Metal Ion Inhibitors and Other Inorganic Toxicants in Anaerobic Biological Treatment Process of Industrial Effluents: A Critical Review

Dr. Mishu Singh

Department of Chemistry, Maharana Pratap Govt. P.G.College, Hardoi, UP, India

Abstract: ***Because of its manifold advantages over pollution control and energy recovery, the anaerobic digestion process is increasingly being used for treatment practice for industrial wastes. It is also advantageous over aerobic treatment for low sludge production and low energy requirements. However, process instability, low biogas yield, and the presence of inhibitory substances are the problems that often encounter in anaerobic digestion, preventing it from being widely applied. Anaerobic degradation is sensitive to toxicants and a wide range of inhibitory substances are the primary cause of anaerobic digester upset or failure since they are present in substantial concentrations in wastes. Extensive efforts were made over the years to identify them, their mechanism of toxicity and the controlling factors of inhibition in anaerobic digestion. In this review, we present a detailed and critical summary of research conducted on the inhibition of anaerobic processes by inorganic toxicants and heavy metals. The inhibitors commonly present in anaerobic digesters include ammonia, sulfides, various light metal and heavy metal ions***

Keywords: Anaerobic digestion, Inhibitors, metals, ammonia, sulphate

1. Introduction

Developing green and sustainable technology for the industrial effluent treatment is a very significant research area in this epoch of industrial and societal development. Phenol is one such major pollutant in the wastewater because of its presence in the effluent of major processing and refining plants. It has very severe short and long term effects on living beings. Phenol is used in different industries such as petrochemical, oil refinery, insecticides, resin, plastic, pharmaceutical, leather, textile and paper (Mohammad Javad et al 2015). The concentration of phenolic compounds in the effluents of these industries is varied between one and hundreds of milligrams per liter (Pan et al., 2008; Quintanilla et al., 2008). Phenolic compounds are classified as mutagenic, teratogenic, and carcinogenic compounds (Quintanilla et al., 2008). Due to their inhibitory effect on ecological systems. The United States Environmental Protection Agency (USEPA) has introduced these compounds as the priority pollutants (Chang et al., 1995; Rappoport, 2003). Phenol has its toxic effects on the life of fishes and consequently threatens aqueous environments above its concentration higher than 1 mg/L (Busca et al., 2008). Therefore, phenol-containing wastewater must be purified before its discharge into the water bodies and land.

Several physical, chemical, and biological methods were used for phenol removal (Karthik et al., 2008). However, phenol removal by the biological method is preferred over physical and chemical methods because of low risk and cost effective (Liu et al., 1996). Various treatment techniques are used for removal of the phenol from wastewater such as adsorption, photodecomposition, volatilization and other biological and non-biological methods. The conception of using biological treatment to remove phenol was first reported in the 1920s (Vipulanandan C et al, 1994). Since then there have been many reports that discuss the general design and operational guidelines for biological treatment of wastewater containing phenolic compounds. The existence of microbes capable of degrading phenolic compounds has been studied in laboratory experiments (Essa et al., 1997). In the light of current global consciousness of environmental sustainability, the anaerobic treatment method is regarded as a promising process and is widely used for the treatment of municipal sludge and limited application in the treatment of organic industrial wastes, including fruit and vegetable processing wastes, packing house wastes, and agricultural wastes (Parkin and Miller, 1983). Despite poor operational stability, preventing it from being widely commercialized (Dupla et al., 2004), anaerobic digestion offers several significant advantages, such as low sludge production, low energy requirement, and possible energy recovery (Ghosh and Pohland, 1974; van Staikenburg, 1997) including additional benefits such as a high degree of waste stabilization, more thorough eradication of viral & bacterial pathogens, and improved post-treatment sludge dewatering (Lo et al., 1985). Anaerobic digesters further contribute to reducing greenhouse gas emissions (L. Yu et al, 2008 ; M. Lantz et al, 2007 ; I. M. Buendía et al, 2009). Generation of nutrient rich digestate, which can be used as fertilizer (] M. Berglund et al, 2006; J. B. H. Nielsen et al, 2009; D. Botheju et al, 2007) is an added advantage. These merits of anaerobic digestion have led to a rapid growth of its application.

In anaerobic digestion, the acidogenic and methanogenic microorganisms differ widely in terms of physiology, nutritional needs, growth kinetics, and sensitivity to environmental conditions (Pohland and Ghosh, 1971). Instability in the reactor is often caused due to failure in maintaining the balance between these two groups of microorganisms (Demirel and Yenigu, 2002). Apart from this, a wide range of reasons has been reported to inhibit anaerobic treatment. Inhibitory substances are often found to be the foremost cause of anaerobic reactor upset and failure since they are present in significant concentrations in wastewaters and cause an adverse shift in the microbial population or inhibition of bacterial growth. Inhibition is usually indicated by a decrease in the steady-state rate of methane gas production and accumulation of organic acids (Kroeker et al., 1979). In the present study, an attempt is made to present the survey of the previous and current research on the inhibition of anaerobic processes by various organic and inorganic compounds, metal ions etc. focusing on their mechanisms of inhibition, the factors affecting inhibition, and problems encountered while operating waste treatment processes.

2. Inhibitors

Inhibition By Inorganic Toxicants

Study of anaerobic digestion shows considerable variation in the inhibition/toxicity levels reported for many organic and inorganic substances and some physical reasons. The major reason for these variations is the complexity of the anaerobic digestion process where the mechanism of acclimatization and complexing significantly affects the inhibition.

Inhibition by Sulfide

Sulfur is a common constituent of many industrial wastewaters that is present in the form of sulfates, sulfides, shulfites etc (O'Flaherty et al., 1998a). Sulfate is reduced to sulfide by the reducing bacteria during anaerobic degradation (Koster et al., 1986; Hilton and Oleszkiewicz, 1988). This reduction is performed by two major groups of SRB including incomplete oxidizers and complete oxidizers. Incomplete oxidizers reduce the compounds such as lactate to acetate and carbon di-oxide, and complete oxidizers completely convert acetate to CO_2 and HCO^{3-}. Inhibition by sulfur exist in two staged due to sulfate reduction. Primary inhibition is due to the presence of organic and inorganic substrates which suppresses methane production(Harada et al., 1994), while the secondary inhibition is due toxicity of the sulfide to various bacterial population. (Anderson et al., 1982; Oude Elferink et al., 1994; Colleran et al., 1995; Colleran et al., 1998). However, it was found that addition of activated carbon at concentrations 2.5% (w/w), removed most of the sulfide in solution. Although activated carbon did not adsorb ammonia, it reduced inhibition of ammonia by removing sulfide, which otherwise would act synergistically with ammonia (Hansen et al., 1999).

Sulfide is toxic to methanogens as well as to the sulfate reducing bacteria themselves (Winfrey and Zeikus, 1977; Karhadkar et al., 1987; McCartney and Oleszkiewicz, 1991; Reis et al., 1992; Okabe et al., 1995). Sulfate reducing bacteria do not degrade natural biopolymers such as starch, glycogen, protein, or lipids and thus depend on the activity of other organisms for providing them with degradation products (Hansen, 1993). Although a few strains of sulfate reducing bacteria have been shown to utilize sugars and amino acids as substrate (Klemps et al., 1985; Min and Zinder, 1990), vigourous growth of sulfate reducing bacteria on typical acedogenic substrates is not common (Hansen, 1993). It is generally agreed that sulphate reducing bacteria cannot effectively compete against the fast-growing fermentative microorganisms involved in monomer degradation (Postgate, 1984; O'Flaherty et al. (1999) conducted tests to detect sulfate reducing bacteria in an anaerobic digester fed with glucose and lactose. No change of their degradation rates was detected upon addition of sulfate, indicating that sulfate reducing bacteria species did not play any substantial role in the degradation of glucose and lactose.

Inhibitiory action between sulfur reducting bacteria and methane producing bacteria is contradictory. Rinzema and Lettinga, 1988; Alphenaar et al., 1993; Stucki et al., 1993; Gupta et al., 1994 reported unbeaten competition of sulfur reducting bacteria, whereas some authors reported supremacy of methane producing bacteria (Colleran et al., 1998; De Smul et al., 1999; Colleran and Pender, 2002, Isa et al., 1986a,b; O'Flaherty et al., 1998a; Omil et al., 1996a; Oude Elferink et al., 1994; Rinzema et al., 1988; Visser et al., 1993). O'Flaherty et al. (1998b) linked the performance of reducting bacteria and methane producing bacteria at different pH values. Oude Elferink et al. (1994) observed that the initial population of SRB played a role in the competition between sulfur reducting bacteria and methane producing bacteria . Colleran and Pender (2002) concluded that aceticlastic methanogens predominated because sulfur reducting bacteria have a lower affinity for acetate than for other substrate

Quite a few processes have been applied to promote the removal of dissolved sulfate to prevent sulfide toxicity in the wastewater stream, although in general this considered uninvited because of the increase in the total volume of wastewater to be treated. An alternative way to reduce the sulfide concentration in an anaerobic system can be by incorporating a sulfide removal step in the whole process that include stripping, chemical coagulation, oxidation, precipitation or partial oxidation to elemental sulfur (Oude Elferink et al., 1994; Song et al., 2001). Adaptation of deagrading bacteria to free hydrogen sulfide in reactor system with fixed biomass, could increase their tolerance to sulfide. Isa et al. (1986a) reported that acclimatized aceticlastic and hydrogenotrophic methane producing bacteria were only slightly withdrawn at more than 1000 mg/L free hydrogen sulphide.

Inhibition By Ammonia

The biodegradation of the nitrogenous matter, which is mostly in the form of proteins and urea, is converted into ammonia (Kayhanian, 1999). Whittmann et al. (1995) proposed a number of mechanisms for ammonia inhibition, such as inhibition of a specific enzyme reaction, change in the intracellular pH or the increase of maintenance energy requirement. Inorganic ammonia exists in the form of ammonium ion and free ammonia in aqueous solution. This free ammonia has been suggested to be the main cause of inhibition as it is freely membrane-permeable (Kroeker et al., 1979; de Baere et al., 1984). The hydrophobic ammonia molecule may diffuse passively into the cell, causing proton imbalance, and/or potassium deficiency (Sprott and Patel, 1986; Gallert et al., 1998). Out of the four types of anaerobic microorganisms, the methanogens are the most intolerant show decrease in growth rate due to ammonia inhibition (Kayhanian, 1994) and with an increase in ammonia concentrations, acidogenic microorganisms in the granular sludge were almost unaffected while the methanogenic population lost 56.5% of its activity (Koster and Lettinga, 1988). Among the methanogens, the strains isolated from sludge digesters, i.e. Methanospirillum hungatei, Methanosarcina barkeri, Methanobacterium thermoautotrophicum, and Methanobacterium formicicum, Methanospirillum hungatei was the most sensitive to free ammonia (inhibition at 4.2 g/L) while the other three strains were resistant to ammonia levels higher than 10 g/L (Jarrell et al., 1987). However, there is contradictory information about the sensitivity and tolerance of aceticlastic and hydrogenotrophic methanogens.

Some research based on the comparison of methane production and growth rate indicated that the inhibitory effect was in general stronger for the acetoclastic than for the hydrogenotrophic methanogens (Koster and Lettinga, 1984; Zeeman et al., 1985; Sprott and Patel, 1986; Bhattacharya and Parkin, 1989; Robbins et al., 1989; Angelidaki and Ahring, 1993; Borja et al., 1996a), while others observed the relatively high resistance of acetate consuming methanogens to high levels as compared to hydrogen utilizing methanogens (Zeeman et al., 1985; Wiegant and Zeeman, 1986). It is believed that ammonia concentrations below 200 mg/L are favourable to anaerobic process since nitrogen is an essential nutrient for anaerobic microorganisms (Liu and Sung, 2002).

A wide range of inhibiting ammonia concentrations has been reported in the literature with the inhibitory total ammonia nitrogen concentration that caused a 50% reduction in methane production ranging from 1.7 to 14 g/L (Angelidaki and Ahring, 1993; Angelidaki and Ahring, 1994; Borja et al., 1996 ; Boardman and McVeigh, 1997; Bhattacharya and Parkin, 1989; Braun et al., 1981; Bujoczek et al., 2000; de Baere et al., 1984; Chamy et al., 1998; De Jarrell et al., 1987; Gallert and Winter, 1997; Guerrero et al., 1997; Gallert et al., 1998; Hashimoto, 1986; Hansen et al., 1998; Hendriksen and Ahring, 1991; Krylova et al., 1997; Kroeker et al., 1979; Kayhanian, 1994; Koster and Lettinga, 1988; Poggi- Varaldo et al. 1998; Parkin and Miller, 1983; Sung and Liu, 2003; Soubes et al., 1994; Zeeman et al., 1985) . The inhibition caused by ammonia can be attributed to the differences in nature of the substrates and the inocula, presence of other metallic and non-metallic ions, temperature & pH of the digester, and acclimatization periods (van Velsen et al., 1979; de Baere et al., 1984; Hashimoto, 1986; Angelidaki and Ahring, 1994).

Around 10% increase in methane yield is reported in presence of combination of Na^+ and K^+ or Na^+ and Mg^{2+} compared to that produced by Na+ alone (Kugelman and McCarty, 1964). Certain ions such as Na+, Ca2+, and Mg2+ were found to be antagonistic to ammonia inhibition, (McCarty and McKinney, 1961; Braun et al., 1981; Hendriksen and Ahring, 1991). Ammonia and sodium showed mutual antagonism, a situation where each ion can antagonize the toxicity produced by another ion. While the concentration of 0.15 M ammonia reduced the methane production from acetic acid by 20%, addition of 0.002–0.05 M Na+ produced 5% more methane compared to a sample without addition of the inhibitor.

An increased process temperature, in general, has a positive effect on the microbial growth rates that also results in a higher concentration of free ammonia. Researchers have found that anaerobic fermentation with a high concentration of ammonia was less inhibited and more stable at mesophilic temperatures than at thermophilic temperatures (Braun et al., 1981; Parkin and Miller, 1983). A decrease in temperature from 60 ^{0}C to 37 ^{0}C in anaerobic digesters with a high ammonia concentration indicated an increase in biogas yield, providing a respite from inhibition as indicated by an increase in biogas yield (Angelidaki and Ahring, 1994; Hansen et al., 1999). At 50^{0}C, thermophilic digestion of cow manure with a total ammonia concentration above 3 g/L was found to be very difficult (Hashimoto, 1983). Contrary to these findings, Gallert and Winter (1997) reported that methane production was inhibited 50% by 0.22 g/L FA at 37 ^{0}C and by 0.69 g/L FA at 55^{0}C, indicating that thermophilic flora tolerated at least twice as much FA as compared to mesophilic flora.

Acclimatization also influence the extent of ammonia inhibition. It was first reported during sludge digestion, dealing with adaptation of methanogens to ammonia by gradually exposing them to a wide variety of potentially inhibitory substances (Melbinger and Donnellon (1971) ; Parkin and Miller, 1983; Speece, 1983; Speece and Parkin, 1983). The adaptation may be the result increased tolerance in the predominant species of methanogenic microorganisms (Zeeman et al., 1985). Hashimoto (1986) reported that ammonia inhibition began at about 2.5 g/L and 4 g/L for unacclimated and acclimated thermophilic methanogens, respectively. Once adapted, they retain their viability at concentrations far exceeding the initial inhibitory concentrations (Kroeker et al., 1979; Parkin and Miller, 1983; Bhattacharya and Parkin, 1989; Angelidaki and Ahring, 1993). Koster and Lettinga (1988) reported that unacclimatized methanogens were unable to produce methane at 0.9–2 g N/L, however, they produced methane at 11 g N/L after adaptation. Successful functioning of anaerobic filters has been achieved at 6 g/L and 7.8 g/L after adaptation (Parkin et al., 1983; de Baere et al., 1984). Parkin and Miller (1983) reported that there was no significant decrease in methane production after acclimatization with the levels of free ammonia as high as 8–9 g/L of TAN. However, the methane yield was lower than that for reactors with a lower ammonia load (Koster and Lettinga, 1988; Borja et al., 1996a).

pH has its effects on the growth of microorganisms during bio-degradation of waste containing nitrogenous matter. (Kroeker et al., 1979; Hashimoto, 1983, 1984; Hansen et al., 1999). Since the FA itself is suggested to be the toxic, an increase in pH would result in increased toxicity (Borja et al., 1996b). Process instability due to ammonia often results accumulation of volatile fatty acids (VFAs), which again leads to a decrease in pH and thereby decreasing concentration of FA. The interaction between FA, VFAs and pH leads to an ‘‘inhibited steady state’’, a condition where the process is running stably but with a lower methane yield (Angelidaki and Ahring, 1993; Angelidaki et al., 1993). However, control of pH within the growth optimum of microorganisms may reduce toxicity caused by ammonia (Bhattacharya and Parkin, 1989). Reducing pH from 7.5 to 7.0 during thermophilic anaerobic digestion of cow manure also increased the methane production by four times (Zeeman et al., 1985). The better performance at pH 7.4 has been attributed to the relief of ammonia-induced inhibition at low pH (Braun et al., 1981). It should also be noted that both methanogenic and acidogenic microorganisms have their optimal pH. Failing to maintain pH within an appropriate range could cause reactor failure although ammonia is at a safe level (Kroeker et al., 1979).

To neutralize ammonia inhibition air stripping and chemical precipitation have been proven to be technically feasible at high ammonia concentrations and in a complex wastewater matrix (Kabdasli et al., 2000).The most common approach was to dilute the manure to a total solid level of 0.5–3.0%, which resulted in increase in waste volume making it economically unattractive (Callaghan et al., 1999). Immobilizing the microorganisms with different types of inert material (clay, activated carbon, zeolite) has been demonstrated to reduce inhibition of the biogas process and make the process more stable (Angelidaki et al., 1990; Nakhla et al., 1990; Borja et al., 1993; Hanaki et al., 1994; Hansen et al., 1998). It was found that increase in biomass retention time resulted in an effluent with a reduced concentration of biomass solids due to improved sedimentation. To allow the reactor to settle was promising ase it was easy and economical (Hansen et al., 1998). Addition of ionic exchangers or adsorbants such as natural zeolite and glauconite with high selectivity for ammonium ion, can remove inhibitors mitigate the ammonia inhibition (Borja et al., 1996a; Borja et al., 1996b; Hansen et al., 1998). Addition of cations such as Mg^{2+} or Ca^{2+} stabilizes anaerobic degradation (McCarty and McKinney, 1961).

Inhibition due to Light Metal Ions

Metals ions (Na, K, Mg, Ca etc) had their toxic effet on treatment process and their toxicity has been studied on the biological pitch for last many decades. High concentration level of these metal salts cause dehydration of bacterial cells due to osmotic pressure (de Baere et al.,1984;Yerkes et al., 1997). The toxicity must be associated with the cations and anions both, however, the toxicity of salts was found to be chiefly determined by the cation present (McCarty and McKinney, 1961). The light metal ions including sodium, potassium, calcium, and magnesium present in the anaerobic digesters are suppose to be released by the breakdown of organic matter present or added of pH adjustment (Grady et al., 1999). In moderate concentrations these cations are required to stimulate microbial growth like any other nutrient, however the excessive amounts slow down the growth and concentrations can cause toxicity (Soto et al., 1993a).

Sodium Ions

Effluent with high sodium content is produced mostly in the food processing industry (Soto et al., 1991). Soto et al (1991,1992, 1993a, 1993b) compared the mesophilic and thermophilic anaerobic filters treating effluents from a mussel cooking unit and reported that mesophilic reactor exhibited better performance than the thermophilic reactor due to the quick adaptation of mesophilic population to the high salinity of the wastewater. Sodium was found more toxic to propionic acid-utilizing microorganisms than to acetic acid-utilizing ones while dedrading volatile fatty acid This was in agreement with the conclusion of Liu and Boone's(1991) experiments who found the NaCl toxicity decreased in the order of lignocellulose-degrading > acetate-utilizing > propionate- utilizing > H_2/CO_2-utilizing organisms.

Because of its role in formation of adenosine triphosphate, sodium is essential for the growth of mesophilic anaerobes at low concentrations in the range of 100–200 mg/L, (Dimroth and Thomer, 1989; McCarty, 1964). The optimal conditions for mesophilic hydrogenotrophic methanogens was reported 350 mg Na+/L (Patel and Roth, 1977). Kugelman and Chin (1971) reported, the optimal sodium concentration for mesophilic aceticlastic methanogens in waste treatment processes was 230 mg Na+/L. The IC50 for has reported to be 5.6–53 g/L depending on the adaptation period, antagonistic/synergistic effects, substrate, and reactor configuration (Patel and Roth, 1977; Rinzema et al., 1988; Liu and Boone, 1991; Soto et al., 1993b; Feijoo et al., 1995; Omil et al., 1995a,b; Aspe´ et al., 1997; Kim et al., 2000; Vallero et al., 2002; Chen et al., 2003; Vallero et al., 2003a,b). At high concentrations, sodium could inhibit the activity of microorganisms and get in the way with their metabolism (Kugelman and McCarty, 1964; Rinzema et al., 1988; Gourdon et al., 1989; Balsleve-Olsen et al., 1990; Mende´z et al., 1995). McCart (1964)reported sodium concentrations of 8000 mg/L to strongly inhibit the methanoges at mesophilic temperatures.

Rinzema et al. (1988) reported no adaptation of Methanothrix sp. to high sodium concentrations even after 12 weeks. Similarly, when treating methanol in a sulfate-reducing reactor, stepwise increases in NaCl could not increase the tolerance of sulfur reducing bacteria to sodium, indicating that the adaptation of thermophilic, sulfidogenic methanol-degrading bacteria to a high NaCl environment was unlikely to occur (Vallero et al., 2002, 2003a,b). This brought to a conclusion that aclimatization of methanogens to high concentrations of sodium over prolonged periods of time was required to increase the tolerance as well as acceptace and shorten the lag phase before methane production begins (de Baere et al., 1984; Feijoo et al., 1995; Omil et al., 1995a,b, 1996b; Chen et al., 2003). Mende´z et al. (1995) reported that IC90 of inocula was 12.0 g/L when sludge was taken from anaerobic reactor after one day of acclimatization and greater than 17.0 g/L when the acclimatization period was 719 days. Anaerobic filter sludge that treating high salinity wastewater for 2 years also exhibited better performance than sludge that had been sampled from a central activity digester employed for wastewater treatment for 1 year (Feijoo et al., 1995).

Potassium Ions

Maintenance of high levels of potassium in culture media or in a digester is undesirable since pure culture studies have shown that high levels of extracellular potassium (1.0 M) lead to a passive influx of potassium ions that neutralize the membrane potential (Jarrell et al., 1984). In addition, potassium is one of the best extractants for metals bound to the exchangeable sites in sludge. Ilangovan and Noyola (1993) observed the increase of micronutrients (Cu^{2+}, Zn^{2+}, Ni^{2+}, Mo^{2+}, Co^{2+}) in a UASB reactor treating molasses stillage containing a high concentration of potassium. The removal of the essential micronutrients from active sludge was believed to be responsible for the low activity of anaerobic methanogenic population. The toxic effect of potassium is rarely referenced in the literature. Low concentrations of potassium (less than 400 mg/L) were observed to cause an enhancement in performance in both the thermophilic and mesophilic ranges while at higher concentrations there was an inhibitory effect that was more pronounced in the thermophilic temperature range. Slug feed studies, in which the concentration of the cation was suddenly increased in actively fermenting cultures, were conducted to determine the toxicity of individual cations (Kugelman and McCarty, 1964). It was observed that 0.15 M K+ caused 50% inhibition of acetate-utilizing methanogens. A series of studies have shown that K+ inhibits the thermophilic digestion of simulated coffee wastes (Fernandez and Forster, 1993, 1994; Shi and Forster, 1994). Information about the sensitivity of different groups of microorganisms to potassium is conflicting. The results of batch tests using acetate as the carbon source showed that the gas production from both the control and samples with elevated K+ were identical, indicating that the inhibition could be at the acidogenic stage (Fernandez and Forster, 1994). Mouneimne et al. (2003) investigated the biotoxicity of potassium using acetate and glucose as substrates and anaerobic sludge as inoculum. The IC50 for acetate-utilizing microorganisms was found to be 0.74 mol/L. However, the degradation rates of glucose were virtually unaffected by potassium, indicating that the acetate-utilizing microorganisms exhibited a greater sensitivity to the toxic effects of cations than the acid-forming ones. Sodium, magnesium, and ammonium were observed to mitigate potassium toxicity, with sodium producing the best results. Combinations of cations produce antagonism superior to that of single cations. The best results were obtained for combinations of sodium and calcium, and combinations of sodium, calcium and ammonia (Kugelman and McCarty, 1964).

Magnesium Ions:

The optimal Mg^{2+} concentration was reported to be 720 mg/L for the anaerobic bacterium Methanosarcina thermophila TM1 and a Methanosarcinae-dominated UASB reactor (Ahring et al., 1991; Schmidt and Ahring, 1993). Cultures could be adapted to 300 mM Mg^{2+} without a change in growth rate, but growth ceased at 400 mg/L Mg^{2+} (Schmidt and Ahring, 1993). Magnesium ions at high concentrations have been shown to stimulate the production of single cells (Harris, 1987; Xun et al., 1988; Schmidt and Ahring, 1993). The high sensitivity of single cells to lysis is an important factor in the loss of aceticlastic activity in anaerobic reactors.

Calcium Ions

Calcium ions have a positive impact of reactors and are an essential cation required for the growth and formation of microbial aggregated of many strains of methanogens (Murray and Zinder, 1985; Thiele et al., 1990; Huang and Pinder, 1995). Very much less toxicity threshold is reported about the toxicity of Ca^{2+} in the anaerobic system (Kugelman and McCarty 1964). Depite presence of large amout of calcium in effluent and the digester, Ca^{2+} concentrations up to 7000 mg/L had no inhibitory effect on anaerobic digestion (Jackson-Moss et al. ,1989). Low Ca^{2+} concentrations from 100 to 200 mg/L were reported to be beneficial for sludge granulation (Cail and Barford, 1985; Mahoney et al., 1987; Yu et al., 2001), whereas its high concentrations (greater than 300 mg/L) were reported unfavourable for microflora (Hulshoff Pol et al., 1983; Thiele et al., 1990; Yu et al., 2001). Its high concentration leads to precipitation of calcium carbonate and calcium phosphate resulting in scaling of reactors and pipes biomass and reduced specific methanogenic activity, loss of buffer capacity and other essential nutrients for anaerobic degradation (Keenan et al., 1993; El-Mamouni et al., 1995; van Langerak et al., 1998). At Ca^{2+} concentrations higher than 120 mg/ L, an accumulation of minerals and a decrease in water content in the biofilm caused an inhibition of cellularmetabolism (Huang and Pinder, 1995).

Aluminum Ions:

Aluminium inhibition on anaerobic digestionin ot much reported in literature. Cabirol et al.,(2003) reported the mechanism of aluminum inhibition. Acetogenic and methanogenic microorganisms showed inhibitionon addition of $Al(OH)_3$. After exposed to 1000 mg/L $Al(OH)_3$ for 59 days, the specific activity of methanogenic and acetogenic microorganisms decreased by 50% and 72%, respectively (Cabirol et al., 2003). Jackson-Moss and Duncan (1991) reported that 2,500 mg/L Al^{3+} could be tolerated by anaerobes after acclimatization.

Inhibition due to Heavy Metal Ions:

Heavy metals such as chromium, iron, cobalt, copper, zinc, cadmium, and nickel present in in municipal sewage and sludge are the major cause of toxicity for digester upset (Jin et al., 1998; Sterritt and Lester, 1980, Swanwick et al., (1969). These metals disrupt of enzymatic function by binding of the metals with organic substrate or by replacing naturally occurring metals in enzyme prosthetic groups (Vallee and Ulner, 1972). Analysis of ten methanogenic strains showed that heavy metals like Fe, Zn, Cu, Ni, Co, Mo are the paert of essential enzymes that take part in many anaerobic reactions (Takashima and Speece, 1989) . It was found that acidogens resist more to heavy metal toxicity than methanogens (Zayed and Winter, 2000). However, Hickey et al. (1989) have speculated that some trophic group(s) or organisms within the anaerobic consortia in digesters might be more severely inhibited by a pulsed addition of heavy metals than the methanogenic populations. Due to the complexity of the anaerobic system, heavy metals participate in many physico-chemical processes such as (1) precipitation as sulfide carbonate and hydroxides (Lawrence and McCarty, 1965; Mosey et al., 1971), (2) formation of complexes in solution with intermediates and product compounds produced during digestion (Hayes and Theis, 1978; Hickey et al., 1989; Callander and Barford, 1983a,b). and (3) sorption to the solid fraction (Shen et al., 1993; Shin et al.,1997). Among these metal forms, only metals in soluble, free form are toxic to the microorganisms (Lawrence and McCarty, 1965; Mosey and Hughes, 1975;

Oleszkiewicz and Sharma, 1990, Bhattacharya and Safferman, 1989; Bhattacharya et al., 1995a,b).

3. Conclusion

Anaerobic biodigestion is the most efficient effeluent treatment method that harnesses natural decomposition to lessen waste volume and generate biogas at the same time. It has been widely accepted for the reatment of waste from many industrial operations. Depending on the production unit or the origin, the waste may ontain inhibitory substances such as ammonia, sulfide, heavy metals, and othe inorganic and organics substances. Presence of these substances at low or high concentrations may cause reactor upsetor even cause possible reactor failure. Also due to the difference in anaerobic microbial species, chemical and physical composition of waste, experimental methods and reactor's physical conditions, physico-chemical parameters, results from previous investigations on inhibition of anaerobic processes vary substantially. So, it cecomes necessary to obtain information on waste components for successful functioning of anaerobic digestor. Digestion with other waste, adaptation of microorganisms toinhibitors and integration of methods to remove the toxicants before digestion can significantly improve the waste treatment efficiency. However, knowledge of the possible contaminants present in the wastewater, their origins, and their degree of toxicity is essential to successful anaerobic treatment.

4. Abbreviations

1. CSTR- continuously stirred tank reactor
2. FA- free ammonia
3. HRT- hydraulic retention time
4. IC50, IC90, IC100 -the toxicant concentration that causes 50%, 90%, and 100% reduction in cumulative methane production, respectively, over a fixed period of exposure time
5. LCFA- long chain fatty acids
6. MPB- methane producing bacteria
7. SRB- sulfate reducing bacteria
8. TAN- total ammonia nitrogen
9. VFA- volatile fatty acids
10. UASB- upflow anaerobic sludge blanket reactor

References

[1] Ahring, B.K., Alatriste-Mondragon, F., Westermann, P., Mah, R.A., 1991. Effects of cations on Methanosarcina thermophila TM-1 growing on moderate concentrations of acetate: production of single cells. Microbiol. Biotechnol. 38, 560–564.
[2] Alphenaar, P.A., Visser, A., Lettinga, G., 1993. The effect of liquid upward velocity and hydraulic retention time on granulation in UASB reactors treating wastewater with a high sulphate content. Bioresour. Technol. 43, 249–258.
[3] Anderson, G.K., Donnelly, T., Mckeown, K.J., 1982. Identification and control of inhibition in the anaerobic treatment of industrial wastewater. Process Biochem. 17, 28–32.
[4] Angelidaki, I., Ahring, B.K., 1993. Thermophilic digestion of livestock waste: the effect of ammonia. Appl. Microbiol. Biotechnol. 38, 560–564.
[5] Angelidaki, I., Petersen, S.P., Ahring, B.K., 1990. Effects of lipids on thermophilic anaerobic digestion and reduction of lipid inhibition upon addition of bentonite. Appl. Microbiol. Biotechnol. 33, 469–472.
[6] Aspe´, E., Martı´, M., Roeckel, M., 1997. Anaerobic treatment of fishery wastewater using a marine sediment inoculum. Water Res. 31 (9), 2147–2160.
[7] Balsleve-Olsen, P., Lynggaard-Jensen, A., Nickelsen, C., 1990. Pilot-scale experiments on anaerobic treatment of wastewater from a fish processing plant. Water Sci. Technol. 22, 463–474.
[8] Bhattacharya, S.K., Madura, R., Uberoi, V., Haghighi-Podeh, M.R., 1995a. Toxic effects of cadmium on methanogenic systems. Water Res. 29 (10), 2339–2345.
[9] Bhattacharya, S.K., Parkin, G.F., 1989. The effect of ammonia on methane fermentation process. J. Water Pollut. Control Fed. 61 (1),55–59.
[10] Bhattacharya, S.K., Safferman, A.G., 1989. Determination of bioavailable nickel concentrations in inhibited methanogenic systems. Environ. Technol. Lett. 10 (8), 725–730.
[11] Bhattacharya, S.K., Uberoi, V., Madura, R.L., Haghighi-Podeh, M.R., 1995b. Effect of cobalt on methanogenesis. Environ. Technol. 16 (3), 271–278.
[12] Borja, R., Sanche´z, E., Duran, M.M., 1996a. Effect of the clay mineral zeolite on ammonia inhibition of anaerobic thermophilic reactors treating cattle manure. J. Environ. Sci. Health A31 (2), 479–500.
[13] Borja, R., Sanche´z, E., Weiland, P., 1996b. Influence of ammonia concentration on thermophilic anaerobic digestion of cattle manure in upflow anaerobic sludge blanket (UASB) reactors. Process Biochem. 31 (5), 477–483.
[14] Borja, R., Sanche´z, E., Weiland, P., Travieso, L., 1993. Effect of ionic exchanger addition on the anaerobic digestion of cow manure.Environ. Technol. 14, 891–896.
[15] Braun, B., Huber, P., Meyrath, J., 1981. Ammonia toxicity in liquid piggery manure digestion. Biotechnol. Lett. 3, 159–164.
[16] Bujoczek, G., Oleszkiewicz, J., Sparling, R., Cenkowski, S., 2000. High solid anaerobic digestion of chicken manure. J. Agric. Eng. Res. 76, 51–60.
[17] Busca, G., Berardinelli, S., Resini, C., & Arrighi, L. (2008). Technologies for the removal of phenol from fluid streams: a short review of recent developments. Journal of Hazardous Materials, 160(2), 265-288.
[18] Cabirol, N., Barraga´n, E.J., Dura´n, A., Noyola, A., 2003. Effect of aluminium and sulphate on anaerobic digestion of sludge from wastewater enhanced primary treatment. Water Sci. Technol. 48 (6), 235–240.
[19] Cail, R.G., Barford, J.P., 1985. The development of granulation in an upflow flock digester and an upflow anaerobic sludge blanket digest treating cane juice stillage. Biotechnol. Lett. 7, 493–498.
[20] Callaghan, F.J., Wase, D.A.J., Thayanithy, K., Forster, C.F., 1999. Codigestion of waste organic solids: batch studies. Bioresour. Technol. 67, 117–122.

[21] Callander, I.J., Barford, J.P., 1983a. Precipitation, chelation, and the availability of metals as nutrients in anaerobic digestion. I. Methodology.Biotechnol. Bioeng. 25 (8), 1947–1957.
[22] Callander, I.J., Barford, J.P., 1983b. Precipitation, chelation, and the availability of metals as nutrients in anaerobic digestion. II. Applications. Biotechnol. Bioeng. 25 (8), 1959–1972.
[23] Chamy, R., Poirrier, P., Schiappacasse, M.C., Alkalay, D., Guerrero, L., 1998. Effect of ammonia content in the biodegradability of the salmon industry wastes. Bioprocess Eng. 19, 1–5.
[24] Chang, Y. J., Nishio, N., & Nagai, S. (1995). Characteristics of granular methanogenic sludge grown on phenol synthetic medium and methanogenic fermentation of phenolic wastewater in a UASB reactor. J. Fermentation Bioeng, 79, 4348-4353
[25] Chen, W.H., Han, S.K., Sung, S., 2003. Sodium inhibition of thermophilic methanogens. J. Environ. Eng. 129 (6), 506–512.
[26] Colleran, E., Finnegan, S., Lens, P., 1995. Anaerobic treatment of sulphate-containing waste streams. Anton. van Leeuw. 67, 29–46.
[27] Colleran, E., Pender, S., 2002. Mesophilic and thermophilic anaerobic digestion of sulphate-containing wastewaters. Water Sci. Technol. 45 (10), 231–235.
[28] Colleran, E., Pender, S., Phipott, U., O'Flaherty, V., Leahy, B., 1998. Full-scale and laboratory-scale anaerobic treatment of citric acid production wastewater. Biodegradation 9, 233–245.
[29] D. Botheju, Ø. Svalheim, B. Rydtun, J. Johansen, T. K. Haraldsen, and R. Bakke, "Fertilizer production by digestate nitrification", in proceedings of the 12th European Biosolids and Organic Resources Conference, Manchester, UK, November 2007.
[30] de Baere, L.A., Devocht, M., van Assche, P., Verstraete, W., 1984. Influence of high NaCl and NH4Cl salt levels on methanogenic associations. Water Res. 18, 543–548.
[31] De Smul, A., Goethals, L., Verstraete, W., 1999. Effect of COD to sulphate ratio and temperature in expanded-granular-sludge-blanket reactors for sulphate reduction. Process Biochem. 34, 407–416.
[32] Demirel, B., Yenigu¨n, O., 2002. Two-phase anaerobic digestion processes: a review. J. Chem. Tech. Biotechnol. 77, 743–755.
[33] Dimroth, P., Thomer, A., 1989. A primary respiratory Na+ pump of an anaerobic bacterium: the Na+-dependent NADH: quinone oxidoreductase of Klebsiella pneumoniae. Arch. Microbiol. 151, 439–444.
[34] Dupla, M., Conte, T., Bouview, J.C., Bernet, N., Steyer, J.P., 2004. Dynamic evaluation of a fixed bed anaerobic-digestion process in response to organic overloads and toxicant shock loads. Water Sci. Technol. 49 (1), 61–68. .
[35] El-Mamouni, R., Guiot, S.R., Mercier, P., Sali, B., Samson, R., 1995. Limiting impact on granules activity of the multiplate anaerobic reactor (MPAR) treating whey permeate. Bioprocess Eng., 47–53.
[36] Essa, M., Farooq, S. and Nackla, G.1997. "Effect of biofilm on the physical properties of sans contaminated with phenol", J. Environ. Sci. Health, A32 (4), 1109-1123.
[37] Feijoo, G., Soto, M., Mende´z, R., Lema, J.M., 1995. Sodium inhibition in the anaerobic digestion process: antagonism and adaptation phenomena. Enzyme Microb. Technol. 17, 180–188.
[38] Fernandez, N., Forster, C.F., 1993. A study of the operation of mesophilic and thermophilic anaerobic filters treating a synthetic coffee waste. Bioresour. Technol. 45, 223–227.
[39] Fernandez, N., Forster, C.F., 1994. The anaerobic digestion of simulated coffee waste using thermophilic and mesophilic upflow filters. Process Safety Environ. Protect. 72 (B1), 15–20.
[40] Gallert, C., Bauer, S., Winter, J., 1998. Effect of ammonia on the anaerobic degradation of protein by a mesophilic and thermophilic biowaste population. Appl. Microbiol. Biotechnol. 50, 495–501.
[41] Gallert, C., Winter, J., 1997. Mesophilic and thermophilic anaerobic digestion of source-sorted organic waste: effect of ammonia on glucose degradation and methane production. Appl. Microbiol. Biotechnol. 48, 405–410..
[42] Ghosh, S., Henry, M.P., Sajjad, A., Mensinger, M.C., Arora, J.L., 2000. Pilot-scale gasification of municipal solid wastes by high-rate and twophase anaerobic digestion (TPAD). Water Sci. Technol. 41 (3), 101–110.
[43] Ghosh, S., Pohland, F.G., 1974. Kinetics of substrate assimilation and product formation in anaerobic digestion. J. Water Pollut. Control Fed. 46, 748–759.
[44] Gourdon, R., Comel, C., Vermande, P., Ve´rom, J., 1989. Kinetics of acetate, propionate and butyrate removal in the treatment of a semisynthetic landfill leachate on anaerobic filter. Biotechnol. Bioeng. 33, 1167–1181.
[45] Grady Jr, C.P.L., Daigger, G.T., Lim, H.C., 1999. BiologicalWaste Water Treatment. Marcel Dekker, New York.
[46] Guerrero, L., Omil, F., Mendez, R., Lema, M., 1997. Treatment of saline wastewaters from fish meal factories in an anaerobic filter under extreme ammonia concentrations. Bioresour. Technol. 61, 69–78.
[47] Gupta, A., Flora, J.R.V., Gupta, M., Sayles, G.D., Suidan, M.T., 1994. Methanogenesis and sulphate reduction in chemostats-1: kinetic studies and experiments. Water Res. 28, 781–793.
[48] Hanaki, K., Hirunmasuwan, S., Matsuo, T., 1994. Protection of methanogenic bacteria from low pH and toxic materials by immobilization using polyvinyl alcohol. Water Res. 28, 877–885.
[49] Hansen, K.H., Angelidaki, I., Ahring, B.K., 1998. Anaerobic digestion of swine manure: inhibition by ammonia. Water Res. 32, 5–12.
[50] Hansen, K.H., Angelidaki, I., Ahring, B.K., 1999. Improving thermophilic anaerobic digestion of swine manure. Water Res. 33, 1805–1810.
[51] Hansen, T.A., 1993. Carbon metabolism of sulfate-reducing bacteria. In: Odom, J.M., Rivers-Singleton, J.R. (Eds.), The Sulfate-reducing Bacteria: Contemporary Perspectives. Springer-Verlag, NY, pp. 21–40.

[52] Harada, H., Uemura, S., Monomoi, K., 1994. Interactions between sulphate-reducing bacteria and methane-producing bacteria in UASB reactors fed with low strength wastes containing different levels of sulphate. Water Res., 355–367.
[53] Harris, J.E., 1987. Spontaneous disaggregation of Mathanosaricina mazei S-6 and its use in the development of genetic techniques for Methanosarcina spp. Appl. Environ. Microbiol. 53 (10), 2500–2504.
[54] Hashimoto, A.G., 1983. Thermophilic and mesophilic anaerobic fermentation of swine manure. Agric. Wastes 6, 175–191.
[55] Hashimoto, A.G., 1984. Methane from swine manure: effect of temperature and influent substrate concentration on kinetic parameter (k). Agric. Wastes 9, 299–308.
[56] Hashimoto, A.G., 1986. Ammonia inhibition of methanogenesis from cattle waste. Agric. Wastes 17, 241–261.
[57] Hayes, T.D., Theis, T.L., 1978. The distribution of heavy metals in anaerobic digestion. J. Water Pollut. Control Fed. 50, 61–69.
[58] Hendriksen, H.V., Ahring, B.K., 1991. Effects of ammonia on growth and morphology of thermophilic hydrogen-oxidizing methanogenic bacteria. FEMS Microb. Ecol. 85, 241–246.
[59] Hickey, R.F., Vanderwielen, J., Switzenbaum, M.S., 1989. The effect of heavy metals on methane production and hydrogen and carbon monoxide levels during batch anaerobic sludge digestion. Water Res. 23, 207–219.
[60] Hilton, B.L., Oleszkiewicz, J.A., 1988. Sulphide-induced inhibition of anaerobic digestion. J. Environ. Eng. 114, 1377–1391.
[61] Hilton, B.L., Oleszkiewicz, J.A., 1990. Sulfide-induced inhibition of anaerobic digestion-closure. J. Environ. Eng. 116, 1007–1008.
[62] Huang, J., Pinder, K.L., 1995. Effects of calcium on development of anaerobic acidogenic biofilms. Biotechnol. Bioeng. 45, 212–218.
[63] Hulshoff Pol, L.W., de Zeeuw, W.J., Velzeboer, C.T.M., Lettinga, G., 1983. Granulation in UASB reactors. Water Sci. Technol. 15, 291–304.
[64] I. M. Buendía, F. J. Fernández, J. Villaseñor, and L. Rodríguez, 2009 “Feasibility of anaerobic co-digestion as a reatment option of meat industry wastes”, Bioresource Technology, vol. 100, pp. 1903- 1909.
[65] Ilangovan, K., Noyola, A., 1993. Availability of micronutrients during anaerobic digestion of molasses stillage using an upflow anaerobic sludge blanket (UASB) reactor. Environ. Technol. 14, 795–799.
[66] Isa, Z., Grusenmeyer, S., Verstraete, W., 1986a. Sulphate reduction relative to methane production in high-rate anaerobic digestion: technical aspects. Appl. Environ. Microbiol. 51, 572–579.
[67] Isa, Z., Grusenmeyer, S., Verstraete, W., 1986b. Sulphate reduction relative to methane production in high-rate anaerobic digestion: mirobiological aspects. Appl. Environ. Microbiol. 51, 580–587.
[68] J. B. H. Nielsen, T. A. Seadi, and P. O. Popiel, “The future of anaerobic digestion and biogas utilization”, 2009. ioresource Technology, vol. 100, pp. 5478-5484.
[69] Jackson-Moss, C.A., Duncan, J.R., 1991. The effect of aluminum on anaerobic digestion. Biotechnol. Lett. 13 (2), 143–148.
[70] Jackson-Moss, C.A., Duncan, J.R., Cooper, D.R., 1989. The effect of calcium on anaerobic digestion. Biotechnol. Lett. 11 (3), 219–224.
[71] Jarrell, K.F., Saulnier, M., Ley, A., 1987. Inhibition of methanogenesis in pure cultures by ammonia, fatty acids, and heavy metals, and protection against heavy metal toxicity by sewage sludge. Can. J. Microbiol. 33, 551–555.
[72] Jin, P., Bhattacharya, S.K., Williama, C.J., Zhang, H., 1998. Effects of sulfide addition on copper inhibition in methanogenic systems. Water Res. 32, 977–988.
[73] Kabdasli, I., Tu¨nay, O., O¨ ztu¨ rk, I., Yilmaz, S., Arikan, O., 2000. Ammonia removal from young landfill leachate by magnesium ammonium phosphate precipitation and air stripping. Water Sci. Technol. 41, 237–240. .
[74] Karhadkar, P.P., Audic, J.-M., Faup, G.M., Khanna, P., 1987. Sulfide and sulfate inhibition of methanoenesis. Water Res. 21, 1061–1066.
[75] Karthik, M., Dafale, N., Pathe, P., & Nandy, T. (2008). Biodegradability enhancement of purified terephthalicacid wastewater by coagulation–flocculation process as pretreatment. Journal of hazardous materials, 154(1), 721-730.
[76] Kayhanian, M., 1994. Performance of a high-solids anaerobic digestion process under various ammonia concentrations. J. Chem. Tech. Biotechnol. 59, 349–352.
[77] Kayhanian, M., 1999. Ammonia inhibition in high-solids biogasification: an overview and practical solutions. Environ. Technol. 20, 355–365.
[78] Keenan, P.J., Isa, J., Switzenbaum, M.S., 1993. Inorganic solids development in a pilot-scale anaerobic reactor treating municipal solid waste landfill leachate. Water Environ. Res. 65, 181–188.
[79] Kim, I.S., Kim, D.H., Hyun, S.-H., 2000. Effect of particle size and sodium ion concentration on anaerobic thermophilic food waste digestion. Water Sci. Technol. 41 (3), 67–73.
[80] Koster, I.W., Cramer, A., 1987. Inhibition of methanogenesis from acetate in granular sludge by long-chain fatty acids. Appl. Environ. Microbiol. 53 (2), 403–409.
[81] Koster, I.W., Lettinga, G., 1984. The influence of ammonium-nitrogen on the specific activity of pelletized methanogenic sludge. Agric. Wastes 9, 2.5–216.
[82] Koster, I.W., Lettinga, G., 1988. Anaerobic digestion at extreme ammonia concentrations. Biol. Wastes 25, 51–59.
[83] Koster, I.W., Rinzema, A., De Vegt, A.L., Lettinga, G., 1986. Sulfide inhibition of the methanogenic activity of granular sludge at various pH levels. Water Res. 20, 1561–1567.
[84] Kroeker, E.J., Schulte, D.D., Sparling, A.B., Lapp, H.M., 1979. Anaerobic treatment process stability. J. Water Pollut. Control Fed. 51, 718– 727.
[85] Krylova, N.I., Khabiboulline, R.E., Naumova, R.P., Nagel, M.A., 1997. The influence of ammonium and methods for removal during the anaerobic treatment of

poultry manure. J. Chem. Tech. Biotechnol. 70, 99–105.

[86] Kugelman, I.J., Chin, K.K., 1971. Toxicity, synergism, and antagonism in anaerobic waste treatment processes. In: Anaerobic Biological Treatment Processes, American Chemical Society Advances in Chemistry Series 105, pp. 55–90.

[87] Kugelman, I.J., McCarty, P.L., 1964. Cation toxicity and stimulation in anaerobic waste treatment. J. Water Pollut. Control Fed. 37, 97–116.

[88] L. Yu, K. Yaoqiu, H. Ningsheng, W. Zhifeng, and X. Lianzhong, "Popularizing household-scale biogas digesters for rural sustainable energy development and greenhouse gas mitigation", Renewable Energy, vol. 33, pp. 2027-2035, 2008.

[94] Lo, K.V., Liao, P.H., March, A.C., 1985. Thermophilic anaerobic digestion of screened dairy manure. Biomass 6, 301–315.

[95] M. Berglund, and P. Börjesson, "Assessment of energy performance in the life-cycle of biogas production", iomass and Bioenergy, vol. 30, pp. 254-266, 2006.

[96] M. Lantz, M. Svensson, L. Björnsson, and P. Börjesson, "The prospects for an expansion of biogas systems in weden - Incentives, barriers and potentials", Energy Policy, vol. 35, pp. 1830-1843, 2007.

[97] MA. Sprott, G.D., Patel, G.B., 1986. Ammonia toxicity in pure cultures of methanogenic bacteria. System. Appl. Microbiol. 7, 358–363.

[98] Mahoney, E.M., Varangu, L.K., Cairns, W.L., Kosaric, N., Murray, R.G.E., 1987. The effect of calcium on microbial aggregation during UASB reactor start-up. Water Sci. Technol. 19, 249–260.

[99] Maillacheruvu, K.Y., Parkin, G.F., Peng, W.C., Kuo, W.C., Oonge, Z.I., Lebduschka, V., 1993. Sulfide toxicity in anaerobic systems fed sulphate and various organics. Water Environ. Res. 65, 100–109

[100] McCartney, D.M., Oleszkiewicz, J.A., 1991. Sulfide inhibition of anaerobic degradation of lactate and acetate. Water Res. 25 (2), 203–209.

[101] McCarty, P.L., 1964. Anaerobic waste treatment fundamentals. Public Works 95 (9), 107–112.

[102] McCarty, P.L., McKinney, R., 1961. Salt toxicity in anaerobic digestion.J. Water Pollut. Control Fed. 33, 399–415.

[103] Mende´z, R., Lema, J.M., Soto, M., 1995. Treatment of seafood-processing wastewaters in mesophilic and thermophilic anaerobic filters. Water Environ. Res. 67 (1), 33–45.

[104] Min, H., Zinder, S.H., 1990. Isolation and characterization of a thermophilic sulfate-reducing bacterium Desulfotomaculum thermoacetoxidans sp. nov.. Arch. Microbiol. 153, 399–404.

[105] Mohammad-Javad Ghannadzadeh, Ahmad Jonidi-Jafari, Abbas Rezaee, Reza Darvishi, Cheshmeh Soltani (2015) Biodegradation of Phenol in Synthetic Wastewater Using a Fixed Bed Reactor With up Flow Sludge Blanket Filtration (FUSBF), Global Journal of Health Science; Vol. 7, No. 7; 2015, pp 120

[106] Mosey, F.E., Hughes, D.A., 1975. The toxicity of heavy metal ions to anaerobic digestion. Water Pollut. Control 74, 18–39.

[107] Mosey, F.E., Swanwick, J.D., Hughes, D.A., 1971. Factors affecting the availability of heavy metals to

[89] Lawrence, A.W., McCarty, P.L., 1965. The role of sulfide in preventing heavy metal toxicity on anaerobic treatment. J. Water Pollut. Control Fed. 37, 392–405.

[90] Liu, J., Wang, B., Li, W., Jin, C., Cao, X., & Wang, L. (1996). Removal of nitrogen from coal gasification and

[91] Liu, S.-M., Wu, C.-H., Huang, H.-J., 1998. Toxicity and anaerobic biodegradability of pyridine and its derivatives under sulfidogenic conditions. Chemosphere 36 (10), 2345–2357.

[92] Liu, T., Sung, S., 2002. Ammonia inhibition on thermophilic aceticlastic methanogens. Water Sci. Technol. 45, 113–120.

[93] Liu, Y., Boone, D.R., 1991. Effects of salinity on methanogenic decomposition. Bioresour. Technol. 35, 271–273.

inhibit anaerobic digestion. Water Pollut. Control 70, 668–679.

[108] Mouneimne, A.H., Carre`re, H., Bernet, N., Delgene`s, J.P., 2003. Effect of saponification on the anaerobic digestion of solid fatty residues. Bioresour. Technol. 90, 89–94.

[109] Murray, P.A., Zinder, Z.H., 1985. Nutritional requirements of Methanosarcina sp. strain TM-1. Appl. Environ. Microbiol. 50, 49–56.

[110] Nakhla, G.F., Suidan, M.T., Pfeffer, J.T., 1990. Control of anaerobic GAC reactors treating inhibitory wastewaters. J. Water Pollut. Control Fed. 62, 65–72.

[111] O'Flaherty, V., Colohan, S., Mulkerrins, D., Colleran, E., 1999. Effect of sulphate addition on volatile fatty acid and ethanol degradation in an anaerobic hybrid reactor. II: Microbial interactions and toxic effects. Bioresour. Technol. 68, 109–120.

[112] O'Flaherty, V., Lens, P., deBeer, D., Colleran, E., 1997. Effect of feed composition and upflow velocity aggregate characteristics in anaerobic upflow reactors. Appl. Microbiol. Biotechnol. 47, 102–107.

[113] O'Flaherty, V., Lens, P., Leaky, B., Colleran, E., 1998b. Long term competition between sulphate reducing and methane-producing bacteria during full-scale anaerobic treatment of citric acid production wastewater. Water Res. 32 (3), 815–825.

[114] O'Flaherty, V., Mahony, T., O'Kennedy, R., Colleran, E., 1998a. Effect of pH on growth kinetics and sulphide toxicity thresholds of a range of methanogenic, syntrophic and sulphate-reducing bacteria. Process Biochem. 33 (5), 555–569.

[115] Okabe, S., Nielsen, P.H., Jones, W.L., Characklis, W.G., 1995. Sulfide product inhibition of Desulfovibrio desulfuricans in batch and continuous cultures. Water Res. 29 (2), 571–578.

[116] Oleszkiewicz, J.A., Sharma, V.K., 1990. Stimulation and inhibition of anaerobic process by heavy metals – a review. Biol. Wastes 31, 45– 67.

[117] Omil, F., Lens, P., Hulshoff Pol, L.W., Lettinga, G., 1996a. Effect of upward velocity and sulphide concentration on volatile fatty acid degradation in a sulphidogenic granular sludge reactor. Process Biochem. 31, 699–710.

[118] Omil, F., Mende´z, R., Lema, J.M., 1995a. Characterization of biomass from a pilot plant digester treating saline wastewater. J. Chem. Tech. Biotechnol. 63, 384–392.

[119] Omil, F., Mende´z, R., Lema, J.M., 1995b. Anaerobic treatment of saline wastewaters under high sulphide and ammonia content. Bioresour. Technol. 54, 269–278.
[120] Omil, F., Mende´z, R., Lema, J.M., 1996b. Anaerobic treatment of seafood processing waste waters in an industrial anaerobic pilot plant. Water SA 22 (2), 173–182.
[121] Oude Elferink, S.J.W.H., Visser, A., Hulshoff Pol, L.W., Stams, A.J.M., 1994. Sulphate reduction in methanogenic bioreactors. FEMS Microbiol. Rev. 15, 119–136.
[122]Pan, G., & Kurumada, K. I. (2008). Hybrid gel reinforced with coating layer for removal of phenol from aqueous solution. ChemEng. J., 138, 194-199
[123] Parkin, G.F., Lynch, N.A., Kuo, W., Van Keuren, E.L., Bhattacharya, S.K., 1990. Interaction between sulfate reducers and methanogens fed acetate and propionate. Res. J. Water Pollut. Control Fed. 62, 780–788.
[124] Parkin, G.F., Miller, S.W., 1983. Response of methane fermentation to continuous addition of selected industrial toxicants. In: Proceedings of the 37th Purdue Industrial Waste Conference, West Lafayette, Ind.
[125] Parkin, G.F., Speece, R.E., 1983. Attached versus suspended growth anaerobic reactors: response to toxic substances. Water Sci. Technol. 15, 261–289.
[126] Parkin, G.F., Speece, R.E., Yang, C.H.J., Kocher, W.M., 1983. Response of methane fermentation systems to industrial toxicants. J. Water Pollut. Control Fed. 55, 44–53.
[127] Patel, G.B., Roth, L.A., 1977. Effect of sodium chloride on growth and methane production of methanogens. Can. J. Microbiol. 23, 893–897.
[128] Poggi-Varaldo, H.M., Arce-Medina, E., Feranadez-Vellagomerz, G., Caffarel-Mendez, S., 1998. Inhibition of mesophilic solid substrate anaerobic digestion by ammonia-rich wastes. Proceedings of 52nd Industrial Waste Conference. Ann Arbor Press, Ann Arbor, MI, pp. 55–66.
[129] Pohland, F.G., Ghosh, S., 1971. Developments in anaerobic stabilization of organic wastes – the two-phase concept. Environ. Lett. 1, 255–266.
[130]Quintanilla-Guerrero, F., Duarte-Va’zquez, M. A., Garcı’a Almendarez, B. E., Tinoco, R., Vazquez-Duhalt, R., & Regalado, C. (2008). Polyethylene glycol improves phenol removal by immobilized turnip peroxidase. Bioresour. Technol., 99, 8605–8611.
[131]Rappoport, Z. (2003). The Chemistry of Phenols. John Wiley& Sons, Ltd.
[132] Rinzema, A., Alphenaar, A., Lettinga, G., 1989. The effect of lauric acid shock loads on the biological and physical performance of granular sludge in UASB reactors digesting acetate. J. Chem. Tech. Biotechnol. 46, 257–266.
[133] Rinzema, A., Boone, M., van Knippenberg, K., Lettinga, G., 1994. Bactericidal effect of long chain fatty acids in anaerobic digestion. Water Environ. Res. 66, 40–49.
[134] Rinzema, A., Lettinga, G., 1988. The effect of sulphide on the anaerobic degradation of propionate. Environ. Technol. Lett. 9, 83–88.
[135] Rinzema, A., van Lier, J., Lettinga, G., 1988. Sodium inhibition of aceticlastic methanogens in granular sludge from a UASB reactor. Enzyme Microbiol. Technol. 10, 24–32.
[136] Robbins, J.E., Gerhard, S.A., Kappel, T.J., 1989. Effects of ammonia in anaerobic digestion and an example of digestor performance from cattle manure protein mixtures. Biol. Wastes 27, 1–14.
[137] Schmidt, J.E., Ahring, B.K., 1993. Effects of magnesium on thermophilic acetate-degrading granules in upflow anaerobic sludge blanket (UASB) reactors. Enzyme Microbiol. Technol. 15, 304–310.
[138] Shen, C.F., Kosaric, N., Blaszczyk, R., 1993. The effect of selected heavy metals (Ni, Co, and Fe) on anaerobic granules and their extracellular polymeric substances (EPS). Water Res. 27, 25–33.
[139] Shin, H.-S., Oh, S.-E., Lee, C.-Y., 1997. Influence of sulfur compounds and heavy metals on the methanization of tannery wastewater. Water Sci. Technol. 35 (8), 239–245.
[140] Song, Z., Williams, C.J., Edyvean, R.G.J., 2001. Coagulation and anaerobic digestion of tannery wastewater. Process Saf. Environ. Prot. 79, 23–28.
[141] Soto, M., Mende´z, R., Lema, J.M., 1991. Biodegradability and toxicity in the anaerobic treatment of fish canning wastewaters. Environ. Technol. 12, 669–677.
[142] Soto, M., Mende´z, R., Lema, J.M., 1992. Characterization and comparison of biomass from mesophilic and thermophilic fixed bed anaerobic digesters. Water Sci. Technol. 25, 203–212.
[143] Soto, M., Mende´z, R., Lema, J.M., 1993a. Methanogenic and nonmethanogenic activity tests: theoretical basis and experimental setup. Water Res. 27, 1361–1376.
[144] Soto, M.,Mende´z, R., Lema, J.M., 1993b. Sodium inhibition and sulphate reduction in the anaerobic treatment of mussel processing wastewaters. J. Chem. Tech. Biotechnol. 58, 1–7.
[145] Soubes, M., Muxı´, L., Ferna´ndez, A., Tarlera, S., Queirolo, M., 1994. Inhibition of methanogenesis from acetate by Cr3+ and ammonia. Biotechnol. Lett. 16, 195–200.
[146] Sterritt, R.M., Lester, J.N., 1980. Interaction of heavy metals with bacteria. Sci. Total Environ. 14 (1), 5–17.
[147] Stickley, D.P., 1970. The effect of chloroform in sewage on the production of gas from laboratory digesters. Water Pollut. Control 69, 585–590.
[148] Stuckey, D.C., Owen, W.F., McCarty, P.L., 1980. Anaerobic toxicity evaluation by batch and semi-continuous assays. J. Water Pollut. Control Fed. 52, 720–729.
[149] Stucki, G., Hanselman, K.W., Hu´ rzeler, A., 1993. Biological sulphuric acid transformation: reactor design and process optimization. Biotechnol. Bioeng. 41, 303–315.
[150]Summers, A.O., 1986. Organization, expression and evolution of genes for mercury resistance. Annu. Rev. Microbiol. 40, 607–634.
[151] Sung, S., Liu, T., 2003. Ammonia inhibition on thermophilic digestion. Chemosphere 53, 43–52.
[152] Swanwick, J.D., Shurben, D.G., Jackson, S., 1969. A survey of the performance of sewage sludge digesters

in Great Britain. J. Water Pollut. Control Fed. 68, 639–653.

[153] Takashima, M., Speece, R.E., 1989. Mineral nutrient requirements for high rate methane fermentation of acetate at low SRT. Res. J. Water Pollut. Control Fed. 61 (11–12), 1645–1650.

[154] Thiele, J.H., Wu, W.-M., Jain, M.K., Zeikus, J.G., 1990. Ecoengineering high rate anaerobic digestion systems: analysis of improved syntrophic biomethanation catalysts. Biotechnol. Bioeng. 35, 990–999.

[155] Vallee, B.L., Ulner, D.D., 1972. Biochemical effects of mercury, cadmium, and lead. Annu. Rev. Biochem. 41, 91–128.

[156] Vallero, M.V.G., Hulshoff Pol, L.W., Lens, P.N.L., Lettinga, G., 2002. Effect of high salinity on the fate of methanol during the start-up of thermophilic (55 _C) sulfate reducing reactors. Water Sci. Technol. 45 (10), 121–126.

[157] Vallero, M.V.G., Hulshoff Pol, L.W., Lettinga, G., Lens, P.N.L., 2003a. Effect of NaCl on thermophilic (55 _C) methanol degradation in sulfate reducing granular sludge reactors. Water Res. 37, 2269–2280.

[158] Vallero, M.V.G., Lettinga, G., Lens, P.N.L., 2003b. Long-term adaptation of methanol-fed thermophilic (55 _C) sulfate-reducing reactors to NaCl. J. Ind. Microbiol. Biotechnol. 30, 375–382.

[159] van Langerak, E.P.A., Gonzales-Gil, G., van Aelst, A., van Lier, J.B., Hamelers, H.V.M., Lettinga, G., 1998. Effects of high calcium concentrations on the development of methanogenic sludge in upflow anaerobic sludge bed (UASB) reactors. Water Res. 32 (4), 1255–1263.

[160] van Staikenburg, W., 1997. Anaerobic treatment of wastewater: state of the art. Microbiology 66, 589–596.

[161] Van Velsen, A.F.M., 1979. Adaptation of methanogenic sludge to high ammonia-nitrogen concentrations. Water Res. 13, 995–999.

[162] Van Velsen, A.F.M., Lettinga, G., den Ottelander, D., 1979. Anaerobic digestion of piggery waste. 3. Influence of temperature. Neth. J. Agric. Sci. 27, 255–267.

[163] Vipulanandan C., Wang S. and Krishnan S., “Biodegradation of phenol remediation of hazardous wastes contaminated soils”, Marcel Dekker, New York, 1994.

[164] Visser, A., Nozhevnikova, A.N., Lettinga, G., 1993. Sulphide inhibition of methanogenic activity at various pH levels at 55 _C. J. Chem. Tech. Biotechnol. 57, 9–14.

[165] Whittmann, C., Zeng, A.P., Deckwer, W.D., 1995. Growth inhibition by ammonia and use of pH-controlled feeding strategy for the effective cultivation of Mycobacterium chlorophenolicum. Appl. Microbiol. Biotechnol. 44, 519–525.

[166] Wiegant, W.M., Zeeman, G., 1986. The mechanism of ammonia inhibition in the thermophilic digestion of livestock wastes. Agric. Wastes 16, 243–253.

[167] Winfrey, M.R., Zeikus, J.G., 1977. Effect of sulfate on carbon and electron flow during microbial methanogenesis in freshwater sediments. Appl. Environ. Microbiol. 33, 275–281.

[168] Xun, L., Boone, D.R., Mah, R.A., 1988. Control of the life cycle of Methanosarcina mazei S-6 by manipulation of growth conditions.Appl. Environ. Microbiol. 54 (8), 2064–2068.

[169] Yerkes, D.W., Boonyakitombut, S., Speece, R.E., 1997. Antagonism of sodium toxicity by the compatible solute betaine in anaerobic methanogenic systems. Water Sci. Technol. 37 (6–7), 15–24.

[170] Yu, H.Q., Tay, J.H., Fang, H.H.P., 2001. The roles of calcium in sludge granulation during UASB reactor start-up. Water Res. 35 (4), 1052–1060.

[171] Zayed, G., Winter, J., 2000. Inhibition of methane production fro whey by heavy metals-protective effect of sulfide. Appl. Microbiol. Biotechnol. 53, 726–731.

[172] Zeeman, G., Wiegant, W.M., Koster-Treffers, M.E., Lettinga, G., 1985. The influence of the total ammonia concentration on the thermophilic digestion of cow manure. Agric. Wastes 14, 19–35