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Effects of thiocyanate on granule-based anammox process and implications for regulation

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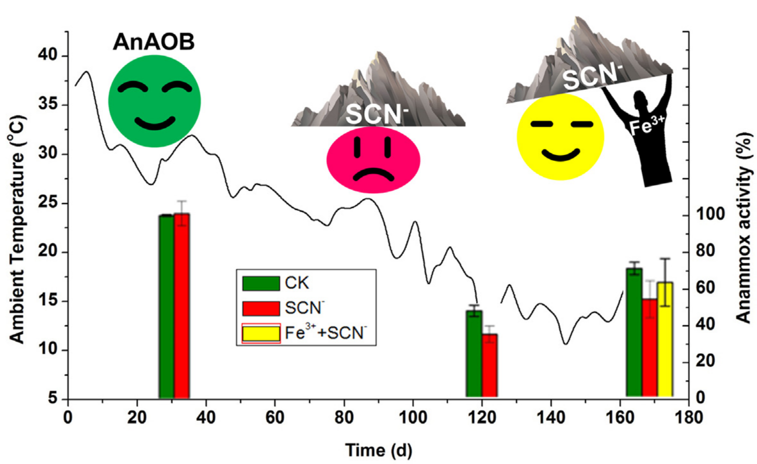
HIGHLIGHTS

- The effects of thiocyanate on anammox granules were evaluated for the first time.
- The mathematical models used to quantify the performance fit the trial data well.
- Thiocyanate changed the granules properties after long-term operation.
- Anammox performance can be restored after thiocyanate stress by Fe(III) addition.

GRAPHICAL ABSTRACT



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ABSTRACT

The feasibility of using anaerobic ammonium oxidation (anammox) process to treat industrial wastewater containing thiocyanate (SCN^-) was examined in this study. Anammox activity decreased with increasing thiocyanate concentration and pre-exposure time in batch tests. A typical noncompetitive model was used to fit the data for thiocyanate inhibition, and the 50% inhibition concentration (IC_{50}) of thiocyanate on anammox was 620.4 mg L^{-1} at 200 mg L^{-1} total nitrogen level. The influent thiocyanate concentration of test reactor (R_1) in phase II gradually increased from 10 to 120 mg L^{-1}, and the average nitrogen removal efficiency (NRE) of R_1 was maintained at 83.0 ± 7.82%. This robustness was attributed to the self-adaptation ability of anammox biomass through long-term acclimatization. The NRE was decreased to 57.1% under 130 mg L^{-1} thiocyanate within two days. However, the NRE of control reactor (R_0) in absence of thiocyanate was 91.23 ± 4.11% in this phase. Under thiocyanate stress, the specific anammox activity, settling velocity and heme c content of the granules significantly decreased, and the extracellular polymeric substances content slightly increased. The short- and long-term performance inhibition could be reversed in the presence of 10 mg L^{-1} Fe(III).

1. Introduction

Complex coking wastewaters contain a mixture with varying and high concentrations of total nitrogen and toxic/recalcitrant

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organic compounds; these wastewaters are produced during industrial processes, such as those used at coking, petrochemical, steel manufacturing and coal gasification factories [1,2]. The total nitrogen in complex coking wastewater contains ammonia (85–121 mg L^{-1}), thiocyanate (SCN^-) (180–642 mg L^{-1}), cyanide (12–95 mg L^{-1}) and organic nitrogen compounds [2–5]. Therefore, it is necessary to treat coking wastewater properly to avoid any adverse long-term environment and ecological impacts to the receiving water body.

Biological treatments, such as anoxic-oxic (A/O) or anaerobic-anoxic-oxic ($A_1/A_2/O$) process, are widely applied in coking wastewater treatment because of the high treatment efficiency and cost-effective advantages [5,6]. Unfortunately, due to the refractory and inhibitory contaminants present in coking wastewater, the above processes are not sufficient in practice to meet the National Discharge Standard of China (GB8978-1996) when accounting for criteria such as the chemical oxygen demand (COD), total cyanide (T-CN) and fluoride, among others [7,8]. To comply with the stringent environmental regulations, physic-chemical processes, such as coagulation or advanced oxidation, have to be involved following the biological process [9].

The combined nitritation and anaerobic ammonium oxidation (anammox) process has been regarded as one of the most efficient ways for autotrophic nitrogen removal [10,11]. In this process, ammonium is aerobically oxidized to nitrite partially by ammonia-oxidizing bacteria (AOB), while the nitrite produced is then anaerobically reduced to dinitrogen gas with the remaining ammonium as electron donor by anammox bacteria. Maybe, anammox based process could be hopefully applied to nitrogen removal from coking wastewater. The anammox granules have several advantages over flocculent sludge, such as a denser and stronger aggregate structure, better settleability, more ensured solid-effluent separation, higher biomass concentration and greater ability to withstand shock loadings and toxicity in industrial wastewaters [12]. The properties of anammox granules are important factors affecting the process performance. Therefore, determining the influence of adverse condition on the sludge characteristics is crucial for practical applications. Thus, the changes of the anammox granules properties under such conditions require investigation to achieve a reliable operation of biological wastewater treatment.

Biological treatments are known to be affected by the operational conditions [13]. The temperature of coke wastewater into reactor usually varies with the change of season and location, which limits the application of the mesophilic anammox process. Due to the large fluctuations in the flow and composition of wastewater, there must be a storage pool. These wastewater produced during industrial processes was not direct to biological degradation process. In addition, the toxic compounds, such as thiocyanate in coke wastewater, would affect the anammox biomass activity and performance by shock-loads or sequentially alternating pollutants events. Although some studies have tested the effects of thiocyanate on nitrification in biological wastewater treatment systems [14,15], adverse conclusions have been reported. Kim et al. [14] showed that thiocyanate exerted a strong negative effect at thiocyanate concentrations higher than 250 mg L^{-1}, while Kim et al. [15] showed that a nitrifying bacterial community is associated with an increase in thiocyanate shock loading. However, no studies have reported the effects of thiocyanate on anammox bacteria. Therefore, widespread application of the anammox process requires reconciliation of the impacts on the physiological characteristics of anammox community caused by those factors. Although the impact of temperature on anammox process performance is frequently reported [13,16,17], no literature is available on the combined influences of temperature and thiocyanate on the physic-chemical characteristics of anammox granules.

Furthermore, there are no studies regarding the effect of thiocyanate pre-exposure on anammox. It has been reported that the concentrations of thiocyanate in coking wastewater were 180–642 mg L^{-1} [2,3]. Although thiocyanate can be biodegraded by specialized biomass [5]. As a result of large fluctuations in the flow and composition of wastewaters, anammox bacteria might also experience famine conditions in under-loaded bioreactors. The impact of thiocyanate on anammox bacteria might vary depending on whether the substrates are actively metabolized. Therefore, the absence of two substrates, which might reduce the tolerance of anammox bacteria to thiocyanate inhibition, should be considered. Furthermore, anammox may suffer higher levels of thiocyanate in one stage nitrification-anammox process or without pre-treatment.

Iron plays an important role in the growth of almost all microorganisms. Iron, at low concentration, is a necessary micronutrient and component of many important protein classes, such as hemochrome, iron-sulfur, and other proteins [18,19]. Therefore, appropriate dosages of iron significantly enhance specific anammox activity (SAA) and improve reactor capacity [20]. Moreover, thiocyanate reacts with iron, generating a series of Fe-complexes, represented by Fe $(SCN)_n^{3-n}$, where n = 1,. . .,6 [21]. Thus, the addition of Fe(III) might be essential for the detoxification of anammox granules suffering from thiocyanate inhibition as a result of the non-toxicity of $Fe(SCN)_n^{3-n}$.

To determine the characteristics of the anammox system under thiocyanate inhibition, the aims of the present study were to (1) evaluate the short-term effects of thiocyanate stress on anammox activity; (2) analyze the long-term effects of the performance of anammox reactors and the properties of anammox granules at room temperature; and (3) investigate the qualitative and quantitative characteristics of the recovery of anammox activity after thiocyanate stress through the appropriate dosing of Fe(III). The information provided here will be useful in facilitating the application of anammox process to treat coking wastewater.

2. Materials and methods

2.1. Synthetic wastewater

Synthetic wastewater containing substrates, bicarbonates and trace elements (similar to the influent described by Yang and Jin [22]) was introduced into the reactor setup as the influent. Equimolar amounts of ammonium and nitrite in the forms of $(NH_4)_2SO_4$ and $NaNO_2$, respectively, were supplied as needed, and the concentration of $(NH_4)_2SO_4$ and $NaNO_2$ in the influent were ranged from 70 to 280 mg N L^{-1}. The influent pH in the continuous flow test was 7.91 ± 0.09 without the addition of acid or alkali. The dissolved oxygen (DO) of reactor was below the limits of detection. To provide thiocyanate, potassium thiocyanate (KSCN) was added to the synthetic medium as required.

2.2. Experimental configuration and operational strategy

Two up-flow anaerobic sludge blanket reactors (UASB), each fabricated from plexiglass, were used for experimental study; the working volume of each reactor was 1.0 L, and the internal diameter was 6 cm. A UASB reactor was assigned to the experimental group (hereafter referred to R_1) that used to study the performance of anammox under thiocyanate stress. The control experiments were conducted in an anammox reactor that was the same to R_1 but without thiocyanate stress (hereafter referred to R_0). Black cloth was used to cover the anammox reactor to prevent light inhibition. Reactors R_0 and R_1 were placed in a laboratory located in Hangzhou, China (30°150′N, 120°10′E) without temperature con-