Journal of Industrial and Engineering Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

# Effects of $Ca^{2+}$ on biological nitrogen removal in reverse osmosis concentrate and adsorption treatment

Hyun Gu Kim, Sung Su Kim, Sung Chul Kim*, Hyun Jong Joo*

*Department of Environmental Energy Engineering, Kyonggi University, 154-42, Gwanggyosan-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do, 16227, Republic of Korea*

ARTICLE INFO

*Article history:*
Received 30 May 2016
Received in revised form 26 January 2017
Accepted 15 August 2017
Available online xxx

*Keywords:*
RO concentrate
Aerobic granular sludge
Nitrate
TDS
Calcium

ABSTRACT

This study aims to investigate the effects of calcium ions present in the reverse osmosis (RO) concentrate on the removal of nitrate nitrogen and the absorption process of calcium ions using various carriers. The results of the analysis show that the denitrification of nitrate nitrogen delayed upon the injection of calcium ions at concentrations 500 mg/L. The adsorption of calcium ion was investigated by the development of adsorption isotherm equation, and aerobic granular sludge was found to be excellent.


## Introduction

As an alternative to recent water shortage, interests and demands for water reuse industry are growing. In particular, among the technologies used for water reuse, the reverse osmosis (RO) process derived from the desalination of seawater is actively in research and is rapidly progressing in Korea and abroad [1]. Not only is the wastewater reuse technology an approach to solve water shortage in Korea by securing alternative water resource, this valuable representative environmental technology can also develop and create value in the water market of foreign countries that suffers from water shortage [2]. The retreatment processes for water reuse used in Korea include sand filtration, activated carbon, microfiltration (MF), nanofiltration (NF), and RO [3,4]. However, these technologies have some problems when used economically and technically for advanced water such as industrial water. In particular, in the case of water reuse using the RO process, the problem of treating reverse osmosis concentrate (ROC) occurs in the process [5,6]. The application of RO process increases with increasing proportion of the reuse of advanced industrial wastewater such as process water and cooling water from the simple reuse of existing stream maintenance water and agricultural water. The amount of ROC is also expected to continuously increase [7].

The wastewater characteristics of ROC are different from that of general household sewage or industrial wastewater, and most of organic matters have been known to be nonbiodegradable substances. Moreover, it shows high salt and nitrogen concentrations. In particular, total dissolved solids (TDS) have been known to significantly inhibit the efficiency of biological treatment [8].

Therefore, some wastewater treatment plants use methods with a big economic burden such as ROC heat evaporation or physical and chemical treatment methods, reprocessing once when returned to the front end of the treatment plant [9,10]. The concentration of nitrogen generated in the ROC is 3–5 times more than that in raw water depending on the concentration and recovery rates upon biological treatment, leading to overload in the treatment plant, thus making the normal operation very difficult. Moreover, ions of TDS existing in ROC are $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $HCO_3^-$, and $SO_4^{2-}$. Among them, calcium ions are strongly adsorbed on the surface of microorganisms, it decreases microbial activity upon biological treatment of nitrogen, and thus decreases the efficiency of nitrogen removal. In the previous studies, the effects of calcium ion on sludge sedimentation, microbial community change, and the effect of calcium ion on biological denitrification under various C/N ratio conditions have been studied. There are few studies on the cause identification and control method of the effect on the denitrification reaction [11–13]. The process for removing refractory organic matters is currently used in the case of the pretreatment process for ROC [9,10]. The quantitative effects of calcium ions on the biological nitrogen removal and appropriate treatment methods have not been

* Corresponding authors.
*E-mail addresses:* mac40@hanmail.net (S.C. Kim), hjjoo@kyonggi.ac.kr (H.J. Joo).

http://dx.doi.org/10.1016/j.jiec.2017.08.027
1226-086X/

studied in details. Thus, the purpose of this study was to investigate the effects of the presence of calcium ions in RO concentrate and assess the calcium ion adsorption using various carriers.

## Experimental methods

### *Materials and reagents*

#### *Effects of calcium ion on nitrate removal*

Synthetic wastewater was used as the inflow to investigate the effects of calcium ions on the removal of nitrate nitrogen. Organic carbon source required for the denitrification was prepared from methanol. $KNO_3$ and $Ca(OH)_2$ were used for the removal of nitrate nitrogen and calcium ion, respectively. Sludge was collected from the anoxic tank of a wastewater treatment plant and used in this experiment. The denitrification microorganisms were cultured by periodical injection and reaction of synthetic wastewater.

#### *Evaluation of calcium ion adsorption*

The adsorption of the inflow was produced by using $Ca(OH)_2$. Metal foam (Alantum Corporation, Korea), aluminum oxide (Kanto Chemical, Japan), granular activated carbon (DY Carbon, Korea), and aerobic granular sludge (BlueBank, Korea) were used as the carriers. Moreover, the surface of the carriers was coated by using coating solution containing sulfur ions to enhance the adsorption capacity of calcium ions. Since all the carriers were selected in the size range ~3–4 mm, the carriers with the same size were used.

### *Laboratory experiments*

#### *Effects of calcium ions on nitrate removal*

The effects of calcium ions on the removal of nitrate nitrogen were investigated by varying the conditions as shown in Table 1. For experimental devices, an acrylic reactor with an effective capacity in 2 L was used. Batch experiments were conducted using a Jar Tester (Chang shin Sci., Korea). Experimental procedures are as follows. 1 L of raw water containing nitrate nitrogen and calcium ion was injected in 1 L of sludge of 3000 mg MLVSS/L after adjusting its pH to 7.0. The efficiency of the removal of nitrate nitrogen was investigated under anoxic conditions for 7 h. Moreover, methanol was selected as the organic carbon source required for denitrification upon the start of the experiment, and the ratio of 2.7 mg $NO_3^-$-N/mg $CH_3OH$ was injected depending on the initial concentration of nitrate nitrogen. The initial concentration of nitrate nitrogen was 55 mg $NO_3^-$-N/L. The concentrations of injected calcium were 0, 250, 500, 750 and 1000 mg $Ca^{2+}$/L.

#### *Investigation of calcium ion adsorption*

The conditions used for the investigation of the calcium ion adsorption are listed in Table 2. For experimental devices, an acrylic reactor with a valid capacity of 2 L was used in the experiments to investigate the effects on the removal of nitrate nitrogen. Batch experiments were conducted by using the Jar Tester. Experimental procedures are as follows. The initial concentration of calcium ion was 200 mg/L, and its pH was adjusted in the range ~7.0–7.1 using $H_2SO_4$ under all the conditions. The weights of the carriers of metal foam, aluminum oxide, granular activated carbon, and aerobic granular sludge were fixed at 0.5, 1.0, 1.5, 2.0, 4.0, and 6.0 g and injected in a reactor. Adsorption experiments were performed by injecting 2 L of raw water containing calcium ions. The equilibrium of adsorption of calcium ions was investigated by conducting the analysis of calcium ion for 12 h. The adsorption by calcium ions was investigated by the Freundlich and Langmuir model. The most popular adsorption model for a single solute system, the Freundlich model, is an empirical equation based on the distribution of solute between the solid and aqueous phases at equilibrium [14]. The basic Freundlich equation is:

$$x/m = K_f C_e^{1/n} \quad (1)$$

where x is the amount of $Ca^{2+}$ adsorbed, m is weight of media, x/m is the concentration of adsorbed $Ca^{2+}$, Ce is the equilibrium concentration of $Ca^{2+}$ in solution, and $K_f$ and n are the empirical constants. Eq. (1) can be written into a linear form:

$$\log(x/m) = \log K_f + (1/n)\log C_e \quad (2)$$

For an X–Y plot of Eq. (2), where $y = \log(x/m)$ and $x = \log C_e$, the slope and intercept are 1/n and log $K_f$, respectively.

The Langmuir adsorption isotherm model was developed for the adsorption of gas on a solid adsorbent. The assumptions of the isotherm model are monolayer surface coverage, identical and equivalent surface sites with equal sorption activation energy of each molecule resulting in homogeneous adsorption and no transmigration or interaction between the adsorbed species in the plane of the surface [15].

The mathematical expression of Langmuir isotherm is as follows:

$$q_e = (q_m b C_e)/(1 + bC_e) \quad (3)$$

where, $q_e$ represents the amount of the adsorbate adsorbed per unit weight of the adsorbent at equilibrium (mg/g) and $C_e$ is the concentration of the solute at equilibrium (mg/L). The parameters, $q_m$ and b, are the Langmuir constants. $q_m$ is represented as the maximum monolayer adsorption capacity and b is related to the binding energy or affinity parameter of the adsorption system. $C_e$ is

**Table 1**
Laboratory-scale experiments for removing of nitrate.

| Condition | Vol., L | pH | DO, mg/L | MLVSS, mg/L | $NO_3^-$-N, mg/L | M.R.[a] | $Ca^{2+}$, mg/L |
|---|---|---|---|---|---|---|---|
| Anoxic | 2 | 7.0 | 0.1–0.2 | 3000 | 55 | 2.7 | 0, 250, 500, 750, 1000 |

[a] M.R.: Methanol required, mg $CH_3OH$/mg $NO_3^-$-N.

**Table 2**
Experimental conditions of adsorption test.

| Experimental conditions | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Condition | Vol., L | pH | Initial $Ca^{2+}$ mg/L | Sampling time, h | Media type | | | |
| Adsorption test | 2 | 7.0–7.1 | 200 | 0–12 | Aluminium oxide | Metal foam | GAC[a] | AGS[b] |

[a] Granular activated carbon.
[b] Aerobic granular sludge.