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Performance of an anaerobic bioreactor with biomass recycling, continuously removing COD and sulphate from industrial wastes

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ABSTRACT

A 30-l anaerobic bioreactor with biomass recycling was used to provide a continuous reduction in sulphate and a continuous COD removal from wastewater, which consisted of the effluent from an industrial pig fattening farm, enriched with technical $FeSO_4 \cdot 7H_2O$, a waste product from ferrous metallurgy. The concentrations of sulphate and COD in the wastewater amounted to 2.73 g l^{-1} and 3.15 g l^{-1}, respectively. The HRT (hydraulic retention time) of 10–1.7 d produced an extent of sulphate and COD reduction which totalled 98% and 88%, respectively. When the HRT was further shortened, the efficiency of reduction in sulphate and COD decreased. The maximum removal rate constants for both the pollutants, calculated by means of a modified Stover–Kincannon model, were 80.9 g COD l^{-1} d^{-1} and 41.8 g SO_4^{2-} l^{-1} d^{-1}, the values of the saturation constants being 91.582 g COD l^{-1} d^{-1} and 42.398 g SO_4^{2-} l^{-1} d^{-1}.

1. Introduction

The use of SRB offers great potential for an effective treatment of industrial wastewaters (Lens et al., 2002). Sulphate are present in a variety of industrial effluents (Lens et al., 1998), e.g. in acid mine drainage (Elliott et al., 1998; Chang et al., 2000), molasses wastewater (Hilton and Archer, 1988), domestic sewage (Silva et al., 2002), textile wastewater (Kabdasli et al., 1995), or tannery effluents (Boshoff et al., 2004), and SBR, as the name implies, are microorganisms with an inherent capability to reduce sulphate. It is essential to note, however, that sulphate can be efficiently removed by SRB only if the wastewater has been polluted with organic matter as well. This is so because sulphate as the terminal electron acceptor in the respiratory chain of SRB and the carbon sources as the electron donors are the primary nutrients for these microorganisms. Thus, the use of SRB has the advantage of providing both the reduction in sulphate and the biodegradation of organic pollutants. The ability of SRB to utilise a broad spectrum of organic compounds has been widely acknowledged (Liamleam and Annachhatre, 2007), and each of them is known to exert a different effect on the behaviour of the bacteria (Shayegan et al., 2005).

Another major benefit of using SRB is the precipitation of many of the heavy metals that are present in the wastewater mainly in the form of sulphides (Lloyd and Lovley, 2001; Tabak et al., 2003; Luptakova and Kusnierova, 2005).

All the uses of practical significance where SRB are applicable have prompted many investigators to aim their researches at the development of sulphate-reducing reactors. In those studies consideration has been given to the packed-bed anaerobic reactor (Silva et al., 2002), the anaerobic hybrid reactor (O'Flaherty and Colleran, 1999) and, also, the stirred tank reactor coupled with a membrane filtration unit (Fuchs et al., 2003). The literature also includes reports on mathematical models describing a microbiological reduction of sulphate (Knobel and Lewis, 2002; Moosa et al., 2002, 2005).

In the work reported on in this paper use was made of an anaerobic bioreactor with biomass recycling. The aim of the study was to examine the performance of the bioreactor in providing continuous COD and sulphate removal from industrial wastewater.

2. Methods

2.1. Experimental set-up

The wastewater was treated in a continuous anaerobic bioreactor with biomass recirculation of a total volume of 30 l. The temperature of the biodegradation processes was maintained at 38 °C. An electric agitator provided biomass mixing in the bioreactor. The bioreactor was connected to a clarifier, from which the settled biomass was continuously recycled. Each experiment began

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Nomenclature

BLR_{COD}	biomass COD loading rate ($g\ COD\ g^{-1}\ d^{-1}$)
BLR_s	biomass sulphate loading rate ($g\ SO_4^{2-}\ g^{-1}\ d^{-1}$)
COD	chemical oxygen demand ($g\ O_2\ l^{-1}$)
E_{COD}	efficiency of COD removal (%)
E_S	efficiency of sulphate reduction (%)
HRT	hydraulic retention time (d)
K_B	saturation constant ($g\ l^{-1}\ d^{-1}$)
MS	mineral solids ($g\ l^{-1}$)
Q	inflow rate ($l\ d^{-1}$)
S_i, S_e	substrate concentration in the influent and effluent ($g\ l^{-1}$)
SRB	sulphate-reducing bacteria
TS	total solids ($g\ l^{-1}$)
U_{max}	maximum substrate removal rate constant ($g\ l^{-1}\ d^{-1}$)
V	reactor volume (l)
VS	volatile solids ($g\ l^{-1}$)
VLR_{COD}	volumetric COD loading rate ($g\ COD\ l^{-1}\ d^{-1}$)
VLR_S	volumetric SO_4^{2-} loading rate ($g\ SO_4^{2-}\ l^{-1}\ d^{-1}$)
VRR_{COD}	volumetric COD removal rate ($g\ COD\ l^{-1}\ d^{-1}$)
VRR_S	volumetric SO_4^{2-} reduction rate ($g\ SO_4^{2-}\ l^{-1}\ d^{-1}$)

with filling the bioreactor with the inoculum in amounts equal to 1/3 of the effective volume of the reactor. Thereafter the wastewater was dosed at an appropriate rate so as to provide the HRT defined in the experiment design. Thus, the HRT (d) for the system amounted to 0.6; 0.75; 0.86; 1; 1.15; 1.43; 1.67; 2; 2.5; 3.33; 4.29; 6 and 10. The gas produced in the reactor was passed through a washer/scrubber filled with 1 M $Zn(COO)_2$ in order to bind the H_2S released during biodegradation.

2.2. Wastewater

The wastewater made subject to examination was the effluent from an industrial pig fattening farm (liquid manure). Samples were collected after passage of the wastewater through the vibrating screens of the treatment facility located at the breeding plant. Since the wastewaters displayed a comparatively low sulphate content, they were enriched with technical $FeSO_4 \cdot 7H_2O$, a waste from ferrous metallurgy. The major parameters of the mixed wastewater (after $FeSO_4 \cdot 7H_2O$ enrichment) were ($g\ l^{-1}$): COD (3.15), SO_4^{2-} (2.73), N-total (0.76), N–NH_4^+ (0.42), P-total (0.44), P–PO_4^{3-} (0.27), alkalinity as $CaCO_3$ (1.89), TS (1.61), VS (1.27) and MS (0.39). The pH and COD/SO_4^{2-} ratio of the mixed wastewater was 7 and 1.154, respectively.

2.3. Inoculum

The inoculum was a mixed anaerobic culture dominated by the species *Desulfovibrio desulfuricans* isolated from the hydrogen sulphide containing curative waters of the spa Busko Zdrój in the south-east of Poland and had a volume of 10 l in each experiment. The TS, VS, MS, COD, SO_4^{2-} and alkalinity of the inoculum were ($g\ l^{-1}$) 14.86, 5.7, 9.16, 0.36, 0.013 and 2.26 as $CaCO_3$ respectively. The pH of the inoculum was 8.2.

2.4. Analyses

The wastewater, inoculum and effluent were analysed for pH, COD, SO_4^{2-}, N-total, N–NH_4^+, P-total, P–PO_4^{3-}, alkalinity, TS, VS and MS according to standard methods (APHA, 1975). The effluent from the bioreactor was sampled once a day, when the system was at steady state (it was assumed that a steady state was reached upon a fivefold change of the content of the bioreactor), and the samples were filtered through a filter paper.

2.5. Kinetic model

The kinetics of substrate (COD and SO_4^{2-}) removal in the bioreactor were estimated using a modified Stover–Kincannon model that, at steady state, has the form (Yu et al., 1998; Büyükkamaci and Filibeli, 2002):

$$dS/dt = (U_{max}(Q \cdot S_i)/V)/(K_B + (Q \cdot S_i)/V) \quad (1)$$

Form (1) can be liberalised as

$$(dS/dt)^{-1} = V/Q/(S_i - S_e) = K_B/U_{max} \cdot V/Q/S_i + 1/U_{max} \quad (2)$$

Form (2) can be used for showing the graph plot that relates the inverse of the substrate loading removal rate ($V/Q/(S_i - S_e)$) to the inverse of the total substrate loading rate ($V/Q/S_i$). If the plot is linear, use can be made of linear regression to estimate the intercept and the slope. The result is a straight line portion of intercept $1/U_{max}$ and a slope of K_B/U_{max}. K_B is saturation constant ($g\ l^{-1}$) and U_{max} is maximum substrate removal rate constant ($g\ l^{-1}$).

3. Results and discussion

Biomass recycling is a well known method for upgrading the performance of the bioreactors used in environmental pollution control (De la Noüe and Eidhin, 1988; Pereira et al., 2001; Hwu et al., 1997). When use is made of this method, the time of biomass adaptation is shorter and the slow growth of some microorganisms has its compensations. Previous research has shown that the generation time for *D. desulfuricans* (the bacterial strain used in our present investigations, which grows on the effluent from an industrial pig fattening farm) is 5.3 d (Kosińska et al., 1995). This is what prompted us to recycle the biomass and thus prevent limitations to the performance of the bioreactor which was aimed to reduce sulphate and remove organic pollutants.

The investigations were conducted with real wastewater, which had been chosen deliberately. The effluent from an industrial pig fattening farm provided the *D. desulfuricans* strain not only with organic substances that could be utilised as carbon and energy sources, but also with nutrients, mainly nitrogen and phosphorus. The $FeSO_4 \cdot 7H_2O$ waste, utilised as a sulphate source, was added in such quantities that enabled the COD/SO_4^{2-} ratio in the mixed wastewater to be maintained within the range of 0.7–1.5. The value of the ratio has an important part in the biodegradation of sulphate (De Smul et al., 1999; Vossoughi et al., 2003; Byun et al., 2004), and a previous study of ours has shown that for the bacterial strain and the industrial effluent used for the purpose of the present study the COD/SO_4^{2-} ratio should take the same values (Kosińska and Miśkiewicz, 1999). Another major advantage of using $FeSO_4 \cdot 7H_2O$ was that S^{2-} ions were bound by Fe^{2+} ions. It was necessary to prevent the inhibitory effect of S^{2-} ions on the activity of the SRB used (Okabe et al., 1992, 1995).

Bioreactor performance was analysed taking into account the efficiencies of COD removal and SO_4^{2-} reduction depending on the HRT that ranged between 0.6 and 10 d. The experimental data are summarised in Table 1. When the HRT was shortened from 10 to 0.6 d, this was paralleled by a rise in the volumetric loading rate for both pollutants. Thus their initial values that were 0.315 g