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Simultaneous ammonium–nitrogen and copper removal, and copper recovery using nitrifying biofilm from the Ultra-Compact Biofilm Reactor

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Abstract

Simultaneous ammonium–nitrogen (NH_4^+–N) and copper removal, and copper recovery in synthetic wastewater using nitrifying biofilm from an ultra-compact biofilm reactor (UCBR) was demonstrated in batch studies, which consisted of three phases: Phase 1 for NH_4^+–N and copper removals, Phase 2 for copper recovery, and Phase 3 for NH_4^+–N removal. The results showed that more than 96.3% of copper was removed within 60 min, while 60.1% of the adsorbed copper was recovered through rinsing the biofilms with 0.1 mM of ethylenediaminetetraacetic acid (EDTA). The nitrifying biofilm was able to adsorb 0.245 mg of copper/g of biofilms. After recovery treatment, 29.4% of copper remained bound within the nitrifying biofilms. No significant inhibitory effects towards NH_4^+–N removal in the presence of 0.92 mg copper/L was noted in Phase 1 compared with the control test. However, lower initial pH condition in the recovery process and the accumulation of copper on the biofilm led to 50% inhibition on NH_4^+–N removal efficiency in the subsequent phase.

Keywords: Ammonia–nitrogen removal; Copper recovery; Extracellular polymer substance; Nitrifying biofilm

1. Introduction

Copper is a common heavy metal pollutant found in many different types of industrial effluents, namely, tanning process (0.06–0.38 mg/L), explosives (0.94 mg/L) and timber products (50–110 mg/L) with ammonia–nitrogen (NH_4^+–N) present at concentrations ranging from 0.40 to 380 mg/L (Dyer and Mignone, 1983). Copper toxicity has been reported in numerous biological wastewater treatment systems especially during nitrification process. This complexity has inevitably hindered the research and development efforts for a single reactor for simultaneous nitrification and copper removal. It was demonstrated that Cu(II) concentration of 0.08 mg/L would exhibit 50% inhibition on the nitrification process of activated sludge (Juliastuti et al., 2003). However, as mixed liquor suspended solids (MLSS) increases, the effect of copper would reduce due to higher copper sorption to the biomass (Kim et al., 2006). Copper can form complex with organic ligands and extracellular polymer substances (EPS) produced by the biomass (Guibaud et al., 2003), which in turn would reduce the available free Cu(II) ions in the bulk media. As the toxicity and bioavailability of metals in the environment are related to the presence of free metal ion concentrations rather than the total or complexed metal concentration (Campbell, 1995), the increase in EPS especially in biofilms would reduce the toxicity effect of copper towards the biomass activity. Adsorbed copper could be further recovered through desorption using desorption agents such as hydrochloric acid (HCl), ethylenediaminetetraacetic acid (EDTA) and water. Although one could

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achieve high copper desorption using HCl (Gupta et al., 2006), its strong acidic properties would be detrimental toward the biomass activity in biological process. Gupta et al. (2006) demonstrated that the desorption of Cu(II) using HCl, EDTA and water from a marine algae, *Spirogyra*, were 95%, 90% and 5%, respectively after 15 min. This finding suggests that the desorption capacity of EDTA is almost comparable with HCl (but with a more subtle acidic condition) could be effectively used for recovery of Cu(II) from biomass. However, the effect of EDTA towards the activity of the biomass after desorption would need to be studied.

The above indicated that biofilm reactors, such as the Ultra-Compact Biofilm Reactor (UCBR), for simultaneous nitrification and copper removal could be of high potentials. EPS in the biofilm structure would also enhance flocculation for good settling (Sponza, 2002) in addition to complexation with copper, while allowing good NH_4^+–N removal (Lee et al., 2004). In addition, the high specific surface area in UCBR (of up to 4000 m^2/m^3) (Ong et al., 2003) would provide a high surface area for copper adsorption and hence would increase the removal capacity. However, the potential of nitrifying biofilm for removal and recovery of copper with simultaneous NH_4^+–N removal in the wastewater is still unexplored. In view of this, this feasibility study was conducted to determine copper removal and recovery efficiency of nitrifying biofilm from the UCBR and effect of copper on NH_4^+–N removal.

2. Methods

2.1. UCBR set up and operating conditions

Nitrifying biofilms collected from a UCBR treating synthetic wastewater were used in this study to investigate the removal and recovery of copper. Fine sand particles with a mean diameter and density of 250 ± 50 μm and 2600 kg/m^3, respectively, were used as biofilm carriers in the UCBR. Sand concentration in the UCBR was maintained at 2.5% (v/v). The NH_4^+–N loading of the UCBR was maintained at 2 kg NH_4^+–N/m^3 d. Each liter of synthetic wastewater contained 1273.7 mg of ammonium chloride, 93.8 mg of di-hydrogen potassium phosphate and 1 ml of trace elements. Each liter of trace elements solution contained (g) $10CaCl_2 \cdot H_2O$, $8FeCl_3 \cdot 6H_2O$, $5MgSO_4 \cdot 7H_2O$, $2CoCl_2 \cdot 6H_2O$, 2thiamine-HCl, $1NaSiO_3 \cdot 9H_2O$, and (mg) $550Al_2(SO_4)_3 \cdot 16H_2O$, $50MnCl_2 \cdot 2H_2O$, $1(NH_4)_6Mo_7O_{24} \cdot 6H_2O$), $1CuSO_4 \cdot 5H_2O$, $1ZnSO_4 \cdot 7H_2O$ and $1H_3BO_4$.

The UCBR was a column reactor with its internal structure divided into two separate sections – riser and downcomer – combined with a three-phase separator mounted at the top. The internal diameters of the riser and downcomer were 50 and 80 mm, respectively, with a downcomer height of 1.0 m. The reactor has a total volume of 6.6 L. Synthetic wastewater was fed into the UCBR using a peristaltic pump (Model no: 7554-85, Cole Parmer Instrument, USA) at a flow rate of 27.4 mL/min. Compressed air was introduced into the riser column via a metallic sparger located at the bottom of the UCBR's riser. Air flow was regulated at 2.2 ± 0.2 cm^3/s using air flow controller (Aalbory, NY, USA) to provide a superficial air velocity (SAV) of 2.0 cm/s. The pH in the UCBR was maintained at 7.0 ± 0.2 using 0.5 M Na_2CO_3 via an alkaline dosing pump (HDpH-P, Barnant, Italy). Fig. 1 illustrates the schematic diagram of the UCBR used in this study.

2.2. Copper removal and recovery using nitrifying biofilms in batch studies

A copper removal and recovery study was conducted to determine the potential of nitrifying biofilm to remove and recover copper, and the effects of copper on NH_4^+–N removal. A control test was carried out to determine NH_4^+–N removal using nitrifying biofilm in the absence of copper. The study was conducted in three batch phases: Phase 1 for nitrification and copper removal, Phase 2 for copper recovery and Phase 3 for NH_4^+–N removal. The three phases were conducted sequentially with a total run time of 8 h for each biofilm sample. A set of triplicates were carried out for each batch experiment.

Phase 1: Copper sulphate (Merck kGaA, Darmstandt, Germany) was dissolved in ultra-pure water and adjusted to pH 7.0 using 1 M of sodium carbonate. The precipitation was then filtered through a 0.45 μm pore size filter paper (GN-6 Grid 47 mm, Gelman Science, USA). Substrate A, containing 191.1 mg of ammonium chloride and 0.01 M of phosphate buffer (consisting 53.3 mg/L of $Na_2HPO_4 \cdot 7H_2O$ and 29.3 mg/L of $NaH_2PO_4 \cdot H_2O$) was added to one liter of filtrate. One hundred milliliters of

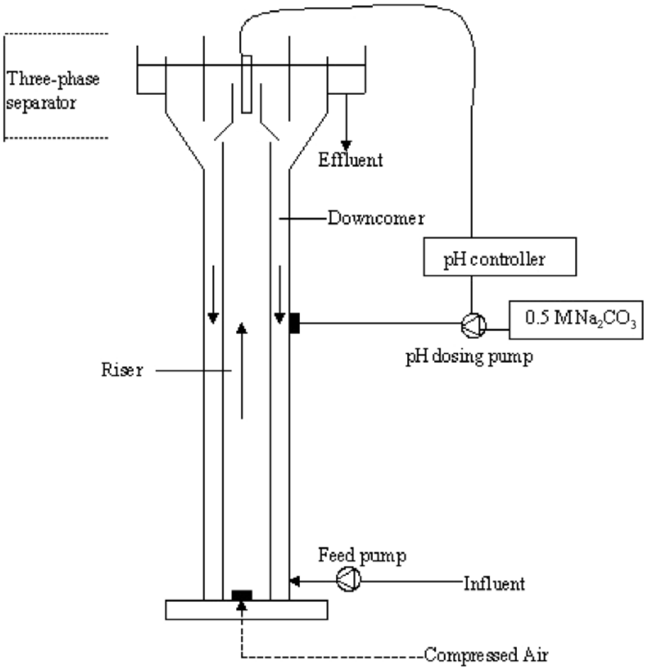

Fig. 1. Schematic diagram of UCBR.