Hidalgo, 2005; Shida et al., 2009). The use of small, porous, fluidized media enables the reactor to retain high biomass concentrations and thereby to operate at significantly reduced HRTs. Fluidization also overcomes operating problems, such as bed clogging and high pressure drops which would be encountered if such high surface area media were used in a packed bed reactor (Haroun and Idris, 2009). A further advantage of using media to retain the biomass within the reactor is the possible elimination of the secondary clarifier.

The performance of two laboratory-scale fluidized bed reactors with natural zeolite as support material when treating high-strength distillery wastewater was assessed (Fernández et al., 2008b). In the first set of experiments, the influences of the OLR, the fluidization level (FL) and the particle diameter (D_p) of the natural zeolite were evaluated. This experimental set was carried out at an OLR from 2 to 5 g COD/(L day), at FL 20% and 40% and with D_p in the range of 0.2–0.5 mm (reactor 1) and 0.5–0.8 mm (reactor 2). OLR and FL were shown to have only a slight influence on COD removal, whereas they had a stronger influence on the methane production rate. COD removal was slightly higher for the highest particle diameter used. The second experimental set was carried out at an OLR from 3 to 20 COD/(L day) with 25% of fluidization and D_p in the above-mentioned ranges for reactors 1 and 2. The performance of the reactors was similar. The COD removal efficiency correlated with the OLR based on a straight line. COD removal efficiencies higher than 80% were achieved in both reactors without significant differences. It was also observed that both COD removal rate and methane production increased linearly with the OLR, independently of the D_p used (Fernández et al., 2008b).

On the other hand, the biomass concentrations attached to zeolite in the above-mentioned reactors was found to be in the range of 40–45 g volatile solids (VS)/L (Fernández et al., 2007a). The methane yield coefficient was 0.29 L CH_4 at STP conditions/g COD consumed and was virtually independent of the OLR applied. Using the scanning electronic microscopy, it was observed that natural zeolite possesses excellent physical characteristics as a support medium (Fig. 2) in anaerobic fluidized bed reactors (Fernández et al., 2007b). A hybridization technique (fluorescence in situ hybridization, FISH) helped determine the predominant anaerobic microorganisms that colonized the zeolite, which were found to be *Methanosaeta* and *Methanosarcinaceae*, observing a reduced number of sulfate-reducing bacteria. The results obtained for reactors 1 and 2 were very similar, showing that the particle size did not significantly influence the microbial community immobilized on zeolite (Fernández et al., 2007a).

A study of the anaerobic treatment of wastewaters derived from red (RWWW) and tropical fruit wine (TFWWW) production was carried out in four laboratory-scale fluidized bed reactors with natural zeolite as bacterial support (Montalvo et al., 2008). These reactors operated at

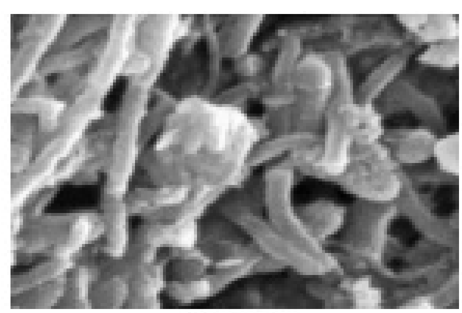

Fig. 2. Colonized zeolite. Photographs taken at: (A) 5000× amplification and B (16000× amplification) (Fernández et al., 2007a).

mesophilic temperature (35 °C). Reactors R1 and R2 contained Chilean natural zeolite, while reactors R3 and R4 used Cuban natural zeolite as microorganism support. The characteristics and composition of both natural zeolites are summarized in Table 2. In addition, reactors R1 and R3 processed RWWW, while reactors R2 and R4 used TFWWW as substrate. The biomass concentration attached to zeolites in the four reactors studied was found to be in the range of 44–46 g VS/L after 90 days of operation time. Both types of zeolites can be used indistinctly in the fluidized bed reactors achieving more than 80%–86% COD removals for OLRs of up to at least 20 g COD/(L day). pH values remained within the optimal range for anaerobic microorganisms (6.8–7.6) for OLR values of up to 20 and 22 g COD/(L day) for RWWW and TFWWW, respectively. Toxicity and inhibition levels were observed at an OLR of 20 g COD/(L day) in reactors R1 and R3 while processing RWWW, whereas the aforementioned inhibitory phenomena were not observed at an OLR of 24 g COD/(L day) in R2 and R4, treating TFWWW as a consequence of the lower phenolic compound content present in this substrate. The volatile fatty acid (VFA) levels were always lower in reactors processing TFWWW (R2 and R4) and these values (<400 mg/L, as acetic acid) were lower than the suggested limits for digester failure. The specific methanogenic activity (SMA) was twice as high in reactors R2 and R4 as in R1 and R3 after 120 days of operation when all reactors operated at an OLR of 20 g COD/(L day) (Montalvo et al., 2008).

The effect of the influent COD concentration on the performance of anaerobic fluidized bed reactors packed with Chilean zeolite as biomass immobilization support treating winery wastewaters from grape-red wine (GRWW) and guava wine production (GWW) was also studied at laboratory scale (Montalvo et al., 2010). Two reactors were used: one treating GRWW (AFB1) and the other processing GWW (AFB2). The behavior of these reactors was compared at mesophilic temperature (35 °C). Influent COD varied from 1 to 24 g/L and the HRT was maintained constant at day 1 throughout the experiment, during which influent and effluent pH, total volatile fatty acids (TVFA), COD and methane gas production were determined. COD removal efficiency increased with the influent COD up to a maximum of around 19 g/L for GRWW and up to around 22 g/L for GWW due to the increase in the concentration of phenols. Process performance was slightly better with guava winery wastewater than with grape-red winery wastewater due to its lower phenolic content (Montalvo et al., 2010).

The zeolite anaerobic fluidized bed reactor was very effective in the treatment of cow manure (COD = 47.1 g/L), a process usually inhibited due to the presence of complex organic compounds and high concentrations of ammoniacal nitrogen (Borja et al., 1994). Two fluidized bed reactors were used for the study, one with freely suspended biomass as a control, and the other with biomass supported on zeolite. The results obtained were evaluated using the Chen–Hashimoto methane production model to obtain values for the maximum specific growth rate μ_{max} and kinetic constant K of the process for each case studied. Use of the support produced a 59% and 35% increase in the values of these parameters, respectively. This behavior is believed to be due to the exchange of ammoniacal nitrogen that occurs in this type of digester between the support and the medium. Anaerobic digestion is shown to be a useful method for purifying the wastewater in question since this method results in a 93%–94% reduction of the initial COD, giving a final COD of between 2.7 and 3.0 g/L (Borja et al., 1994).

Table 2
Chemical and mineralogical compositions of Chilean and Cuban natural zeolites (Montalvo et al., 2008).

Chemical composition (%)			Mineralogical composition (%)		
Compound	Chilean	Cuban		Chilean	Cuban
SiO_2	67.74	66.62	Clinoptilolite	53	35
Fe_2O_3	3.60	2.08	Mordenite	40	15
CaO	3.46	3.19	Montmorillolite	–	30
Al_2O_3	13.01	12.17	Others[b]	7	20
MgO	0.78	0.77			
Na_2O	–	1.53			
K_2O	0.53	1.20			
IW[a]	10.50	11.02			

[a] Ignition wastes.
[b] Others: calcite, feldespate and quartz.

The use of the zeolite anaerobic fluidized bed digester for treatment of landfill leachate has also been researched (Turan et al., 2005). COD removals of up to 90% were achieved at OLRs as high as 18 g COD/(L day) after 80 days of operation. A good biogas production yield (Y_{gas}) of 0.53 L biogas per gram of removed COD with a methane (CH_4) content of 75% was obtained. The attached biomass concentration increased along the column height from bottom to top, and its mean value was found to be 6065 mg/L after 100 days of operation.

6. The role of zeolite in other reactor configurations and processes

6.1. Zeolite and sludge granulation

Most theories on granulation confirm that the acetotrophic methanogen *Methanosaeta* plays a key role therein. Some believe that *Methanosarcina* clumps enhance granule formation (Hulshoff Pol et al., 2004). The only theory that states that other organisms cause granulation is the Cape Town Hypothesis, which is based on the excessive ECP (extracellular polymers) production of the *Methanobacterium* strain *AZ* under conditions of high H_2-partial pressures, unlimited ammonium and cysteine limitation. There is considerable consensus that the initial stage of granulation is bacterial adhesion (a physical–chemical process) parallel to the early stage of biofilm formation (Hulshoff Pol et al., 2004). However, treating bacterial adhesion as a mere physico-chemical process limits explaining its complexity. Bacteria are not made up of a sharp surface boundary, simple geometry or a uniform molecular surface composition. In fact, internal chemical reactions can lead to changes in molecular composition both in the interior and on the surface, and molecules and ions may cross the bacterium/water surface and these processes continue after adhesion. In any case, this physico-chemical approach is valuable in that it forms a framework in which biological factors can be added to form a unifying theory of granulation (Hulshoff Pol et al., 2004).

Although much attention in granulation theories is given to the conditions affecting bacterial adhesion, the selective wash-out of disperse sludge, resulting in an increased growth of retained (heavier) sludge agglomeration is more crucial for the granulation process. In this light, the presence of inert particles serving as surfaces on which bacteria can adhere is clearly advantageous. Nevertheless, the particles should be extremely settleable, otherwise unwanted sludge wash-out may occur (Rough et al., 2005).

A typical example of the use of zeolite in granulated bed reactors is the anaerobic expanded micro-carrier bed (MCB) process, in which fine zeolite (50–100 μm) support materials were used as expanded bed media (Yoda et al., 1989). This reactor configuration was capable of cultivating granular sludge similar to that formed in an upflow anaerobic sludge blanket (UASB) process. Specifically, two laboratory-scale MCB reactors were studied with VFA and glucose wastewaters to clarify the role of the micro-carrier and the influence of substrates on granular sludge formation. Granular sludge 1.0–2.0 mm large was found after a time of 20 days, *Methanotrix* being the predominant bacteria observed. Based on these results, a scale-up model with a reactor volume of 800 L was successfully operated using molasses wastewaters to demonstrate the feasibility of granular formation in the MCB process (Yoda et al., 1989).

In the same way, this MCB process with fine particles of zeolite as expanded bed media to enhance granular sludge formation, was also applied for the treatment of a wastewater from a brewery yeast processing plant (Yoda et al., 1991). Based on the results of the pilot study, in which 97% to 99% COD removals were maintained at 13 to 24 kg COD/(m^3 day), a full-scale MCB plant with a total reactor volume of 985 m^3 was constructed at Asahi's Koganei plant. Cobalt and nickel were found to be deficient in the wastewater and had to be supplemented during the start-up of the full-scale plant. However, sufficient granular sludge was cultivated so that the reactor could accept the design loading within 3 months of operation and achieve average COD removal of 93.5% at 9.8 kg COD/(m^3 day). Thus, it was clearly demonstrated in the full-scale installation that the MCB process could provide a reliable and predictable way to cultivate granular sludge necessary for efficient anaerobic treatment (Yoda et al., 1991).

6.2. Zeolite in the Anammox process

The removal of the nitrogen present both in municipal and industrial wastewaters (basically as ammonium) is conventionally carried out by means of nitrification and denitrification processes. This procedure is suitable for the treatment of wastewaters with a high ammonia content and rich in biodegradable carbon, but is expensive for the treatment of wastewaters with low carbon to nitrogen (C/N) ratios, such as effluents derived from anaerobic sludge digestion (Fernández et al., 2008a). The treatment of these effluents involves important amounts of dissolved oxygen for nitrification and the addition of an external source of organic matter for the denitrification step, with the consequent increase in operational costs. The use of a combined system made up of a process of partial nitrification of ammonium to nitrite and the Anammox (anaerobic ammonium oxidation) process leads to a reduction in costs (Furukawa et al., 2009; Strous et al., 1999).

In the Anammox process, ammonium (NH_4^+) is anaerobically utilized as an electron donor for the reduction of nitrite (NO_2^-), yielding nitrogen gas (N_2) as the final product (Boumann et al., 2009). The bacteria capable of performing this biochemical reaction were initially identified in wastewater treatment systems, but have now also been detected in various oxygen-limited fresh water and marine ecosystems. Today, anammox bacteria play a key role in the low-cost and environmentally friendly removal of ammonium in wastewater reactors and sewage treatment. They belong to the *Planctomycetales* order and form a distinct phylogenetic cluster composed of the genera *Candidatus* “Kuenenia”, *Candidatus* “Brocadia”, *Candidatus* “Scalindua”, *Candidatus* “Jettenia” and *Candidatus* “Anammoxoglobus propionicus” (Boumann et al., 2009).

The application of the Anammox process is limited because of its long start-up periods due to the very low growth rates and biomass yields of the microorganisms involved (Boumann et al., 2009; Fernández et al., 2008a). Minimizing the wash-out of biomass from the reactor by improving its retention becomes critical when biomass with long duplication time (0.003 h^{-1}) is used (Strous et al., 1998). In order to reduce the duration of the start-up period and provide better conditions to implant the Anammox process at industrial scale, improvements in biomass retention are needed. In reactors where biomass grows in the form of biofilms or granules, the formation of compact aggregates increases the settling velocity of the biomass and improves its retention and the amount of biomass growing in suspension is minimized (Boumann et al., 2009). In this respect, the addition of zeolite particles as support material in reactors containing suspended biomass seemed to be very effective in promoting the retention of the anaerobic biomass (Lahav and Green, 2000; Lee et al., 2001). Recently some researchers (Fernández et al., 2008a) have demonstrated that zeolite particles improve the operation and performance of the Anammox process. To be precise, the use of zeolite particles (clinoptilolite) 0.5–1.0 mm big as carrier material for Anammox biofilm formation has been reported, which allowed the reduction of the biomass wash-out in the effluents to values as low as 3 mg VSS/L. As a consequence, the biomass concentration increased significantly inside this reactor. In addition, the specific anammox activity (SAA) of the biomass was also enhanced increasing from 0.35 up to 0.50 g N/(g VSS day) (Fernández et al., 2008a). This approach allows biomass retention to improve and could be a good strategy for the application of the Anammox process in low salinity wastewaters.

6.3. Zeolite in anaerobic moving-bed biofilm reactors

The moving-bed biofilm reactor (MBBR) is a highly effective biological treatment process that was developed on the basis of a conventional activated sludge process and a fluidized-bed reactor. It is a completely mixed and continuously operated biofilm reactor, where the biomass is grown on small carrier elements that have a slightly lighter density than water and are kept in movement along with a water stream inside the reactor. The fluidization inside the reactor can be caused by a mechanical stirrer in an anaerobic reactor (Chen et al., 2008). Over the past few years, this reactor has been successfully used for the treatment of many industrial effluents. Researchers have proven that MBBR possesses many excellent characteristics such as high biomass, high COD loading, strong tolerance to loading impact, is a relatively smaller reactor and has no sludge bulking problems (Borghei and Hosseini, 2004; Im et al., 2001; Johnson et al., 2000).

The performance of a MBBR system with an anaerobic–aerobic arrangement has recently been reported as treating landfill leachate for simultaneous removal of COD and ammonium. This reactor contained an organic polymer (high density polyethylene) as biomass carrier which was mixed with nano-sized zeolite, which was used to enlarge the surface area and roughness of the carrier for better microorganism accommodation (Chen et al., 2008). It was found that the anaerobic MBBR played a major role in COD removal due to methanogenesis, and the aerobic MBBR acted as a COD-polishing and ammonium removal step. The contribution of the anaerobic MBBR to total COD removal efficiency reached 91% at an OLR of 4.1 kg COD/(m^3 day), and gradually decreased to 86% when the OLR feed was increased to 15.7 kg COD/(m^3 day). Because of the complementary function of the aerobic reactor, the total COD removal efficiency of the system showed a slight decrease from 94% to 92% even though the OLR feed was increased from 4.1 to 15.7 kg COD/(m^3 day). HRT had a significant effect on NH_4^+–N removal; more than 97% of the total NH_4^+–N removal efficiency could be achieved when the HRT of the aerobic MBBR was more than 1.25 days. The anaerobic–aerobic system had a strong tolerance to shock loading. A decrease in COD removal efficiency of only 7% was observed when the OLR was increased by 4 and shock duration was 24 h. The system could recover the original removal efficiency in 3 days. The average sludge yield of the anaerobic reactor was estimated to be 0.0538 g VSS/g $COD_{removed}$ (Chen et al., 2008).

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