

# 1 Introduction

The use of anaerobic sewage treatment in tropical regions is a consolidated practice as primary treatment (van Haandel and Lettinga, 1994; Chernicharo, 1997; van Starckenburg 1997; Foresti, 2001; Wiegant 2001, Jordao and Volschan 2004, Mbuligwe, 2004; Aiyuk, 2004). The attributes of an anaerobic process that render it an attractive and appropriate option include the requirement of low initial investment and energy for operation, lower sludge production and easier maintenance compared to conventional aerobic processes (Van Haandel and Lettinga, 1994; Kalogo and Verstraete, 2001).

However, it is recognized that a sulphate-rich wastewater can cause some significant problems resulting from sulphate reduction in the anaerobic treatment process. In anaerobic conditions the sulphate-reducing bacteria start to work, breaking down the organic matter by sulphate respiration and thus producing hydrogen sulphide. Hydrogen sulphide,  $H_2S$ , is toxic to aquatic animal life in very low concentrations and has a very unpleasant odour. The threshold limit value for fresh or salt water fish is 0.5 ppm (EPS, 1984).

Because of the toxicity of sulphide and last but not least also due to the bad odour of  $H_2S$ , such anaerobically pre-treated wastewater needs further steps of post-treatment. For sulphide oxidation/detoxification in wastewater several methods are available such as chemical oxidation (Fagan and Walton, 1999; Witherspoon et al., 2004) using hydrogen peroxide ( $H_2O_2$ ), sodium hypochlorite ( $NaOCl$ ) and iron chloride ( $FeCl_3$ ). Physical methods include the use of activated carbon (Boudou et al., 2003), but the regeneration cycles and the costs of the chemicals are disadvantageous. Another possibility to control the problem is by microbial processes in special bioreactor with phototrophic bacteria but the need of light sources and intensity are not economically

appropriate technologies for implementation in Latin America.

Due to restricted financial budgets simple methods/systems like ponds or wetlands are often preferred (Kadlec and Knight, 1996; Al-Malack et al., 1998; Mbuligwe, 2004). The wastewater treatment in constructed wetlands is a relatively new emerging technology with some advantages: no energy for aeration is needed – roots of special plants (helophytes) allow the transport of oxygen to the rooted soil (Armstrong et al., 1990). Different variations of water flow can be realized (surface flow and subsurface flow); by this direct transfer of the volatile  $\text{H}_2\text{S}$  into the atmosphere can be minimized. There are a lot of reports about carbon and nitrogen removal (Kadlec et al., 2000; Vymazal, 2002; Stottmeister et al., 2003; Sousa et al., 2003; Mashauri et al., 2003; García et al., 2004; Kaseva, 2004). Comparably, knowledge regarding the dynamics of sulphur compounds like sulphate, sulphide, elemental sulphur etc., under the gradient redox conditions in constructed wetlands is still limited (Wiessner et al., 2005a).

In the past, little attention has been paid to the sulphur metabolism in constructed wetlands. In the case of an industrial wastewater loaded with  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  (area-specific load of  $1.1 \text{ g S m}^{-2}\text{d}^{-1}$ ) and without significant concentrations of heavy metals, Winter and Kickuth (1989a) showed that constructed wetlands can act as an important sink for sulphur. However, the importance of the sulphur transformation processes in the case of treatment of domestic wastewater has not yet been sufficiently evaluated (Wiessner et al., 2005a), even more sulphide oxidation, immobilization/remobilization of sulphide and elemental sulphur transformation with other redox processes and the toxic effect of sulphide upon plants and microorganisms.

In model experiments with a laboratory-scale constructed wetland Wiessner et al. 2005a showed that also the sulphate-sulphur of domestic sewage can play an important role as

an electron acceptor for the removal of the organic carbon load and influences the ammonia removal.

Knowledge regarding the dynamics of sulphide, elemental sulphur, sulphite, thiosulphate, polythionates, sulphate, etc. and their interactions under gradient redox conditions in planted soil filters is highly limited. According to the interactive potential of sulphur species in wetland systems, it has been ascertained that:

- Sulphur input to wetlands may cause sulphur deposits of elemental and organic sulphur (Winter and Kickuth, 1989b), but the balances were mostly incomplete and there exist no information about the remobilization, particularly under redox-dynamic conditions;
- Sulphate in wetlands initiates Eh and pH changes, C-transformation and, indirectly the mobilization of nutrients (Feng and Hsieh, 1998; Lamers et al., 1998)— all these processes are of importance for carbon, nitrogen, phosphorous-removal but not yet sufficiently evaluated;
- Sulphide may be highly toxic to microorganisms and macrophytes, and is a competitor for the consumption of oxygen (Armstrong et al., 1996a; Chambers et al., 1998; Lee, 1999; Koch et al., 2001; Pedersen et al., 2004);
- The potential microorganisms of the sulphur cycle coexist very closely with all other microorganisms involved in the removal processes in microbial mats and sediment layers, especially under micro-scale gradient conditions (Overmann and van Gemerden, 2000; Liesack et al., 2000; Blaabjerg and Finster, 1998; Wind and Conrad, 1997).

Therefore, the role of sulphide loads of wetlands for the post-treatment of anaerobically treated domestic wastewater should be revisited in terms of treatment effectiveness. The

sulphur-cycle processes inside the rhizosphere and their role in the complex network of transformation processes are necessary for better understanding of the “black box” rhizosphere and for optimum design and operation of wetland systems.

Using a system of planted fixed bed reactor- PFBR and planted and unplanted laboratory-scale subsurface horizontal flow constructed wetlands concentrations of reduced sulphur species and hydraulic loading condition were varied and the dynamics of sulphur compounds, removal efficiencies and constitution of the plants were evaluated.

### **1.1 Objectives**

The objective of this work is to assess the effects of the plants on the cycling of sulphur compounds in wetland prototypes. The research was focused on following aspects:

- Toxicity of sulphide to plants
- Nature of sulphur compounds formed within the different zones of the constructed wetland
- The effectiveness of constructed wetlands to remove S-compounds
- Possibilities for improvements of sulphide removal in constructed wetlands

### **1.2 Problem**

The developing countries face the enormous challenges of promoting quality of life usually under very adverse condition of financial resources availability. Sanitation, environmental protection and natural resources conservation are among those items that

have deserved less attention and received less investment that needed for the improvement of living conditions. For these countries, the option for low cost systems that provide sanitation associated to environmental protection and natural resources conservation is mandatory.

The applicability of anaerobic reactors for the treatment of domestic sewage is definitively established in tropical and sub-tropical regions. It is well known that effluents from anaerobic reactors cannot be discharged into receiving water without further post-treatment. In this way, the search for post-treatment alternative arose to permit the application of anaerobic reactors even under very restrictive situations.

The search for alternative solutions related to wastewater treatment systems has taken advantages of some favourable environmental condition that amplify the range of applications of non-conventional systems. This is the case of the anaerobic processes for wastewater in some developing countries, including Colombia.

The effluent of Up Flow Anaerobic Sludge Blanket- UASB contains sulphide concentration of about 10-20 mg L<sup>-1</sup> ("Rio Frio", wastewater treatment plant, Bucaramanga-Columbia, 2004) and the legal limits of sulphide concentration in wastewater are in a range of 1 - 2 mg L<sup>-1</sup> (Zartner-Nyilas and Deutsch, 2004). It means that anaerobic effluent cannot be discharged directly in the water bodies; a second post-treatment step is necessary. In order to remove these contaminants, biological treatments are preferred technologies rather than physical-chemical methods, which are expensive and may generate toxic residues.

The anaerobic digestion step can be linked with further treatment in a constructed wetland but because of insufficient experiences some questions such as possible sulphide toxicity effects on plants, the transformation processes of the sulphur

compounds, the different redox processes turnover in the rhizosphere of helophyte and other influencing factors are unknown.

## 2 Literature Review

### 2.1 Chemical methods for H<sub>2</sub>S removal in wastewaters

There are numerous chemical compounds available to control H<sub>2</sub>S odour. Although these chemicals can oxidize H<sub>2</sub>S, their use depends on environmental, economic and operational conditions, which make it highly different for each application.

**Chlorine gas** (Cl<sub>2</sub>), environmental and safety concerns surrounding its use are some of the disadvantages and the use of Cl<sub>2</sub> produces chlorinated by-products (Fagan and Walton, 1999).

**Sodium hypochlorite** (NaOCl) is an oxidant that oxidizes sulphide to sulphate. This compound does not act selectively for sulphide; therefore, the actual dose required depends on other chemicals/materials present within the wastewater to be treated (Witherspoon et al., 2004). Chlorine is not regenerated in the process, so it may result in a high operational cost. Moreover, in the presence of organic compounds, chlorine oxidation is not attractive due to the formation of undesirable organic chloride compounds.

**Hydrogen peroxide** (H<sub>2</sub>O<sub>2</sub>), the oxidation rate of sulphide with hydrogen peroxide is relatively slow (Cadena and Peters, 1998). Twenty to 30 min contact time is normally required for a complete reaction. The mechanism of oxidation of H<sub>2</sub>S by hydrogen peroxide is not well understood; however, it is suggested that direct oxidation of sulphide by hydrogen peroxide depends on the reaction with oxygen released during gradual decomposition of hydrogen peroxide. The benefits of its use include dissolved