Assessment of a UASB reactor with high ammonia concentrations: Effect of zeolite addition on process performance

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ABSTRACT

The UASB process for wastewater treatment has been extensively studied, but the use of zeolite to improve UASB reactor performance has rarely been explored. In this study, a UASB reactor modified with natural zeolite operating at high nitrogen concentrations (0.5 g/L, 0.7 g/L and 1 g/L) was evaluated. Two laboratory bioreactors, one with zeolite and one without, were operated at ambient temperatures ranging between 18ºC and 21°C. The experimental phase had a start-up period of 21 days. In the reactor with zeolite, the pH was found to be between 7.9 and 9.1, with a COD removal efficiency of about 60% after 80 days of operation at ammonia concentrations of between 0.229 and 0.429 g/L in the effluent. In the reactor without zeolite, the pH was between 8.3 and 9.3, and the COD removal efficiency was about 40% at ammonia concentrations between 0.244 and 0.535 g/L in the effluent. The addition of zeolite also decreased the volatile suspended solids (VSS) concentration in the effluent, generating a biomass with larger granules and higher settling rates as compared to a UASB reactor without zeolite. Taking the lower ammonia concentration, the higher COD removal and the improved granulation into account, it can be concluded that natural zeolite positively influenced the behavior and performance of the UASB reactor operating with high nitrogen concentrations.

Keywords: ammonia, UASB, zeolite, granulation, COD removal.

1. INTRODUCTION

Many industries generate liquid residues which, besides containing biodegradable organic matter, contain nitrogen concentrations that can frequently pollute the water course receptors [1-3]. Nitrogen is found in its different forms in wastewaters [4-7]. It is a by-product of industrial processes, mainly from the fertilizer, food, agricultural and livestock industries [8].

It is well-known that one form of nitrogen, ammonia, has an inhibitory effect on anaerobic digestion. Recently, Yenigün and Demirel [9] presented a review on this subject, showing that above threshold concentrations ammonia is a powerful inhibitor in an anaerobic digester and can easily cause process instability which is identified by a decrease in both biogas and methane yields. This can eventually lead to reactor failure. Ammonia is produced by the biological degradation of the nitrogenous matter, mostly from proteins and urea. Several mechanisms for ammonia inhibition have been proposed, such as a change in the intracellular pH, an increase in energy maintenance requirements, and the inhibition of a specific enzyme reaction [9]. Ammonium ion (NH_4^+) and free ammonia (FA) (NH_3) are the two principal forms of inorganic ammonia nitrogen in aqueous solution. It has been suggested that FA is the main cause of inhibition since it is freely membrane-permeable. The hydrophobic ammonia molecule may diffuse passively into the cell, causing proton imbalance, and/or potassium deficiency [9]. Salerno et al.[10] showed the inhibitory effect of ammonia on hydrogen production at a concentration of 2 g N/L. Sossa et al.[11] studied the effect of ammonia on the specific methanogenic activity (SMA) in a biofilm enriched with methyalminothropic methane-producing *Archaea*, showing that inhibition appears at ammonia concentrations above 148.8 mg/L. Calli et al. (2005a) [12] showed that propionate-degrading acetogenic bacteria are more sensitive to ammonia than *Archaea*, while Calli et al. (2005b) [13] compared the ammonia inhibition of UASB, upflow filters and hybrid reactors treating landfill leachates, and concluded that anaerobic filters and hybrid reactors were more efficient. The latter study showed that UASB reactors can be improved if ammonia inhibition can be decreased.

The use of natural zeolites to decrease the ammonia level in wastewater has been studied, showing the effectiveness obtained by including zeolite in the reactor [14]. Cintoli et al. [15] used natural zeolite for the pre-treatment of piggery wastewater, and in so doing decreased the concentration of ammonia from 1,500 to 300 mg/L, which in turn reduced the toxicity towards the anaerobic microbial population, thus improving the performance of a UASB reactor treating this waste. Milan et al. [16] studied the application of zeolite in the range of 0.2–10 g/L in batch anaerobic digestion of piggery waste, achieving the best results at doses of 2–4 g/L, while Kotsopoulos et al. [17] found that at zeolite doses of between 4 and 12 g /L, with an optimum dose of 4 g/L, both methane production and volatile solids removal were significantly higher compared to the control in the thermophilic anaerobic digestion of pig waste. Milan et al. [16] also found that zeolite reduces the concentration of both ammonia and ammonium ion which are produced during anaerobic degradation of proteins, aminoacids and urea.

The UASB reactor is an ideal anaerobic process for organic matter removal, but to achieve the best results, preventing the removal of the microbial granules from the reactor is paramount [18]. In the light of this, the presence of inert particles such as zeolite, serving as surfaces to which bacteria can adhere, is clearly advantageous. Scanning electron microscopy (SEM) showed that unmodified natural zeolite is made of rounded particles with an irregular rough surface and a sandy appearance [19]. Numerous irregularities contributing to the increase of its surface area were observed. This is an advantage to the anaerobic process because these irregularities can increase the colonization and immobilization of the microorganisms in the support medium. This study also reveals that the anaerobic populations immobilized on zeolite can provide a specific enzymatic activity as an addition to the natural consortium activities, e.g. hydrolytic activity to increase recalcitrant biomass degradation, thus resulting in higher methane yields in batch-culture experiments [19, 20].

A typical example of the use of zeolite in a granulated bed reactor is the anaerobic expanded micro-carrier bed (MCB) process, in which fine zeolite (50-100 μm) support materials were used as expanded bed media [20]. This reactor configuration was capable of cultivating granular sludge similar to that formed in an UASB process. Specifically, two laboratory-scale MCB reactors were studied with volatile fatty acids (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 in size was found after 20 days, *Methanotrix* being the predominant bacteria observed [20]. 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.

The feasibility of using natural zeolites as support media for immobilizing microorganisms in different high-rate reactor configurations has been pointed out [20]. It would appear that the modification of a UASB with zeolite as biofilm support is an interesting means for the improvement of performance within the UASB. Furthermore, in reactors where biomass grows in the form of biofilms or granules, the formation of compact aggregates increases the sedimentation rate of the biomass and improves its retention, which leads to the amount of biomass growing in suspension being minimized [21]. In this respect, the addition of zeolite particles as support material in reactors containing suspended biomass seemed to be a very effective way to promote the retention of the anaerobic biomass [22, 23]. More recently, researchers have shown that zeolite particles also improve the operation and performance of the Anammox process [24], autotrophic denitrification [25] and sewage treatment [26]. However, the use of zeolite in the treatment of wastewater using the UASB reactor at high ammonia concentrations has not been reported to date.

Keeping this in mind, a study was made of the performance of UASB reactors modified with natural zeolite in the presence of high amounts of ammonia. Characteristics such as COD removal, ammonia elimination, formation of granules and sedimentation rate were also studied and evaluated.

2. MATERIALS AND METHODS

2.1. Equipment

Two UASBs consisting of two plastic acrylic cylindrical columns labelled R-1 and R-2 without zeolite and with zeolite, respectively, were used. Each reactor was composed of a cylindrical section in which the anaerobic process took place, and a decantation section located at the top of the reactor. The change in column diameters was achieved by a truncated cone situated at the top of the cylindrical section. Figure 1 shows a schematic diagram of the UASB reactor used including all dimensions. The larger diameter determined a decrease in fluid velocity, which facilitated the settling of the support particles. A liquid–gas separator was placed at the top of the decantation section in order to guarantee the separation of the solid, liquid and gas fractions.

2.2. Characteristics of the zeolite and inoculum used

The chemical composition (% w/w) of the zeolite used was 66.62% SiO_2, 12.17% Al_2O_3, 2.08% Fe_2O_3, 3.19% CaO, 0.77% MgO, 53% Na_2O, 1.20% K_2O and 11.02% residue on ignition. Its mineralogical composition was 35% clinoptilolite, 15% mordenite, 30% montmorillonite, and 20% others (calcite, feldespate and quartz). Other characteristics of the zeolite used were: framework density (FD) 20.6 tetrahedral atoms (T-atoms) per 1000 Å^3, 32.03% porosity, and grain density (ρ_A) 2.12 g/cm^3. The zeolite particles used in UASB reactor R-2 were 1 mm in diameter.

Each reactor was inoculated with 1,250 mL of methanogenically active biomass from an anaerobic sludge digester processing sewage sludge located at “La Farfana” treatment plant in Santiago, Chile. The inoculum had a concentration of volatile suspended solids (VSS) of 76 g/L.

2.3. Characteristics of the wastewater

Table 1 shows the main characteristics of the substrate used in the experiments. The main difference in the synthetic wastewater used throughout this study was the inlet nitrogen concentration used, which varied between 0.5 and 1 g/L.

2.4. Start-up of the UASB reactors, acclimatization stage and experimental procedure

A mixture of 900 mL of the previously dried zeolite and 1,250 mL of inoculum was homogenized and poured into the top of reactor R-2, completing the missing volume with the synthetic influent with the lowest nitrogen load (0.5 g/L). Similarily, in reactor R1 without zeolite, 1,250 mL of inoculum were added to the reactor and the volume was completed with the synthetic influent with the lowest nitrogen load (0.5 g/L). To favor the formation of granules, the reactors were allowed to decant for one day and were then operated at a rate of 0.25 m/h with full recirculation for two days. On the fourth day the complete recirculation was maintained at the rate of 0.25 m/h for three weeks. The organic load rates (OLRs) and hydraulic retention times (HRTs) of this stage are shown in Table 2. After this acclimation stage, sets of experiments were carried out in continuous mode as shown in Table 2.

The change from one experimental condition to another was made after the steady state of the previous condition had been reached, which was assumed to have taken place after a period equivalent to 15 times the HRT values, and also when several parameters remained almost constant. Once the steady state was reached, triplicate samples were taken three times a week from the influent and effluent of each UASB. The steady-state value of a given parameter was taken as the average of these consecutive measurements for that parameter when the differences between the observed values were less than 5% in all cases.

2.5. Chemical analysis and calculations

The samples were analyzed to determine COD, BOD, alkalinity, pH and solids according to the Standard Methods for the Examination of Water and Wastewater [27]. Specifically, COD and BOD were determined according to the standard methods 5220 and 5210, respectively. Ammonia nitrogen and pH were determined by selective electrodes. The Stat graphics plus 5.0 program was used for processing the experimental data.

In order to compare the effect of zeolite on alkalinity, parameter α, which relates the partial alkalinity with total alkalinity, was calculated as follows:

$$\alpha = \frac{\text{Partial alkalinity (as CaCO}_3\text{)}}{\text{Total alkalinity (as CaCO}_3\text{)}} \qquad (1)$$

Alkalinity was determined by titration using 0.1 N HCl (or another strong acid) at two equivalent points:

- pH 5.75 or partial alkalinity.
- pH 4.3 or total alkalinity.

The fluidization potential of the sludge bed was evaluated by measuring particle size distribution, and calculating the sedimentation rate from these data [28]. The sedimentation rate of a spherical particle can be estimated as follows:

$$V_p = \sqrt{\frac{4g(\rho_s - \rho)d_p}{3C_d\rho}} \qquad (2)$$

where

V_p = terminal sedimentation rate of particles.

d_p = particle diameter, m.

ρ_s = solid particle density, kg/m^3.

ρ = liquid medium particle density, kg/m^3.

C_d = drag coefficient.

g = gravitational acceleration, m/s^2.

The density of the solid particles was measured experimentally according to:

$$\rho_s = \rho_w \cdot x_w + \rho_s \cdot x_s \qquad (3)$$

where x is the weight/weight percentage, and the subscripts w and s refer to water and dry solid, respectively. The solid particle diameter was calculated from

$$d_p = \frac{1}{\sum_{i=1}^{n} \frac{x_i}{d_{p,i}}} \qquad (4)$$

where

x_i = weight fraction of the mass retained by sieve “i” in relation to the sample's total mass.

$d_{p,i}$ = average of the opening of the upper sieve and that of the sieve on which mass m was retained.

To calculate the particle diameter, the mean surface diameter or Sauter diameter was used, which represents the diameter that a hypothetical particle with the same volume to surface area ratio as that of the sample's whole volume and whole surface would have. The Sauter diameter concept is usually the one most commonly used because it relates better to processes in which friction between the fluid and the particle's outer surface are important [29]. Values of x_i and $d_{p,i}$ were based on the total suspended solids (TSS) obtained by sifting, i.e., the total mass present on the sieves, which means the biomass plus the retained residual water for the reactor without zeolite, and for the reactor with zeolite, the biomass, the retained residual water and the zeolite. This happens because if fluidization occurs, since we are dealing with a solid-liquid system, it takes place homogeneously, implying a rise of the biomass to the upper part of the reactor. The opening or size of the sieves 1, 2, 3, 4 and 5 (bottom) used in this study were 2, 1, 0.65, 0.25 and 0 mm, respectively.

The particle distribution of the inoculum was 2444, 3886, 4926, 13814 and 81242 mg TSS/L on the sieves 1, 2, 3, 4 and 5 (bottom), respectively.

The C_d for various particles is a function of the Reynolds number:

$$C_d = \frac{24}{\mathrm{Re}_p} + \frac{3}{\sqrt{\mathrm{Re}_p}} + 0.34 \qquad (5)$$

The Reynolds number, Re, for sediment particles is defined as

$$\mathrm{Re}_p = \frac{V_p d_p \rho}{\mu} \qquad (6)$$

where μ is the viscosity of the liquid medium. Knowing the values of d_p, the values of V_p can be obtained by successive iterations.

3. RESULTS AND DISCUSSION

3.1. Start–up period

The start-up period of the reactors lasted a total of 21 days. During this stage the reactors operated at an organic loading rate of 6 kg COD/m^3 d. Although that loading rate is twice the recommended one [30, 31], the reactor was started up in a shorter time than that estimated theoretically, due to the system characteristics. According to Pol and Lettinga [32] (Table 3), a granular sludge operating at 20ºC with 50% inhibition takes approximately 72 days to reach a volumetric loading rate of 15 kg COD/m^3 d, starting from an initial sludge concentration of 10 g VSS/L, under conditions of 100% contact and 0% dragging. These conditions approach those existing in the tests made in the present study. It should be noted that the volumetric loading rates achieved in the present study were 12 and 18 kg COD/m^3 d, therefore the difference with the 15 kg COD/m^3 d load of Table 3 is less than 20%. The sludge comes from an anaerobic domestic sludge digestion plant, but due to the short start-up time, its performance is close to that of a granular sludge, as shown in Table 3. With respect to particle dragging, because of the start-up technique used during the first 72 hours (1 day of decantation and 2 days of complete recirculation), particle drag is less than 50%.

In spite of the high influent nitrogen concentration and the low hydraulic retention time, the start-up time was short compared to the values reported in Table 3. This can be explained by the amount of inoculum used. Table 3 is the result of an initial inoculum concentration of 10 g VSS/L. The inoculum concentration of 35.21 g VSS/L at the beginning of the experiments as presented in this paper may have decreased the start-up time. This is in line with Vadlani and Ramachandran's proposal [30] – they used a large amount of initial inoculum (40% of the reactor's volume), which improved the start-up of the UASB reactor. These authors also demonstrated that the presence of non-active biomass delayed the start-up operation of UASB reactors [30]. In addition, the fact that the carbon source was glucose may have had an influence on this relatively fast start-up because glucose is easily dissociated in an aqueous medium, facilitating the availability of carbon to the microorganisms.

To confirm that all the stable operating conditions had been reached, COD and ammonia concentrations were measured in the effluents of both reactors for one week, and the results shown in Figure 2. As can be seen, there were no significant variations of those values in the analyzed time period. In particular, there were no variations in the ammonia concentrations of the two reactors during this stage.

3.2. Effect of zeolite on the removal of ammonia and COD

The evolution of the concentration of ammonia and COD in the effluent of the reactors is shown in Figure 3. On average, the study was made at a nitrogen concentration 10 times greater than that considered inhibitory [9, 33], with COD/N ratios of between 1 and 2, with the boundary value below which the inhibition process is started at 15. Figure 3 shows that in the reactor with zeolite there is approximately 25% less ammonia than in the reactor without zeolite, a difference that is achieved at upflow velocities of 0.75 m/h. This is due to the cation exchange ability of zeolite, which consists in the exchange of ammonium nitrogen (NH_4^+) from the medium for one of its own cations, mainly Ca^{2+} and Na^+ [20]. As there is less total nitrogen in the medium, the amount of ammonia formed is less, and this affects the other control parameters. With respect to the stage at 0.5 m/h (days 21-59), the performance of the reactor was more unstable, because a sustained increase of ammonia was observed in both reactors. The above is associated with the change of pH that takes place in the liquid phase of the reactor (Figure 4B), since as the pH of the medium is increased, the chemical equilibrium of the NH_3-NH_4^+ couple favors the formation of NH_3, increasing N content as ammonia. Therefore, as the nitrogen load increased, the pH increased and so did the N in the form of NH_3. Recent batch anaerobic digestion experiments of swine manure with 10% total solids and 60 g/L of zeolite addition revealed simultaneous K^+ and ammonium (NH_4^+) (580-600 mg/L) adsorptions onto zeolite particles, which contributed to an increase of 20% in the biogas yield, resulting in alleviated inhibition effects of ammonium on acidogenesis and methanogenesis [34].

With respect to the variation of COD in the effluent as a function of the upflow velocity (Figure 3B), it was observed that the COD concentration in the reactor with zeolite is approximately 40% the inlet COD concentration (60% removal) for both operating conditions (upflow velocities of 0.5 and 0.75 m/h), while the reactor without zeolite achieves only 30% removal in the first stage (0.5 m/h) and 40% COD removal in the second stage (0.75 m/h). In addition, a greater COD removal at higher organic loads applied has been observed. This behavior is explained by the greater formation of granules and the less significant loss of biomass in the second stage (Figures 5 and 6).

The lower COD removal efficiency achieved in this study with respect to that obtained in other studies [35, 36] can be accounted for by various factors:

- Working temperature: the optimum working temperature for an anaerobic reactor in the mesophilic range is 35ºC - 37ºC. In the present work the operating temperature of the reactors was approximately 20ºC, which can be considered as an average ambient temperature although it is far from the optimum mesophilic temperature. However, the removal efficiencies obtained were of the same order of magnitude as those reported at temperatures close to 20°C. For instance, Esparza-Soto et al. [37] achieved efficiencies between 60% and 79% working at temperatures of 17ºC to 18°C. Syutsubo et al., 2011 [38] also observed a considerable decrease in the TSS and BOD removal efficiencies (lower than 60%) during the continuous operation at ambient temperature (16ºC-29ºC) in a pilot-scale UASB reactor for sewage treatment at an HRT of 9.7 h when the sewage temperature dropped to 20ºC.

- Low hydraulic retention time (HRT): this factor is perhaps the parameter that has the greatest influence on the low efficiency in the elimination of organic matter. In fact, various researchers [39, 40] working at temperatures that varied between 13ºC and 25ºC achieved removals of COD between 70% and 90% in UASB reactors, but operating at HRTs of between 4.7 h and 7 days, more than twice those used in this study. Related to this parameter is the volumetric organic loading rate. Halalsheh et al. [41], operating a UASB of 96 m^3 for an extended period (2.5 years) found that for the operating temperature range of 18ºC – 25ºC, COD removal efficiencies between 51% and 62 % were obtained, but operating with moderate organic loads of between 2.9 and 5 kg/m^3d, more than three times lower than those used in this work.
- Ammonia concentration: when the COD/N ratio was analyzed, it was observed that the amount of nitrogen is approximately 10 times higher than the inhibitory limit, so the operation was carried out under conditions of possible inhibition according to previous reports [9, 11]. Specifically, these authors reported that the threshold inhibition concentration of free ammonia for anaerobic digestion is 100-120 mg/L [9].
- Increased pH: methanogenic cells have an optimum operating pH of between 6.8 and 7.2, while the pH of the reactors used in this work varied between 8.5 and 9, which could also contribute to the decrease in the removal efficiency. Some authors have recommended the control of the pH value of the influent, e.g. diluting some raw wastewaters, to ensure a free ammonia nitrogen concentration below the above-mentioned threshold inhibition value [9, 33].

Therefore, in spite of the system's extreme operating conditions, the COD removal efficiency of the reactor with zeolite approached 60%, indicating the robustness of this kind of zeolite-modified UASB reactor in the removal of organic matter.

3.3. Effect of zeolite on the variation of alkalinity and pH

Figure 4 shows the evolution of α and pH throughout the experiments. Figure 4A shows that the parameter α of both reactors remains without great variations in the measurements from day 28 through day 59, when they operated at an upflow velocity of 0.5 m/h. On day 60, which corresponds to the first measurement operating at 0.75 m/h, there was a slight decrease in alkalinity. This happened because a rise in the upflow velocity brings about an increase in the organic load entering the reactor, which aggravates the methanogenic archaea, since acidogenic bacteria, which have greater activity than methanogenic archaea, adapt more rapidly, increasing the amount of volatile fatty acids inside the reactor. It was also observed in all cases that α was close to 1 and always greater than 0.5 (the minimum recommended value) which indicates that in spite of the decrease on day 59, the reactors operated with good buffering capacity and consumption of the volatile fatty acids, showing an appropriate stability.

Figure 4B shows that the pH of the reactors with and without zeolite was very similar, reaching values close to 9, higher by 1.5 pH units than that of the influent. This can be explained by the hydrolysis of urea, which increases the ammonium ion levels, thereby increasing the pH. These higher levels of pH because of the increased urea loads was also reported by Sterling et al. [42], who found pH values between 8.2 and 9.0 in the effluent for nitrogen concentrations of 600 and 3,000 mg/L, respectively. Although the pH values in the reactors with and without zeolite differed by about 0.4 and 0.15 pH units, they tended to yield higher values in the reactor without zeolite, which is attributed to the nitrogen levels within. The decrease of nitrogen as NH_4^+ and NH_3 in the reactor with zeolite diminished the presence of this weak base, leading to smaller pH increases in the reactor with zeolite. Therefore, the addition of zeolite could reduce both NH_4^+ (by ion exchange delivering Mg^{2+}, Ca^{2+} and Na^+ to the digester liquor) and NH_3 (by adsorption of this species on the active areas of the material). Both processes were favorable for anaerobic digestion [16].

3.4. Effect of zeolite on the variation of VSS, TSS and sedimentation rate

Figure 5 shows the variation of VSS and TSS in the reactors with and without zeolite. As can be seen, the amount of VSS was approximately 80% of TSS, with the VSS consisting mainly of cells that were expelled from the reactor. It was observed that the reactor with zeolite released fewer solids than the reactor without zeolite under all the operating conditions studied. This happened because the zeolite increased the density of the sludge blanket ($\rho_{\text{sludge without zeolite}} = 1050$ kg/m^3, $\rho_{\text{sludge with zeolite}} = 1450$ kg/m^3) decreasing the particles dragged, and in addition favoring granulation. This was reflected in higher sedimentation rates calculated for the reactor with zeolite (Table 4), showing the improvement of the UASB reactor modified with zeolite in the decrease of the system's biomass loss. The values obtained for the densities of the granules agree with those reported by Vlyssides et al. [43], who point out that the densities of the granules can vary between 1,000 and 1,400 kg/m^3, depending on the system's VSS/TSS ratio. Since the VSS/TSS in the system with zeolite decreased, its density increased, coinciding with the behavior reported by Vlyssides et al. [43].

Table 4 shows the mean Sauter diameters in the reactors with and without zeolite, and the sedimentation rates at different operation times. As can be seen, except for day 28 the sedimentation rate of the reactor with zeolite was greater than that of the reactor without zeolite, and this can be attributed to the fact that the density of the sludge mantle of the reactor with zeolite was higher than that of the reactor without zeolite, requiring a higher velocity to drag it out of the reactor. Moreover, in most cases the reactor with zeolite had larger particles which also increased the sedimentation rate. The average granule size determined in both reactors coincides with the lower range of diameters determined elsewhere. Specifically, Bhunia and Ghangrekar [28] found diameters that varied between 0.25 and 3.03 mm, larger than those found in the present work. Fang et al. [44] working with phenolic wastewaters, found 1-2 mm granules, while Fang and Zhou [45] and Tay et al. [46] reported 0.5-3 mm granules, similar to Subramanyam and Mishra’s findings [47]. The lower values obtained in our work can be attributed to the high ammonia concentrations used in the assays [48]. With respect to the sedimentation rates, Table 4 shows that the values obtained in the reactor with zeolite were much higher than those obtained in the reactors without zeolite. This is attributed to the fact that the granule density obtained in the reactor with zeolite ($\rho_s = 1450$ kg/m^3) is 38% greater than that in the reactor without zeolite ($\rho_s = 1050$ kg/m^3). This difference can be attributed specifically to the use of zeolite, which decreases the VSS/TSS ratio and increases sludge density [46].

For the reactor without zeolite, the sedimentation rates found coincide with those expected for the diameters and densities obtained. Bhunia and Ghangrekar [28] indicated that for granules with densities of between 1,010 and 1,050 kg/m^3 (assuming that ρ_{water} = 1,000 kg/m^3), the rates varied between 2.5 and 25 m/h for diameters lower than 0.5 mm. Ghangrekar et al. [49] also obtained rates between 11.26 and 92.12 m/h under different loading rates (1.48 and 9.50 kg COD/m^3 d). Subramanyam and Mishra [47] also found sedimentation rates in the range of 30–75 m/h for granule diameters between 0.5 and 2.5 mm. The sedimentation rates in the reactor with zeolite are close to those obtained for much higher diameters, between 0.8 and 3 mm [28, 47]. A sedimentation rate of about 60 m/h is considered to be very good for the granular sludge [50], showing, therefore, that the use of zeolite improves the settleability of the sludge in a UASB reactor.

3.5. Effect of zeolite on granulation

Figure 6 shows the variation of granule size over time for the reactors with and without zeolite. For the reactor without zeolite (Fig. 6A), it was observed that for holes of 1 and 2 mm there was a small percentage of solids (less than 15%), and, therefore, a small number of granules reached diameters greater than 1 mm. The bottom plate contains biomass smaller than 0.25 mm, which corresponds to biomass that did not come to form granules. This biomass did not exceed 15% of the total, and it decreased as the experiment proceeded. On day 28 it was observed that the largest amount of VSS was on the 0.25 mm sieve and the second largest mass was on the 0.65 mm sieve. On day 80 the previous distribution was inverted, i.e., the largest VSS mass was at 0.65 mm and the second largest was at 0.25 mm. Furthermore, on day 80 the VSS concentration at 1 mm was slightly larger than on day 28. This shows that granule size in the reactor without zeolite increased with time, with its largest percentages (45% and 27%) between 0.65 and 0.25 mm diameter. It should be noted that even though the sifting was done gently to avoid breaking the granules, it is probable that some of the granules did break, slightly increasing the amount of VSS present in the smaller sieves. Despite this, it has been reported that a granulometry procedure based on manual humid sieving, as used in the present work, was an appropriate technique for determining the granule size distribution of UASB sludge, compared to other techniques (microscope sizing, image and laser analysis), which have the disadvantage of being tedious, imprecise or expensive and hardly ever applied in full-scale treatment plants [51].

With respect to the reactor with zeolite, Figure 6B shows a trend similar to that of the reactor without zeolite. For the 2 mm holes, it increased from 3% on day 28 to 7% on day 35, and then remains steady at around 5%. In the case of the 1 mm holes, it begins with a small amount of biomass, but as time goes by (between days 28 and 42), the amount of VSS increased suddenly, indicating an increase in granule size. The same behavior was observed for the 0.65 mm hole, which increased from 30% to 40% between days 28 and 81. For the 0.25 mm hole there was a gradual decrease in the number of granules in this size range, dropping from 42% on day 28 to 22% on day 80. Finally, for the bottom plate, values very similar to those obtained for the reactor without zeolite, between 22% and 5%, were found. This is due to biomass that did not become attached to (or came off) the zeolite, or biomass that became attached to very fine zeolite (with diameters of less than 0.25 mm that might have been included with the zeolite 1 mm in diameter). Therefore, it can be concluded that the granule size in the reactor with zeolite increased with time, with its highest percentages (40% and 27%) between 1 and 0.65 mm in diameter.

In general, both granulation processes were similar in the sense that in both reactors the amount of VSS in the larger holes increased to a stable value. However, in the reactor with zeolite the increase in granule size (increased amount of VSS in the larger holes) was displaced from the 0.65 and 0.25 mm holes to those of 1 and 0.65 mm, while for the reactor without zeolite the displacement occurred only from 0.25 to 0.65 mm. Therefore, in the reactor with zeolite larger granules were formed, due to the possible formation of biofilm over the zeolite [20]. It should be noted that in spite of the tendency seen in the growth of the granules, further growth may be possible as this phenomenon can take up to eight months [43, 52].

4. CONCLUSIONS

The modification of a UASB reactor by including natural zeolite improved its performance when treating synthetic waste water with a high nitrogen load. Natural zeolite reduced the reactor's pH by 0.4-0.15 pH units, decreasing the amount of ammonia in the reactor by up to 25%. It also increased the COD removal rate by 50% with respect to the reactor without zeolite.

The addition of zeolite decreased the amount of biomass removed from the reactor, generating a denser sludge blanket with larger granules and much higher sedimentation rates than those of a UASB reactor without zeolite operating under the same conditions.

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Table 1

Characteristics of the synthetic wastewater used in the study.

Synthetic wastewater (SWW)	Urea (g/L)	Nitrogen (g/L)	Potassium phosphate (g/L)	Glucose (g/L)	Chemical Oxygen Demand (COD) (g/L)	$NaHCO_3$ (g/L)
Assays 1 and 4	1.071	0.50	0.005	0.9375	1	1
Assays 2 and 5	1.607	0.75	0.005	0.9375	1	1
Assays 3 and 6	2.142	1.00	0.005	0.9375	1	1

Table 2

Operating conditions of the sets of experiments carried out including start-up.

Period (days)	Upflow velocity (m/h)	Hydraulic retention time (HRT) (h)	Organic load rate (OLR) (kg COD/m^3 d)	Nitrogen load rate (kg N/m^3 d)
Start-up: 0 – 20	0.25	4	6	3
Assay 1: 21 - 33	0.5	2	12	3
Assay 2: 34 - 46	0.5	2	12	9
Assay 3: 47 - 59	0.5	2	12	12
Assay 4: 60 - 72	0.75	1.33	18.05	9.02
Assay 5: 73 - 85	0.75	1.33	18.05	13.53
Assay 6: 86 - 100	0.75	1.33	18.05	18.05

Table 3

Minimum time (in days) to achieve a load of 15 kg COD/m^3 d assuming an initial sludge concentration of 10 g VSS/L.[32]

Kind of inoculum	Activity (g COD-CH_4/g VSS d)	Conditions	30ºC		20ºC	
			Without inhibition	50% inhibition	Without inhibition	50% inhibition
River sludge	0.05	Ideal	58	129	129	286
		50% drag	115	259	259	573
		50% drag and 50% contact	143	315	315	685
Cow dung	0.020	Ideal	44	101	101	230
		50% drag	88	202	202	461
		50% drag and 50% contact	116	258	258	573
Digested domestic	0.100	Ideal	27	69	69	166
		50% drag	55	138	138	331
		50% drag and 50% contact	83	194	194	443
Granular sludge	1.00	Ideal	4	22	22	72
		50% drag	8	44	44	145
		50% drag and 50% contact	36	100	100	257

Table 4

Granule diameters and sedimentation rates for the UASB reactors with and without zeolite.

	Reactor with zeolite		Reactor without zeolite	
Day	d_p (mm)	V_t (m/h)	d_p (mm)	V_t (m/h)
28	0.247	42.738	0.376	11.940
35	0.442	105.303	0.422	14.649
42	0.563	145.438	0.513	20.495
59	0.551	141.493	0.521	21.035
69	0.585	152.613	0.501	19.693
80	0.588	153.587	0.530	21.643

Figure Captions

Figure 1: Schematic diagram of the UASB reactor used including all dimensions.

Figure 2: Evolution of COD and ammonia concentration in the reactor effluents during start-up. Legends: ♦: COD with zeolite; ■: COD without zeolite; ▲: ammonia with zeolite; X: ammonia without zeolite.

Figure 3: Evolution of ammonia and COD in the effluents of the experimental runs carried out. A) Ammonia; B) COD. Legends in Fig. 3A: ♦: NH_3 SWW; ■: NH_3 with zeolite; ▲:NH_3 without zeolite. Legends in Fig. 3B: ▲: COD SWW; ♦: COD with zeolite; ■: COD without zeolite.

Figure 4: Variation of pH and α in the effluents of the UASB reactors. A) parameter α; B) pH. Legends in Fig. 4A: ♦: parameter α with zeolite; ■: parameter α without zeolite. Legends in Fig. 4B: ▲: pH SWW; ♦: pH with zeolite; ■: pH without zeolite.

Figure 5: Evolution of total suspended solids and volatile suspended solids in the effluents of the two UASB reactors assessed. Legends: ♦: TSS with zeolite; ■: TSS without zeolite; ▲: VSS with zeolite; X: VSS without zeolite.

Figure 6: Evolution of granulation over time. A) Reactor without zeolite; B) Reactor with zeolite. Legends in Fig. 6A: ♦: 2 mm; ■: 1 mm; X: 0.65 mm; *: 0.25 mm; ●: bottom. Legends in Fig. 6B: ♦: 2 mm; ■: 1 mm; ▲: 0.65 mm; X: 0.25 mm; ***:** bottom.

Figures

Figure 1

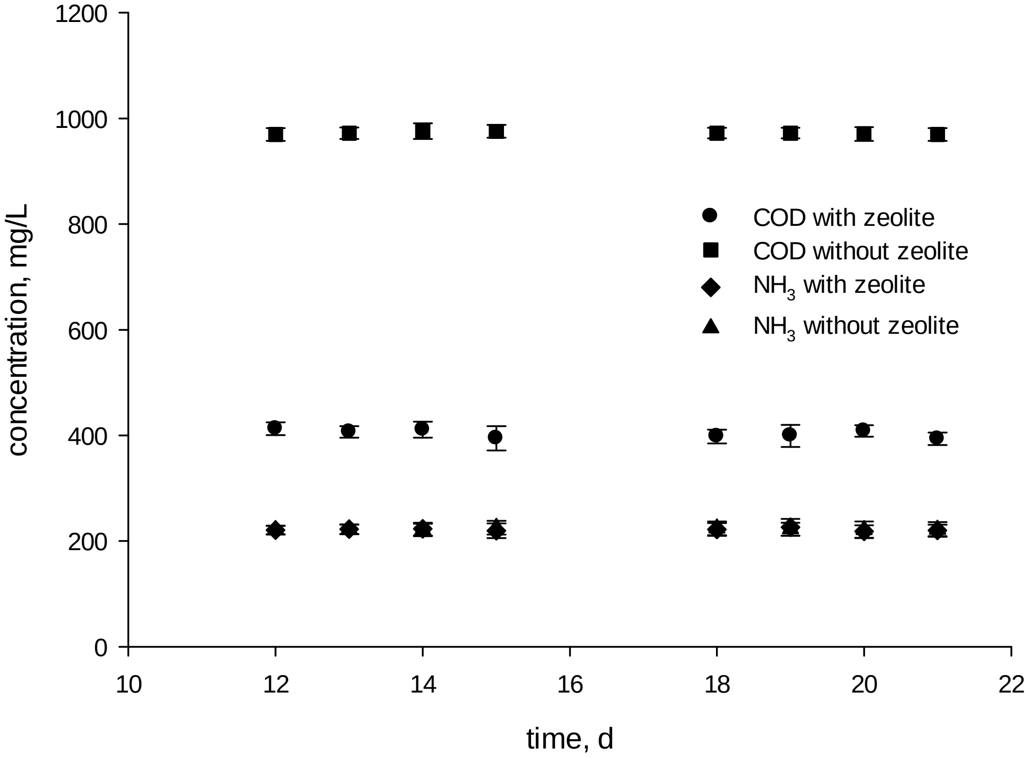
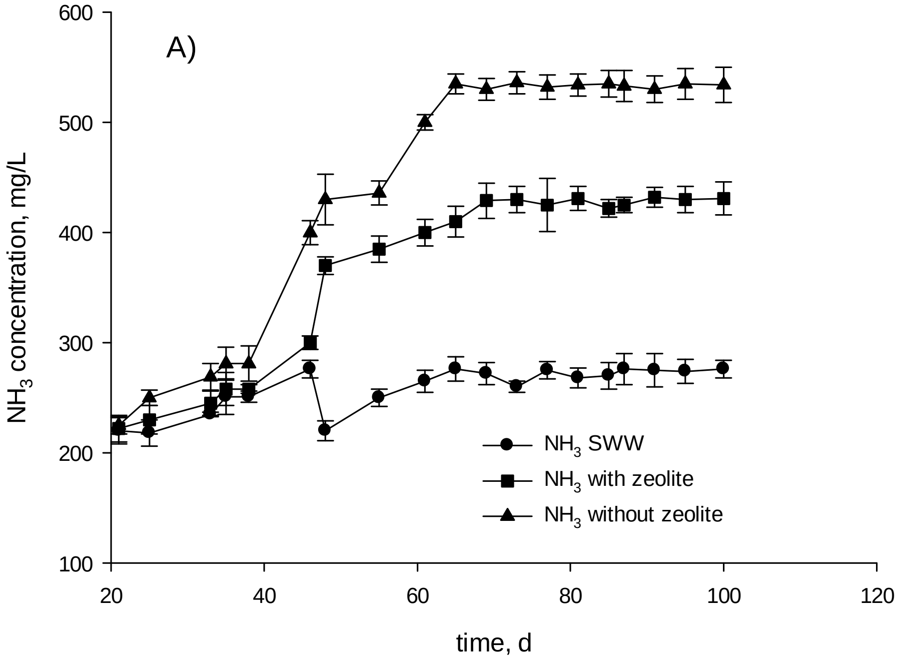


Figure 2


A)
NH$_3$ concentration, mg/L
600
500
400
300
200
100
20
40
60
80
100
120
time, d
NH$_3$ SWW
NH$_3$ with zeolite
NH$_3$ without zeolite

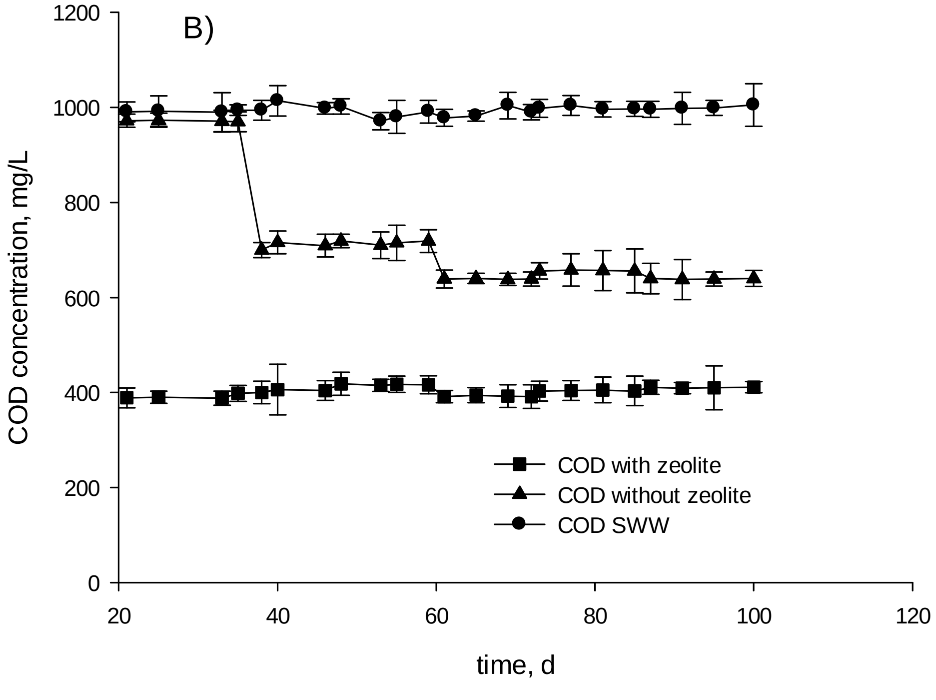

B)
COD concentration, mg/L
1200
1000
800
600
400
200
0
20
40
60
80
100
120
time, d
COD with zeolite
COD without zeolite
COD SWW

Figure 3

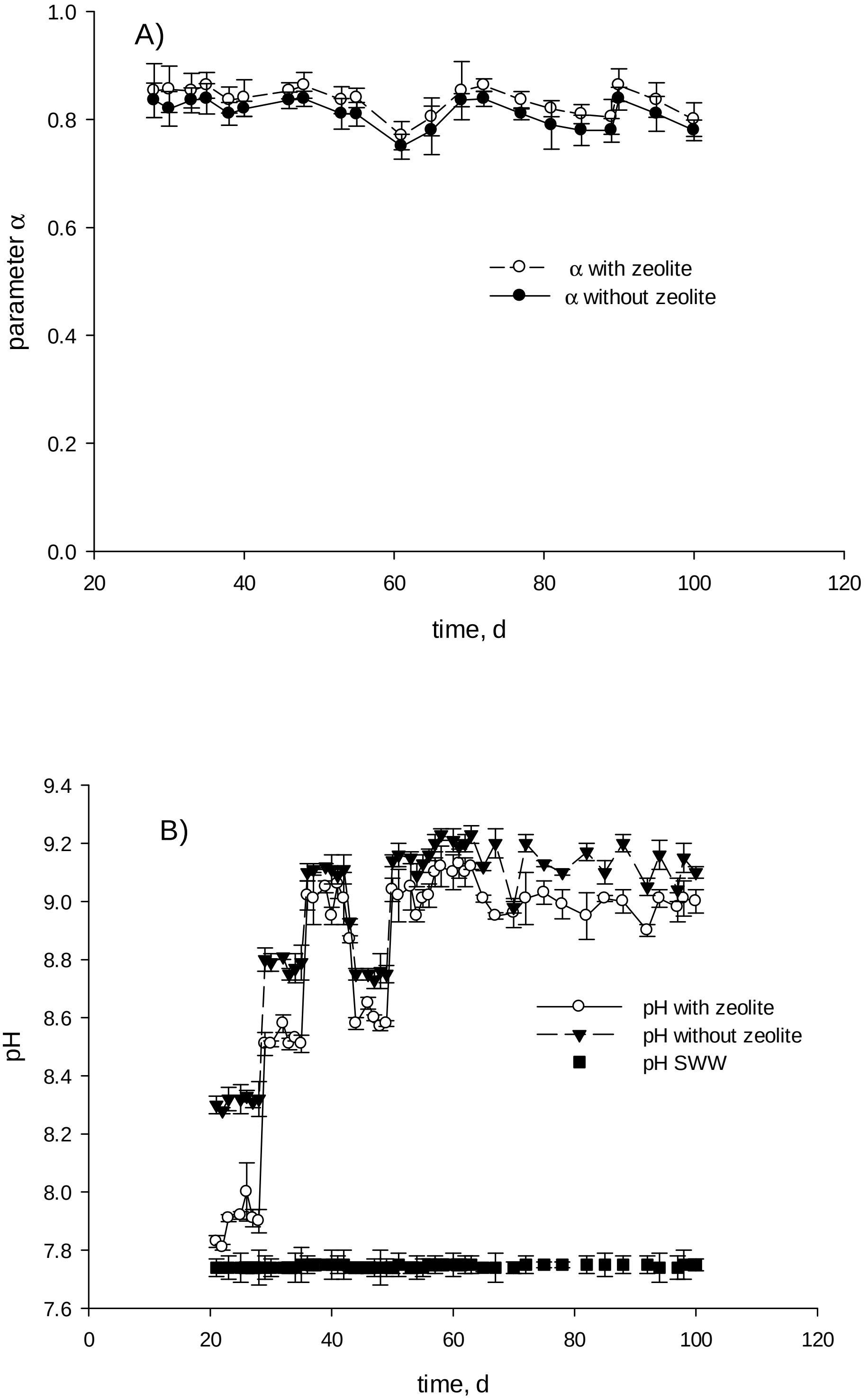

A)
parameter α
1.0
0.8
0.6
0.4
0.2
0.0
20
40
60
80
100
120
time, d
α with zeolite
α without zeolite
B)
pH
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
0
20
40
60
80
100
120
time, d
pH with zeolite
pH without zeolite
pH SWW

Figure 4

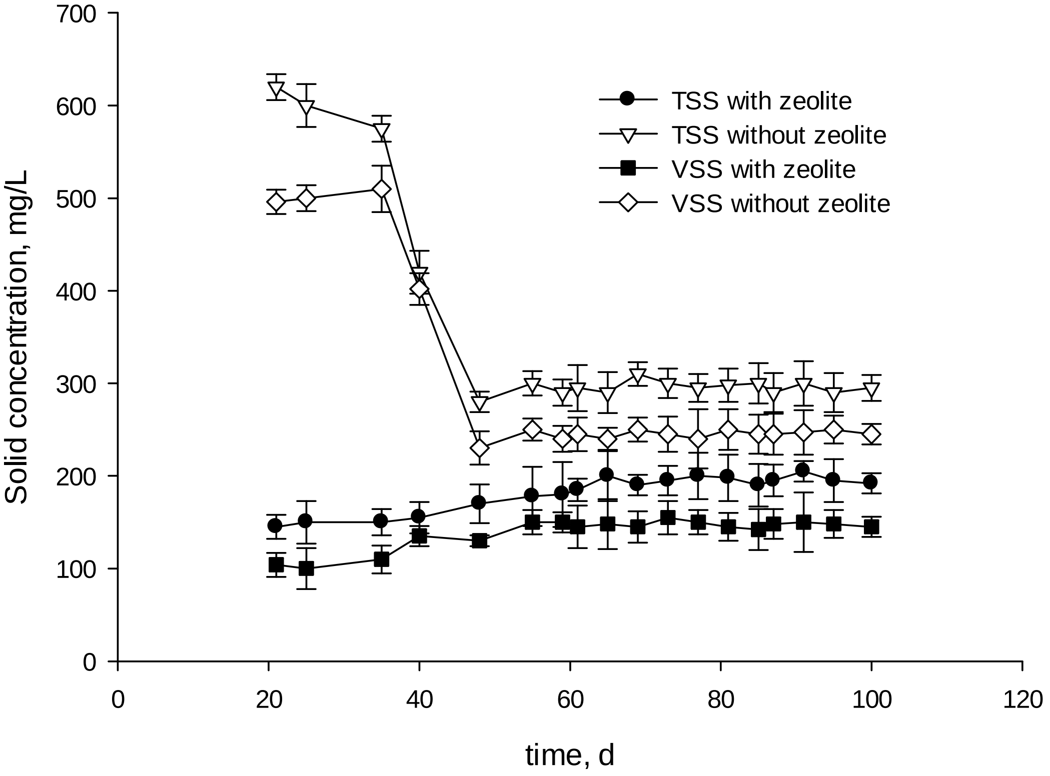
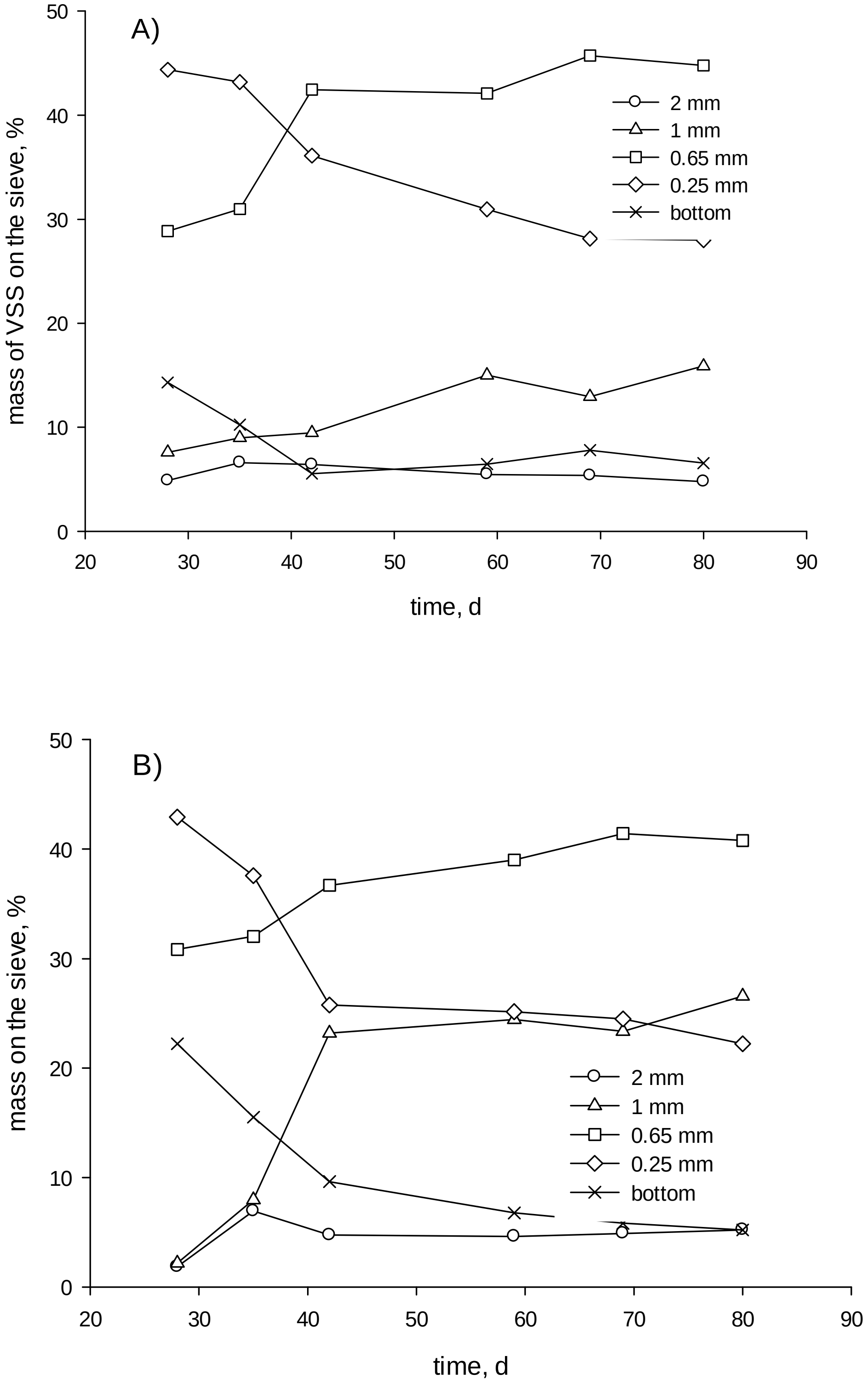

Solid concentration, mg/L
700
600
500
400
300
200
100
0
0
20
40
60
80
100
120
time, d
TSS with zeolite
TSS without zeolite
VSS with zeolite
VSS without zeolite

Figure 5


A)
mass of VSS on the sieve, %
time, d
0
10
20
30
40
50
20
30
40
50
60
70
80
90
2 mm
1 mm
0.65 mm
0.25 mm
bottom
B)
mass on the sieve, %
time, d
0
10
20
30
40
50
20
30
40
50
60
70
80
90
2 mm
1 mm
0.65 mm
0.25 mm
bottom