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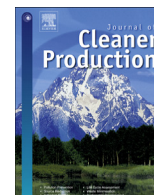

Experimental and modelling study of treatment and regeneration of ferrous-nitrilotriacetate solution scrubbed with nitric oxide by an up-flow anaerobic biofilm reactor

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ABSTRACT

This paper deals with an integrated biochemical process for the treatment of stationary gaseous emissions containing nitric oxide. The process involves absorption of nitric oxide in a solution of ferrous nitrilotriacetate, followed by regeneration of the solution by microbial reduction of nitrosyl adduct of ferrous nitrilotriacetate and ferric nitrilotriacetate present in the solution generated during absorption. A laboratory-scale up-flow anaerobic biofilm reactor using polyurethane foam cubes as support matrix for biofilm was employed for the treatment of 20 mM ferrous nitrilotriacetate solution scrubbed with synthetic nitric oxide gas mixture. The biofilm was developed by fed-batch operation for 30 days by using enriched bacterial culture capable of reducing nitrosyl adduct and ferric nitrilotriacetate using ethanol as organic electron donor. Under steady-state conditions, the nitrosyl adduct reduction efficiency reached >90% at a loading rate of 0.24 mML^{-1} h^{-1} while ferric nitrilotriacetate reduction efficiency was 15–20%. The average biofilm thickness was about 550 μm, decreasing the porosity of the matrix. Reactor hydrodynamics was studied by tracer (methyl orange) experiments. The analysis based on residence time distribution theory involved axial dispersion flow model and tracer diffusion with linear adsorption inside the biofilm. Peclet number value of 28 was obtained allowing the plug-flow assumption for the reactor model. The experimental profiles of the nitrosyl adduct reduction in the reactor were explained by using a kinetic model of first order reaction coupled with NO diffusion inside the biofilm.

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1. Introduction

Nitrogen oxides or NOx are one of the major air pollutants, responsible for severe toxic and environmental hazards (Olivieri and Scoditti, 2005; Gallego et al., 2009; Pandey and Chandrashekhar, 2014). Various physicochemical approaches such as selective catalytic reduction (SCR) and selective non catalytic reduction (SNCR) have been developed to mitigate the emission of NOx from stationary sources. But these processes have certain drawbacks such as relatively high cost and the concerns on the use of toxic ammonia and urea (Muzio et al., 2004; Neuffer and Laney, 2007). The poisoning of SCR catalysts due to sulphur compounds present in the gas is also a major concern (Seo et al., 2011). Other physico-chemical technologies have been proposed and investigated at different scales to reduce the cost of gas denitrification, such as low temperature oxidation by ozone (Lin et al., 2004 and corona induced plasma (Lee et al., 2003). But such processes are very costly and therefore have not been implemented at large scale. Removal of NOx by scrubbing is a promising and economical approach. But nitric oxide (NO) which is the major component of NOx is sparingly soluble in water; therefore various additives such as hydrogen peroxide (Zhang et al., 2014) and sodium hydroxide (Myers and Overcamp, 2002) have been used to enhance the solubility of NO. The aqueous solution of ferrous-chelates are more promising since they dramatically enhance the mass transfer of NO into from the gas to liquid phase, without changing the oxidation state of NO by formation of a stable but reversible Fe^{II}chelate-NO adduct (Gambardella et al., 2005).

In order to make the scrubbing process using Fe^{II}chelate cost effective, many biological treatment methods have been investigated to reduce and regenerate the scrubbed ferrous-chelate

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solution for its recycle to the scrubber. This has led to the development of an integrated process for NOx removal, also known as BioDeNOx (van der Maas et al., 2008; Dilmore et al., 2009). In this process, NOx is first absorbed into an aqueous solution of Fe^{II}EDTA (ethylenediamine tetraacetate) in a wet scrubber and the spent scrubber solution is treated in a bioreactor where the Fe^{II}EDTA-NO and Fe^{III}EDTA adducts formed during absorption are reduced by dedicated NOx and iron-reducing bacteria. The entire process is operated as a closed loop and the corresponding chemical reactions in the integrated chemo-biochemical process using Fe^{II}EDTA are shown in Table 1. This is a promising approach, however the biological reduction of Fe^{II}EDTA-NO and Fe^{III}EDTA is rather slow and hence the biological regeneration of the scrubbing solution is the critical step in this process (Dilmore et al., 2006; Dong et al., 2013). Different types of bioreactors viz. sludge blanket reactors, bioelectrode reactor have been investigated in the past for this purpose (Gao et al., 2011). But such bioreactors usually suffer from low biomass growth, low iron-reduction efficiency and other complexities which could make them non-feasible for large scale application, especially for longer periods.

The present study deals with the biological treatment of ferrous nitrilotriacetate (Fe^{II}NTA) based NOx scrubbing solution in an up-flow anaerobic biofilm reactor using polyurethane foam (PUF) as the packing material. Biofilm reactor or fixed bed bioreactors have the advantage that they provide higher biomass density per unit volume, higher reaction rates, higher biomass-liquid specific interfacial contact areas and simplicity of operation as compared to suspended growth bioreactors. As the reduction of NO adduct is affected by substrate inhibition mechanism (Dilmore et al., 2006); a fixed bed bioreactor may be suitable for this purpose. Mohanty et al., 2016 have also demonstrated the effectiveness of an up-flow packed bed anaerobic reactor for biological nitrogen removal. Polyurethane foam has the advantages that it provides homogenous biofilm thickness, high surface area for biomass retention, high porosity and easy installation. NTA was used instead of EDTA due to several advantages such as being cost effective due to lesser molecular weight and less toxicity. The complex Fe^{II}NTA-NO, is less stable than Fe^{II}EDTA-NO (Wolak and Eldik, 2002) which can facilitate faster reduction of NO. NTA also encourages iron reduction by solubilization of ferric oxides by various mechanisms (Luu and Ramsay, 2003). Higher biomass yields and biological NOx reduction rates in Fe^{II}NTA as compared to Fe^{II}EDTA was found in our previous study (Chandrashekhar et al., 2013); hence, use of NTA as a substitute for EDTA could provide additional advantages.

In our earlier work, the start-up and operation of an up-flow anaerobic biofilm reactor for continuous NO removal was described (Chandrashekhar et al., 2015). The performance of the bioreactor in a continuous system for a longer period was monitored and the dynamics of the bio-process with respect to substrate utilization was also explained using different kinetic models. The work presented in this paper further explains the biomass growth and steady state kinetics of Fe^{II}NTA-NO reduction in the bioreactor during continuous operation, using diffusion based kinetic model.

2. Materials and methods

This section provides the details of the chemicals and microorganisms, experimental set-up and methodology used for carrying out this research work.

2.1. Chemicals

Disodium nitrilotriacetic acid (Na_2NTA) and Ferric chloride ($FeCl_3$) along with other chemicals used for scrubber solution and cultivation medium preparation were purchased from Himedia Labs Pvt Ltd., India. NO (250 ppm in N_2, v/v) and N_2 (99.99%) were obtained from Chemtron Science Laboratories, India. Air was used as the source of oxygen. The reagents used for analysis were prepared in the laboratory from commercially available reagents and chemicals, used without further purification.

2.2. Microorganisms and cultivation medium

A mixed bacterial culture capable of reducing both Fe^{II}NTA-NO and Fe^{III}NTA (Chandrashekhar et al., 2013) was used as inoculum for the bioreactor. The culture was pre-cultivated at 37 °C and pH 7 in a synthetic medium consisting of potassium nitrate (KNO_3) – 5 mM, dipotassium hydrogen phosphate (K_2HPO_4) – 3 mM, potassium dihydrogen phosphate (KH_2PO_4) – 4 mM, magnesium chloride ($MgCl_2$) – 0.002 mM, magnesium sulphate ($MgSO_4.7H_2O$) – 0.4 mM, sodium sulphite (Na_2SO_3)– 0.5 mM, ferrous sulphate ($FeSO_4$) – 0.06 mM, copper sulphate ($CuSO_4.5H_2O$) – 0.03 mM, and sodium molybdate (Na_2MoO_4) – 0.02 mM with ethanol as electron donor under denitrifying conditions before inoculation. pH was maintained by adding HCl or NaOH from concentrated stocks.

2.3. System configuration, start-up and operation

The schematic and details of laboratory scale system used for this investigation is depicted in Fig. 1. The dimensions of the bioreactor used are provided in Table 2. The absorption of NO in Fe^{II}NTA solution was carried out in an absorption unit (agitated tank reactor of 1.5 L working volume). The spent scrubber solution was pumped to an up-flow anaerobic biofilm reactor (UABR) where it was exposed to the biofilm immobilized on polyurethane foam matrix, containing a population of denitrifying (NO reducing) bacteria and iron reducing bacteria to regenerate the spent Fe^{II}NTA solution. The treated effluent from the top of the UABR was sent back to the absorption unit as shown in Fig. 1.

The system was operated for 164 days in two distinct phases. In Phase-I, the entire system was operated without the absorption unit (Loop I). The UABR was inoculated with approximately 1 L of biomass containing 1.2 g dry cell weight (DCW) per litre and balance volume was filled with the synthetic medium containing 20 mM Fe^{III}NTA to grow iron reducing bacteria in the bioreactor. Once most of the Fe^{III}NTA was reduced, the Fe^{II}NTA-NO complex was generated by adding $NaNO_2$ to the feed tank. Ethanol was added at required concentrations (to maintain C:N = 4 approximately) with other nutrients to the feed tank. Nitrite was added manually to the feed tank in required amount whenever the

Table 1
Important reactions taking place in the process.

Absorption stage	Biological regeneration stage
Reaction of Fe^{II}EDTA with NO	*Reduction of Fe^{II}NTA-NO using EtOH*
$Fe^{II}NTA^{2-} + NO \leftrightarrow Fe^{II}NTA{-}NO^{2-}$	$6\ Fe^{II}NTA\text{-}NO^{2-} + C_2H_5OH \rightarrow 2HCO_3^- + 2H^+ + 3N_2 + H_2O + 6\ Fe^{II}NTA^2$
Reaction of Fe^{II}NTA with O_2	*Reduction of Fe^{III}NTA using EtOH*
$4\ Fe^{II}NTA^{2-} + O_2\ (aq) \rightarrow 4\ Fe^{III}NTA^- + 2H_2O$	$12Fe^{III}NTA^- + C_2H_5OH + 5H_2O \rightarrow 2HCO_3^- + 12Fe^{II}NTA^{2-} + 14H^+$

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