

Treatment of recycled wastewaters from fishmeal factory by an anaerobic filter

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Fishmeal industries processes produce effluents with high load organic matter. These effluents, after recycling and physical-chemical pretreatment, have a high organic content (5–6 g COD/l), proteins (3–5 g/l), salinity close to sea water, sodium chloride (30 g/l) and sulphate (1–3.3 g/l). An anaerobic filter was used for the treatment of this wastewater, with marine sediment as anaerobic inoculum. Anaerobic filter removed up to 70% of the influent COD concentrations at organic loading rates (OLR) of 9.5 and 14.3 (g/l-d) and sulphate up to 80% at OLR of 7.1 and 14.3 (g/l-d) whereas the pH ranged between 7.0 and 7.5. These results show that anaerobic filter systems are applicable to recycled wastewaters from fishmeal.

Introduction

The process of fish meal production involves the hydraulic discharge of fishes from ship loads with loss of soluble proteins to the sea (Roeckel *et al.*, 1996). Recycling the water used in the fish unloading from ships to factories will reduce the environmental impact (Roeckel *et al.*, 1994). These recycled fishmeal wastewaters show high contents of chemical oxygen demand (COD) protein and salinity (sodium, chloride, sulphate) (Roeckel *et al.*, 1996). Several configurations of fixed biomass anaerobic reactors have been successfully developed and applied to the treatment of fish canning factory effluents, reaching high organic loading rates (OLR) (Soto *et al.*, 1993; Veiga *et al.*, 1994).

The anaerobic filter (AF) is able to treat effluents, with high soluble COD and high OLR when used as a recycle reactor. Other properties include a fast start-up and stability towards hydraulic, organic, toxic or pH overloads, and ability to work with intermittent feeding, useful when dealing with fish industry effluents (Veiga *et al.*, 1994). This work demonstrates the start-up operations and efficiency key parameters of an AF reactor treating recycled fish meal effluents showing high salinity.

Materials and methods

Anaerobic filter reactors

The AF (Figure 1) was operated at 37°C. The reactor was 44.5 cm height and 8.5 cm internal diameter with a working volume of 2.5 l. The supporting material consisted of corrugated PVC Rashing rings of 1.6 cm

diameter with a specific surface of 270 m²/m³, leaving 20% v/v for the head space with a device to allow solid/liquid/gas separation. The recirculation ratio was 10:1; assuming more than 90% of the reactor volume as mixed, as shown in Figure 2. The reactor performance was continuously assessed by means of determination of flow rate and composition of the influent and effluent, biogas production and composition. The COD removal (%COD_r) and sulphate removal (%SO_{4r}) were used as criteria of process efficiency. The percentage of methanization (%M) is defined as the fraction of COD transformed into methane.

Inoculum

The inoculum was obtained from marine sediment and was treated according to Urrutia *et al.* (1993).

Analytical methods

The following parameters: Volatile Suspended Solid (VSS), Total Suspended Solid (TSS), Chemical Oxygen Demand (COD), Protein, Total Kjeldahl Nitrogen (TKN) and Sulphate were measured by Standard Methods (APHA, 1985). The intermediate alkalinity (IA) and total alkalinity (TA) were measured according to Ripley *et al.* (1986). Gas production in the reactor was measured with gas-meter. Gas composition (CH₄ and CO₂) was analyzed with a Hach Carle, Series 100 AGC, gas chromatograph using a thermal conductivity detector. The oxidation-reduction potential and ammonium-nitrogen were measured using an ion selective electrode.

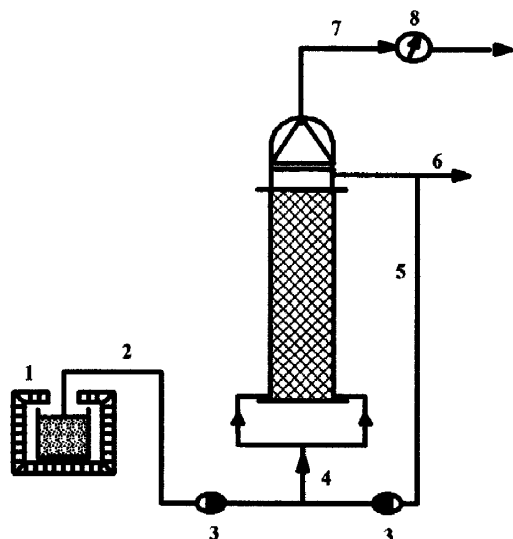


Figure 1 Upflow anaerobic filter. 1: stock feed; 2: feed; 3: pump; 4: influent; 5 recycle; 6: effluent; 7: gas; 8: gas meter.

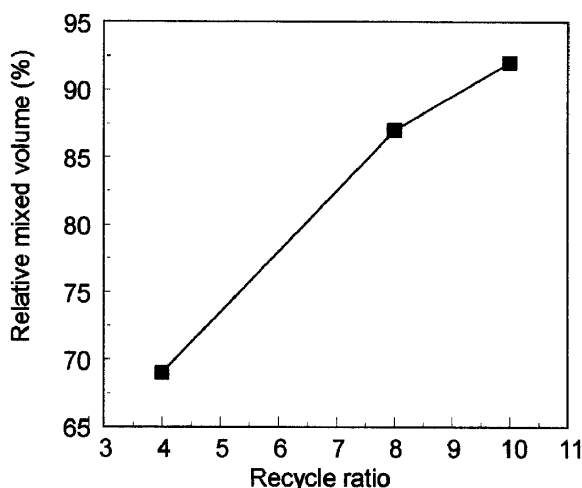


Figure 2 Mixed volume in the AF.

Table 1 Wastewater characteristics from recycling internal process.

Parameters	Value
pH	6 – 7
COD (g/l)	5.0 – 6.3
TSS (g/l)	11.0 – 22.0
VSS (g/l)	3.9 – 8.0
TKN (g/l)	0.48 – 0.8
Protein (g/l)	3.0 – 5.0
Phosphates (mg/l)	6.5 – 6.7
Sulphates (g/l)	0.98 – 3.3

COD: Chemical Oxygen Demand. TSS: Total Suspended Solid. VSS: Volatile Suspended Solid. TKN: Total Kjeldahl Nitrogen.

Anaerobic batch assay

The methodology used for the tests of anaerobic methanogenic activity and methanogenic toxicity assays was that described by Soto *et al.* (1993).

Wastewater

The wastewaters used to feed the reactor were effluents coming from the internal recycling process, pretreated according to Martí *et al.* (1994). As can be seen in Table 1, this raw effluent contains high concentrations of organic matter (COD) and proteins. No additional nutrients were used since the COD/N/P ratio was larger than 600/7/1.

Results and discussion

Figure 3 shows the AF performance with reference to the OLR, pH, and alkalinity ratio. During the start-up of the AF, a stepwise increase of COD loading was used (Figure 3), with an initial OLR of 0.76 g/l·d for 25 days. Then, as HRT decreased, the OLR increased to 1.53 g/l·d. The pH ranged between 8 and 9; after the 50th day it stayed almost stable, with values between 7 and 7.5, by keeping the value of the total alkalinity above 6 g CaCO₃/l and the alkalinity ratio between 0.05 and 0.25 (see Figure 3C).

Concentrations of 30 g NaCl/l in this wastewater had no toxic effect due high salinity, attributed either to the use of a marine sediment as inoculum (Urrutia *et al.*, 1993), or to anaerobic bacterial adaptation to concentrations over 9 g Na⁺/l (Veiga *et al.*, 1994), and over 10 g Cl⁻/l (Veiga *et al.*, 1994; Soto *et al.*, 1993).

Figure 4 shows the percentage of methanization (%M), COD removal (%CODr) and sulphate removal (%SO₄r) with reference to OLR.

The maximal %M and %CODr values were obtained at an OLR of 7.1 g/l·d. Sulphate abatement also increased with greater OLRs because of the available COD content. The effect of sulphate on methanogenesis was a reduction of methane yield per unit of converted COD. During anaerobic treatment, the reduction of 1.5 g SO₄⁻² requires the oxidation of 1 g COD, resulting in a decrease of 233 l in the methane yield for every 1 g SO₄⁻² reduced (Veiga *et al.*, 1994).

Figure 5 shows the methanogenic toxicity due to the sulphide produced from sulphate reduction. It can be seen that 7 g SO₄⁻²/l produced an activity reduction of 50% for this type of biomass; this value is high compared to 120 mg H₂S/l, reported by Koster *et al.* (1986). Concentrations in the AF effluent up to 1 g H₂S/l were found, while the pH ranged between

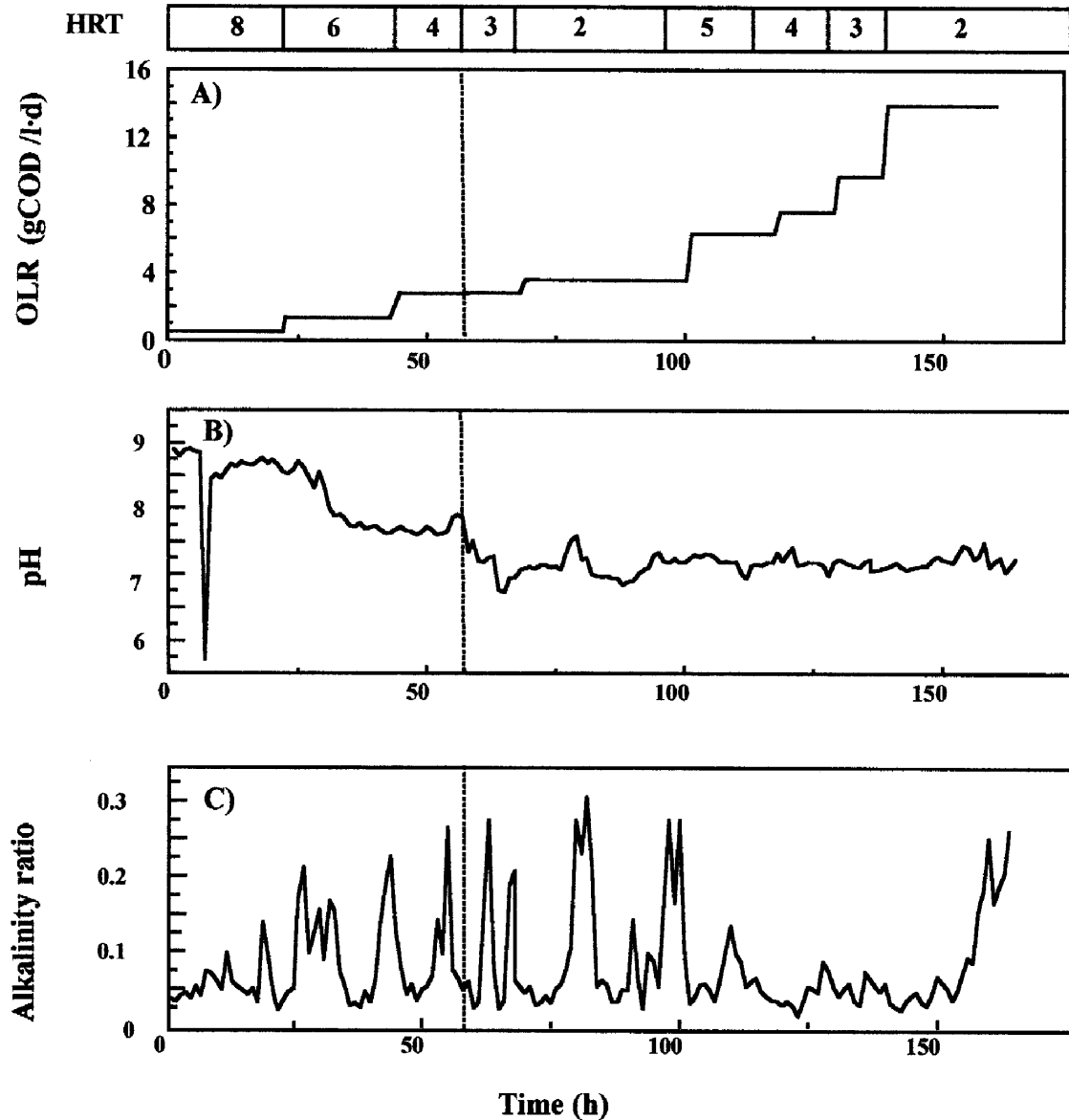


Figure 3 Operation parameters of the AF. A) OLR; B) pH; C) alkalinity ratio (IA/TA).

7.0 and 7.5. The equilibrium between undissociated hydrogen sulphide (free H_2S), bisulphide ion and sulphide ion is very much controlled by the medium pH, and neutral pH the $H_2S:HS^-:S^{2-}$ ratio is $1.1:1:10^{-5}$, which shifts towards the dissociated forms at increasing pH values (Van Gernerden and De Wit, 1986). Previous papers in AF have reported that at a pH below 7.25, the presence of H_2S in the liquid phase causes instability in the process (Soto *et al.*, 1991). In this study, the AF influent was pretreated with $FeCl_3$ producing Fe_2S_3 precipitate and avoiding toxicity in the reactor; similar results were reported by Van Gernerden and De Wit (1986).

The relation between pH, efficiency in COD removal (%CODr) and effluent ammonia is shown in Figure 6. As the pH increased the ammonia nitrogen increased and %CODr decreased due to the degradation of proteins leading to inhibitory ammonium-nitrogen in the first step of the anaerobic digestion. The ammonia concentration in the effluent ranged between 400 and 480 mg/l, whereas the pH ranged between 7.0 and 7.5.

According to this, the selection of the operating pH is a key factor for the successful treatment of these wastewaters; and for this purpose the buffering capacity of

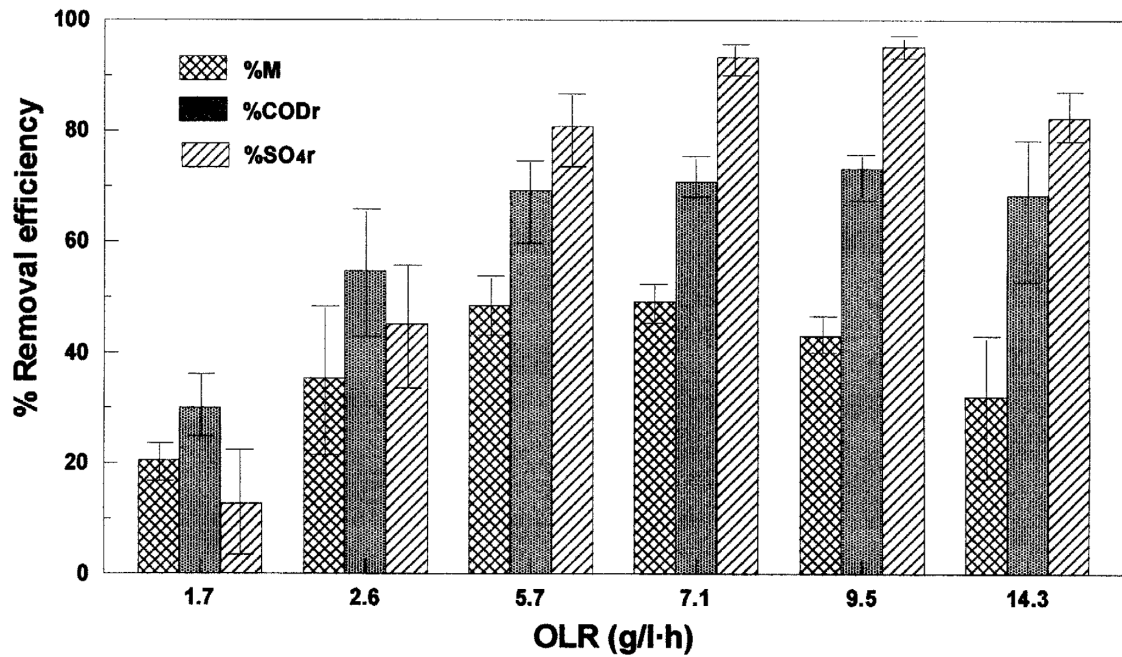


Figure 4 Performance of AF.

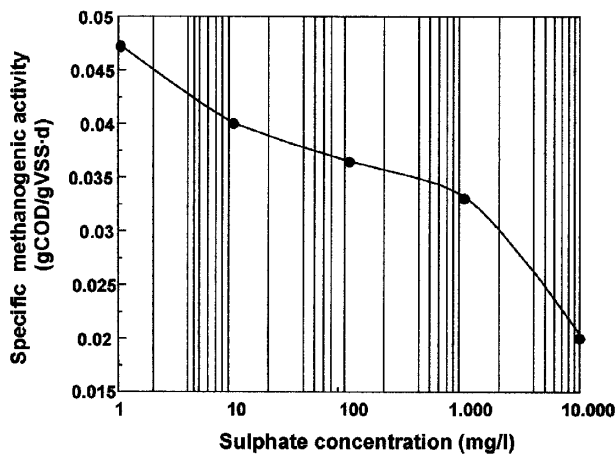


Figure 5 Methanogenic toxicity by sulphate.

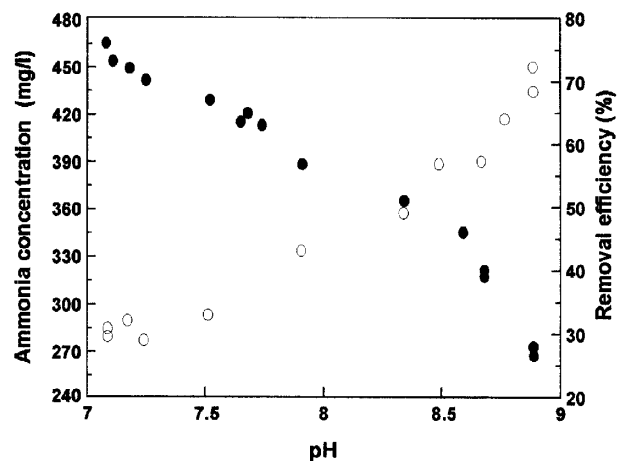


Figure 6 Removal COD efficiency (●) and ammonia (○) vs pH in the AF.

the carbon dioxide/bicarbonate system is essential. Omil *et al.* (1995) have reported that a pH value around 7.6 minimises both free ammonia and sulphide concentrations.

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