Use of construction waste in the removal of Hydrogen Sulfide

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XI Brazil-Japan International Workshop. IFSP-Caraguatatuba; Universidade Estadual de Campinas; Gifu University; Tokyo University of Agriculture and Technology. Caraguatatuba [SP], Brasil. 11/09/2013. [Conpadre n.16/2013].

Abstract
The human being has been using the biodegradation principle into the effluent sewage treatment in order to achieve the standards of quality required for the release of effluent in the water bodies' receivers. However, under anaerobic conditions, there is the formation of gaseous compounds such as carbon dioxide and methane, the damage happens when the effluent contains sulfur compounds, resulting in the formation of sulfide hydrogen, toxic gas, offensive and corrosive odor, requiring treatment. This paper presents an overview of the use of the construction waste, which should receive special attention in the management of solid waste, the removal of this gas, presenting a potential field of study, given the high rates and low efficiency obtained cost of implementation and operation.

Keywords
Alkaline system, biogas, H_2S, wastewater treatment.

MEIRA, L. H. R.; CALHEIROS, H. C. Use of construction waste in the removal of Hydrogen Sulfide. **Labor & Engenho**, Campinas [Brasil], v.7, n.4, p.47-56, 2013. Disponível em: <www.conpadre.org>.

Introduction

For a long time the raw sewage has being released into the receiving bodies or soil, however when there is no proper treatment it might occur the deterioration of the environment as a whole or, as the characteristics of the effluent and environmental conditions, it can be purged by the action of microorganisms that reduce the matter (ANDRADE NETO; CAMPOS, 1999).

Observing the action of these degrading microorganisms, which promotes a series of anabolic and catabolic reactions to convert the organic matter, human beings started to use them in effluent treatment plants (WWTP), resulting into the reduction of the hydraulic retention time and increasing the efficiency of degradation reactions, getting faster and effective treatment, reaching the standards established by the specific legislations. However, when the treatment occurs in the absence of oxygen catabolism there is the formation of gaseous compounds such as carbon dioxide (CO_2) and methane (CH_4) (ANDRADE NETO; CAMPOS, 1999; MIKI, 2010).

The anaerobic systems have some advantages when compared to the aerobic system (table 1), mainly in the categories of implementation, operation costs and area demanding for its operation, on the other hand they produce large amounts of biogas, which depending on their composition can exhale a bad odor, among other problems. It is estimated that in the anaerobic treatment the conversion rate of organic matter into biogas is within 70 to 90%, the remainder is expected from 5 to 15% to be incorporated into the sludge and from 10 to 30% is not degraded as shown in Figure 1 (CHERNICHARO *et al*., 1999; 2001).

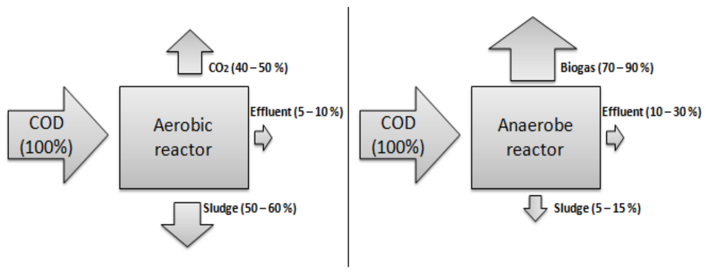

Figure 1. Differences of the conversion in aerobic and anaerobic systems. Source: Chernicharo *et al.* 2001.

Table 1. Advantages and disadvantages of the anaerobic treatment.

ADVANTAGES	DISADVANTAGES
Low cost to install and operate	Long time to match system
Efficient removal of BOD and COD with a 65-75% range	
Easy operability	Exhaling of bad odors
Easily dehydrated sludge	Post-treatment is required
Small area for its construction and operation	
Little solids production	Low toxic loads toleration
Quick restart after long stagnation	

Source: Cernicharo et al. 1999.

Recalling that in the absence of oxygen for the production of gaseous compounds, mainly CO_2 and CH_4 as a result from the biological degradation of organic matter it is important to note that the CH_4 may be used as biofuel. However, when the effluent contains sulfur compounds, the reaction of this substrate and sulfate-reducing bacteria combined with anaerobic condition results into the formation of hydrogen sulfide gas (H_2S), a process called sulfidogenic. This gas is toxic, smelly (characteristic odor of rotten eggs) and corrosive. Generally, the biogas produced during the anaerobic digestion contains from 70 to 80% of methane, 10 to 25% of nitrogen, 5 to 10% of carbon dioxide and hydrogen sulfide in the range from 0.11 to 0, 39% (AGRAWAL; HARADA; OKUI, 1997; GLÓRIA, 2009; NOYOLA; MORGAN-SAGASTUME; LÓPEZ-HERNÁNDEZ, 2006; SOUZA, 2010).

To use the biogas for power generation, it must be purified (mainly for the removal of water and sulfide hydrogen) with the goal of raising its calorific value and increase the lifetime and performance of the equipment, besides power generation facilities (COELHO *et al.,* 2006).

Equation 1 represents the sulfate reduction process which results into the formation of H_2S (ALVES *et al.*, 2004).

$$CH_3COOH + SO_4^{-2} + 2\ H + \rightarrow H_2S + 2\ H_2O + 2\ CO_2 \text{ (Equation 1)}$$

Table 2 contains the main advantages and disadvantages of hydrogen sulfide formation in the anaerobic treatment.

Table 2. Advantages and disadvantages of the formation of H_2S.

ADVANTAGES	DISADVANTAGES
Removal of oxidized sulfur compounds (sulfate, sulfite and thiosulfate)	COD removal efficiency reduction
	Corrosion
Removal of heavy metals	Inert material accumulation such as metal sulfides in the sludge
	Methane formation decrease
Metal sulfide precipitation	Biogas quality decrease, requiring its removal
	Odor exhalation
	Toxic potential

Source: POL et al. (1998).

The WWTPs that use the anaerobic treatment produce biogas. However, the untreated biogas emission into the atmosphere creates a problem relating to the stations which are installed near the housing area, as the population has rejected these practices due to the presence of odor, health problems associated to odoriferous substances and estate speculation (BELLI FILHO; LISBOA, 1999; BELLI FILHO *et al.*, 1999; LILIAMTIS; MANCUSO, 2003; SILVA, 2007).

Krischan, Makaruk and Harasek (2012) highlight the importance of studying a H_2S removal selective technique, further using cheap and environmentally safe reagents.

This article presents an overview of the potential use of construction waste, which is a problem for solid waste management during the hydrogen sulfide gas treatment.

Hydrogen sulfide and its main characteristics

Studies have been conducted to better understand the effect of hydrogen sulfide on the human body when exposed to low concentrations, since the biggest part of the investigations are performed after leakage accidents of this gas. There are also researches aiming to evaluate occupational exposures in limited populations. It is known that the population most susceptible to the effects of toxic H_2S are fetuses, cardiac, asthmatic children (large volume of inspired air in relation to their weight) and alcohol consumers (SANDRES; MAINER, 2009; WHO, 2003).

In the human body the gas penetrates the alveoli wall reaching then the bloodstream, where it is neutralized and oxidized. However, in the presence of enzymes that contain metals, this gas can react culminating into metal sulfides formation, which leads to sensitivity loss. In more severe cases, when the concentration of inhaled H_2S exceeds the body's ability to oxidize it, hydrogen sulfide remains in its original structure resulting in neurological effects and it can lead to respiratory arrest and consequently death (MAINIER; VIOLA, 2005).

Table 3 contains the main effects of hydrogen sulfide on human health according to the inhaled concentration and exposure time.

Table 3. Effects on human health due to H_2S exposure.

H2S CONCENTRATION (PPM)	EXPOSURE TIME	EFFECT IN HUMANS
0,05 to 5	1 minute	Odor characteristics detection
10 to 30	6 to 8 hours	Eye Irritation
50 to 100	30 minutes to 1hour	Conjunctivitis, breathing difficulties
150 to 200	2 to 15 minutes	Smell loss
250 to 350	2 to 15 minutes	Eye Irritation
350 to 450	2 to 15 minutes	Unconsciousness, convulsions
500 to 600	2 to 15 minutes	Breathing and circulatory disturbances
700 to 1500	0 to 2 minutes	Collapse, death

Source: MAINER; VIOLA, 2005.

Campagna *et al.* (2004) conducted a survey in order to correlate the exposure of the citizens from South Dakota and Sioux, during the years 1998 and 2000, to reduced sulfur compounds and to H_2S with the cases of asthma and other respiratory diseases increase. The authors indicate an association between these compounds and the studied effects, requiring protection for the residents who live in areas where there is emission of these compounds.

On the other hand, Liliamtis and Mancuso (2003) studied the odor perception of hydrogen sulfide coming from a wastewater treatment plant in the city of Pereira Barreto - São Paulo. The authors reported there was a complaint about odor of "rotten eggs" in addition to health problems, such as headaches, nausea, mood swings and dizziness. These symptoms disappeared when the WWTP started applying ammonium nitrate to minimize such odors.

Besides health problems, the hydrogen sulfide is potentially corrosive and it can cause chemical corrosion (it occurs in the absence of water) or electrochemical corrosion where hydrogen sulfide acts directly on metal, concrete, or other compounds present in the structures of the stations and structures close to the gas emitting source (LAHAV *et al.*, 2004; SANDRES; MAINIER, 2009).

According to the Environmental Protection Agency (EPA, 1991) this gas can quickly cause damage to concrete, metal pipes, equipment, instruments and electrical control and in large quantities.

A case study in Burdekin Shire Council (North Queensland, Australia) identified a number of failures that occurred in the tubes of the sewer / storm water and sluice gates, culminating into the break of 345 meters from the main pipe system. After the event the tubing was covered with PVC before reestablishing the sewage flow, because it was detected that the corrosion occurred due to the presence of hydrogen sulfide in the system which is operated under gravity (CHANDLER; TICKNER, 2011).

Civil Construction waste in H_2S removal

One way that hydrogen sulfide gas has been treated is the application of an alkaline system, where the gas passes through a column containing the reagent material. The choice of an alkaline compound is based on the fact this condition facilitates the absorption / adsorption (CANAS, 1986; NOYOLA; MORGAN-SAGASTUME; LÓPEZ-HERNÁNDEZ, 2006 apud MANSFIELD *et al.*, 1992).

Furthermore, Chernicharo *et al.* (2010) claims that the adsorption presents a moderate cost, easy operability, requires a small area for its construction, it also requires little retention time, and it is stable and can remove the gas in a selective way depending on the applied adsorbent.

Participating countries of ECO 92 pledged with certain measures contained in Agenda 21. An important aspect of this text is the highlight of the recycling importance through solid waste management plan. Over 50% of this waste is originated from construction and demolition, also studies that aim to find a way to reuse them are primarily important. A concern about these residues is that civil works will always exist because there will be constructions, demolitions and renovations (MENEZES; PONTES; AFONSO, 2011).

Unfortunately, a way to dispose these wastes is to place them into vacant lots, public areas and water bodies. Another major part is discarded in landfills, which can cause the contamination of the area if its composition contains harmful materials such as solvents and fluorescent lamps. Generally, these wastes contain concrete, plaster, wood, cement, pipes among other materials depending on the type of work (MENEZES; PONTES; AFONSO, 2011).

Table 4 contains the percentages of construction and demolition waste types.

Table 4. Percentage of waste from construction and demolition.

RESIDUE / PERCENTAGE	
SOIL / 32 %	
CERAMIC / 63 %	CONCRETE / 13%
	MORTAR (hardened cement and lime) / 40%
	POTTERY (bricks, tiles, ceramics, tile, glass, plaster) / 47%
OTHER (metals and organic materials) / 5 %	

Source: MENEZES; PONTES; AFONSO (2011).

According to Table 4, it can be seen that most of the residues belong to the group of ceramics, and among them there are alkaline materials such as calcium oxide (CaO - lime), which can react with hydrogen sulfide according to the equation 2 (EFTHIMIADIS; SOTIRCHOS, 1992) and therefore it is a good compound to be used in a column of this type of system.

$$CaO(s) + H_2S \rightarrow CaS(s) + H_2O \text{ (Equation 2)}$$

Other material of potential use would be the concrete because it has similar alkaline characteristics to lime, making its study interesting in the hydrogen sulfide removal (XU; TOWNSEND; BITTON, 2011).

On the other hand, mortar can also be reused for the removal of hydrogen sulfide, since it is composed of mineral aggregates and binders, such as cement, hydrated lime, hydraulic lime, gypsum and chemical adjuvants (Paul, 2006).

Some research has been conducted in order to understand the reaction of calcium oxide with H_2S, like Efthimiadis and Sotirchos' (1992), who investigated through thermogravimetry and structural study of nonreactive solid after the biogas adsorption process, the reaction from lime derivatives (with a high content of calcium carbonate> 95%) with a mixture containing the hydrogen sulfide and nitrogen gases (N_2). The calcination was carried out in the temperature range of 750-850 ° C and sulfation occurred at temperatures from 650 to 750 ° C. The authors noticed that there is a strong correlation between particle size and rate of CaO reactivity, because smaller particles (53-105 mM) had a bigger conversion rate of CaS to CaO in a shorter period of time when compared to particle with sizes of 210-350 micrometers. In addition, they also could conclude that the calcination temperature influences the subsequent reactions, however the temperature of sulfation showed no significant relation to the conversion process, because at different temperatures the conversion rates were close, reaching its maximum efficiency at about 5 minutes for smaller particles (up to 100% conversion) and 10 minutes for the larger particles (with conversion to the order of 80%).

Another study in this aspect is Sohn and Won's (1985), who evaluated the reaction of CaO with hydrogen sulfide through a thermogravimetric experiment, for this they used H_2S with 99.5% purity, along with helium (99, 9955 purity), hydrogen gas (99.98% pure) and calcium oxide in a single batch. They observed that for a quantity of powdered CaO 46 ± 1.3 mg and 750 ° C and higher flow rates of 1.03 dm3 per minute, the speed of the reaction is independent of the flow gas rate. They also verified that the sample of lime with a lower moisture content has a lower reaction rate than a sample with a higher moisture content, for example, the initial reaction rate of a lime sample with initial moisture content 13 9% was about nine times greater than one of a sample with a moisture content of 0.9%, this may be due to the increased contact surface (porosity). Another study reported that the reaction rate increases with rising temperature, with an initial rapid reaction followed by a period of very low speed. Finally, they could also conclude that the higher the concentration of H_2S, the higher the conversion rate, and the reaction of the lime powder with hydrogen sulfide has an energy of energy of 76.1 kJ / mol.

Regarding to the use of construction waste, and construction and demolition in the removal of hydrogen sulfide, some researchers have obtained significant results, such as Xu, Townsend and Reinhart (2010) who concluded in his research that covering of landfill with sandy soil modified with hydrated Lime (1% to 3%) results in an efficiency of 90% adsorption of H_2S after 10 minutes.

Yang *et al.* (2006), on the other hand, declare in their study that the concrete placed in landfill reduces the production of hydrogen sulfide by the increase of pH, discouraging the action of sulfate-reducing bacteria, or performing a process of adsorption or absorption of this gas.

And Plaza *et al.* (2007), in their study, investigated kinds of materials for covering landfill and evaluated that the thin concrete (particles 2.5 centimeters or less) was obtained in 99.3% efficiency in removing hydrogen sulfide, and is more efficient than the thick concrete (particles 2.5 centimeters or more) who obtained the removal rate of 2.4%.

Finally, Xu, Townsend and Reinhart (2010) conducted a field study and in laboratory scale, in order to test different soil covers for landfill that reduce the emission of hydrogen sulfide gas (H_2S). First of all, in the study field, emissions of H_2S were measured in a landfill with different cover crops, then the experiment was conducted in a laboratory in order to support the results obtained in the field. They evaluated the use of sandy soil, compost yard, thin concrete, sandy soil modified with hydrated lime (1% and 3%) and sandy soil modified with 10% of agricultural lime (CaCO3), as a landfill cover to mitigate the emission of hydrogen sulfide. They concluded that the thin concrete was the most efficient in the removal of hydrogen sulfide, reaching 90% in 5 minutes adsorption.

Final considerations

It is noticed that most of work that uses construction waste in hydrogen sulfide removal is focused on the application of them as landfill cover, however, this idea can be used, once it applies these materials in alkaline systems columns to support wastewater treatment plants, as a cheap and effective alternative in of H_2S treatment, avoiding problems associated with corrosion coming from this gas and its toxic effects to human beings.

Finally, it’s concluded that the study of construction waste is very important for this purpose, because this system is easy to be operated, has a low cost and is environmentally correct.

Acknowledgements

This research was supported by the Coordination for the Improvement of Higher Education Personnel (CAPES) and the Sanitation Research Group at Itajubá Federal University (GES/UNIFEI).

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