

연속회분식 반응조에서 생화학흡착제로서 바이오세라믹의 영향에 관한 연구

A Study on the Effect of Bioceramics as Biochemosorption Material in Sequencing Batch Reactor

이승환^{1,*} · 이슬람² · 강미아³

Seunghwan Lee^{1,*} · M.S. Islam² · Meea Kang³

1 School of Civil and Environmental Engineering, Kumoh National Institute of Technology, Gumi 730-701, Korea

2 Foundation Engineering, Curtin University of Technology, Sarawak Campus, CDT 250, Miri 98009, Malaysia

3 Dept. of Environmental Engineering, Andong National University, Andong 760-749, Korea

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Abstract

Sequencing Batch Reactor (SBR) is well adopted for community wastewater treatment for its simplicity, performance and various advantageous treatment options. SBR is now drawing attention for its process modification such as coupled with membrane bioreactor, reverse osmosis or applying different media to achieve high removal efficiency. This study focused on the improved efficiency of carbon, nitrogen and phosphorous removal by applying zeolite materials called bioceramics to the SBR. Two laboratory-scale SBR units were operated in the same operating conditions - one with bioceramics called Bioceramic SBR (BCSBR) and the other without bioceramics used as control. Routine monitoring of COD, TP, NH₃-N, NO₃-N was performed throughout this study. COD removal was about 80% to 100% and phosphorous removal was about 60% in the process whereas NH₃-N removal efficiency was found to be 99.9% in the BCSBR unit. Addition of bioceramics also improved sludge characteristics such as sludge dewaterability, specific gravity and particle size. BCSBR can withstand high ammonia shock loading leading to the better treatment capacity of high ammonia containing wastewater. The cause of improved removal efficiencies within the biological reactor could be attributed to the biochemosorption mechanisms of bioceramics. Absorption/adsorption or desorption capacity of bioceramics was tested through laboratory experiments.

Key words: Bioceramics, sequencing batch reactor, ammonia nitrogen removal, shock loading

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*Corresponding author Tel: +82-54-478-7632, FAX: +82-54-478-7629, E-mail: dlee@kumoh.ac.kr (Lee, S.H.)

1. INTRODUCTION

Biological processes for nitrogen removal is very important for wastewater treatment because discharge of nitrogen into surface water results in oxygen depletion and algae bloom. In order to enhance the nitrogen removal from ammonium-rich wastewater, several studies on pretreatment such as air stripping and chemical precipitation with magnesium ammonium phosphate have been conducted. These processes, however, require complicated configuration and have difficulties in maintenance due to the scale formation (Liao et al., 1995; Li et al., 1999; US EPA, 1993). Sequencing batch reactors (SBR) have proven a viable alternative to continuous-flow reactors (CFR) in handling fluctuating wastewater flows (Irvine et al., 1997). Furthermore, the operational flexibility of SBRs makes them capable of mimicking many types of processes in CFR systems and yield similar or superior performance (Grady et al., 1999). Another recently described advantage of SBRs over CFRs is the possible formation of granular activated sludge, which can greatly improve sludge settleability and increase treatment capacities (Morgenroth et al., 1997). The mechanism of granulation is mostly unknown, although it may be related to adaptation to inhibitory compounds and severe environments (Razo-Flores et al., 1996). Biochemical processes have a tremendous capacity for the removal of many organic and inorganic compounds from wastewaters. This capacity can be enhanced by subjecting reactors to sequential or alternating redox environments (e.g., anoxic/aerobic conditions), as is well established for biological nutrient removal (BNR). It has also been known that such sequential environments may be beneficial for the removal of soluble organic carbons (SOCs). Nevertheless, it may be challenging to efficiently remove both nutrients and refractory organic contaminants concomitantly, because many SOC inhibit autotrophic nitrification, the first step in nitrogen removal (Hockenbury and Grady, 1977). Several researchers have developed hybrid biological ion exchange systems, using

the zeolite as ion exchange material (Semmens and Kleive, 1981). It was recently presented (Green et al., 1996) a dual mode process consisting of ion exchange and bioregeneration mode in a single reactor using zeolites for ammonium removal, followed by bioregeneration. In addition to the ammonium removal step with bioregeneration, however, a denitrification step should be provided for complete nitrogen removal from nitrogen stream generated from bioregeneration. This study investigates wastewater treatment by modified sequencing batch reactor (SBR) using absorbing media for better nutrients removal.

The effect of media on the process of biological nitrification and denitrification, and also on the physical and biological characteristics of activated sludge is of prime importance for the improvement of nutrients removal. Biological processes are limited by the amount of active biomass present in the system or to the extent of efficiency (Morgenroth et al., 2000). The inherent capacity to compensate for variable loading conditions in biological systems for wastewater is limited by a relatively slow adaptation of the mass of active bacteria in the system. Adjusting treatment plant operation on the quality of wastewater has become feasible today with an increasing availability of reliable treatment options and increasing process wastewater (Mazumder, 2002). SBR is one of the most promising processes for small size wastewater treatment plants (Furumai and Kazmi, 2000). Equalization, primary clarification (in most cases), biological treatment, and secondary clarification can be achieved in a single reactor vessel while operating flexibility and control, minimal footprint, potential capital cost savings can be made by eliminating clarifiers and other equipments. Hence the feasibility of using absorbing media for improved nutrient removal is necessary to be studied both in terms of clean environment and efficient treatment process. Bioceramics are such types of biological support media made from oceanic silica, zeolite and other elements. The main objective of this study is to identify the physical composition, characteristics and phenomena of

bioceramics in biological process. This paper presents enhanced nitrification and denitrification capacity of Bioceramic-SBR(BCSBR) system due to the biochemosorption mechanism of bioceramic supporting media.

2. THEORETICAL CONSIDERATION

Bioceramics was manufactured at high temperature by combining zeolite and mineral that can be effective for the removal of $\text{NH}_3\text{-N}$. Zeolites are naturally occurring ion exchange materials used for cation removal (Metcalf and Eddy, 2002). Zeolites have characteristics of high selection of absorption and cation exchange capacity. It supports individual development and helps eliminating $\text{NH}_3\text{-N}$ from municipal, industrial and agricultural wastewater. The biochemical activity of activated sludge can be increased with the addition of porous additives, such as those with high surface area to which bacteria adhere and are thus immobilized (Smith, 1999). Ceramic materials have been considered potentially useful for preparation of porous carriers for supporting microbial adhesion and growth. Therefore, the effects of the surface structure of porous ceramics on adhesion of microorganisms and the biological purification abilities were investigated by using surface-modified ceramics (Nagata, 1995). It is well known that bioceramics maximize nitrogen removal efficiency through ammonia ion exchange, i.e., increase of biological treatment efficiency through biochemosorption, and work for effective microorganism attachment to the surface. The ion exchange mechanism is shown in **Fig. 1**. The ion exchange capacity of bioceramic material is influenced by the size and shape of the media, ion atmosphere, pH, temperature of wastewater and the size and concentration of the hydrated ions in the reactor. As cations that have strong affinity to geolite based media are K^+ , NH_4^+ , Na^+ and Ca^{2+} in decreasing order (Jama and Yucel, 1990). Thus NH_4^+ ion easily replaces Na^+ at higher ammonium ion concentrations.

The equilibrium exchange reaction between the NH_4^+

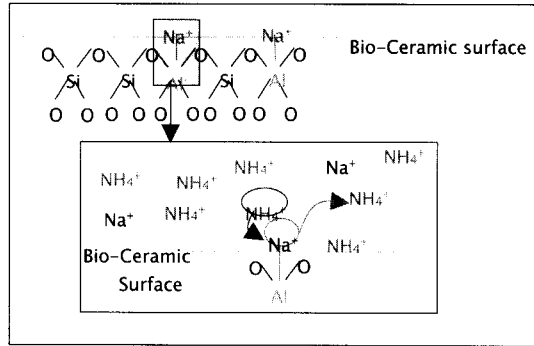


Fig. 1. Ion exchange mechanism.

ion in the solution and the Na^+ ion attached to the bioceramic can be expressed as stoichiometric reaction as shown in Eq. 1;



The selectivity of various ions is dependent on the size, electron, and electric structure of cations. Once the bioceramic is saturated with ammonium, chemical regeneration is possible when the large amount of sodium chloride is added into the solution. As soon as the ammonium-saturated bioceramic is placed in solution, a small amount of ammonium will be displaced according to Eq. 2;



The ion-exchange equilibrium between ammonium and sodium for clinoptilolite was expressed as shown in Eq. 3.

$$[\text{NH}_4^+] = \frac{X_{\text{NH}_4^+} [\text{Na}^+]}{a(1 - X_{\text{NH}_4^+})} \quad (3)$$

where $[\text{NH}_4^+]$ is the concentration of ammonium ion in solution (meq/L), $[\text{Na}^+]$ the concentration of sodium ion in solution (meq/L), is the ionic fraction of ammonium in the bioceramic phase and a is the selectivity coefficient.

Table 1. Chemical composition of bioceramics

Components	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Na ₂ O	Fe ₂ O ₃
Percentage (%)	64.3	26.5	3.28	2.61	0.18	3.1

3. MATERIALS AND METHODS

In this study, bioceramics was manufactured in spherical shaped media for microorganism growth at the surface. It acts both as supporting media and biochemosorption media within the biological treatment system with its high capacity of biological sustainance, chemosorption and ion exchange. Bioceramics is aluminosilicate that has tetrahedral structure, which allows relatively wide distance between the constituting elements. Ions and water molecules can travel through the cavity (empty space between the elements) easily. Negatively charged aluminum in AlO₄/Al₂O₃ is combined with cations such as Na⁺ or K⁺. Due to the characteristics of electric attraction to ammonium ions, aluminosilicate media with higher aluminum density can be considered as better media. Nitrification is inhibited by unionized ammonia or free ammonia, and unionized nitrous acid (HNO₂). The inhibition effects are dependent on the total nitrogen species concentration, temperature and pH. It was revealed (Alleman and Irvine, 1980) that a free ammonia concentration of 0.6 mg/L was capable of inhibiting the nitrobacter species. Bioceramic has an ammonia adsorption and exchange capacity, which is suitable for biological process where NH₄⁺ ion is exchanged in BCSBR to render greater efficiency of treatment system. Compared to activated carbon, bioceramics used in this study has advantages in terms of high sorption capacity, special selectivity, good temperature stability, and strong radiation resistance. The chemical composition and physical characteristics of the bioceramics are shown in **Table 1** and **Table 2** respectively. The ratio of Si/Al is an important factor in the bioceramic structure. When the ratio is less than 4.0, the bioceramic is a clinoptilolite-type one. On the contrary, if the ratio is less than 4.0, the clinoptilolite-type

Table 2. Physical characteristics of the bioceramics

Items	Values
Average diameter (mm)	12
True density (ρ)	1.73
Surface area ($^{\circ}$ C)	49.6
Pore size (θ)	52.0

bioceramic would be somewhat shifted to a heulandite-type one (H.S. Lee and H.G. Kim, 2003). The ratio of Si/Al for bioceramic used is about 2.64, which means that heulandite-type bioceramic is predominant. Although the commonly occurring sedimentary mineral, clinoptilolite, is generally considered to be an isostructural variant of heulandite, there is no sufficient evidence for the conclusion (Breck, 1974)

Three sequencing batch were operated in a day at a cycle of 8 h. One-third of the reactor working volume was decanted during a cycle. Hydraulic retention time was 1 day, and 30 days of solid retention time was maintained by discharging the proper amount of sludge. Operating condition of the control reactor consisted of an anoxic-fill phase (0.5 h), an aeration-mixing phase (3 h), an anaerobic phase (2.0 h), a settling phase (1.5 h), and a decanting phase (45 min) and idle phase (15 min). The concentrations of NO₃-N, NH₃-N were measured at influent and effluent points in a daily basis according to the standard methods for the examination of water and wastewater (APHA, 1998). **Fig. 2** shows the experimental set-up in this study. Two reactors were operated with the same experimental condition to investigate the effects of bioceramics in SBR unit. Cycle sequences were controlled by an automatic timer in each reactor.

The absorption and desorption of ammonia by bioceramics were tested in the laboratory by jar test experiments. Detailed experimental operating conditions are summarized in **Table 3**. **Table 4** shows the composition of synthetic wastewater used in this

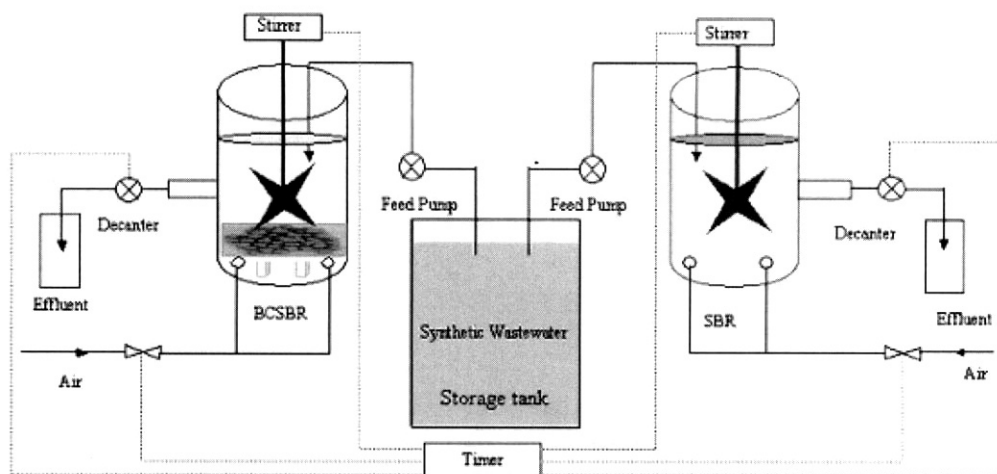


Fig. 2. Experimental Set-up of BCSBR and SBR units.

Table 3. Detailed experimental operating condition

Volumetric loading rate (kg COD/m ³ .d)	0.2
MLSS (mg/L)	2000
F/M ratio (mg COD/mg MLSS.d)	0.1
Fill to React ratio	0.1
Recycle volume (L)	5
Recycle ratio (%)	34
Sludge age (d)	10
HRT (d)	1

Table 4. Composition of synthetic wastewater

Compounds	Amount/Concentration
Glucose (g)	188
(NH ₄)Cl (mg/L)	5,10,20,30
K ₂ HPO ₄ (g)	15
MgSO ₄ ·7H ₂ O (g)	10
CaCl ₂ ·2H ₂ O (g)	10
NaCl (g)	50
FeSO ₄ ·7H ₂ O (g)	2

experiment. Synthetic wastewater was prepared in 10 L of storage tank.

Ammonium in the microbial sludge and bioceramics was measured as described in the previous paper (Semmens and Porter, 1979). Samples for ammonium analysis of the liquid phase and solid phase were taken from each sequencing batch reactor. Samples for extractable (solid phase) ammonium taken from the BCSBR were immediately poured into test tubes with a 2 N KCl solution on a 1:1 volumetric basis. Then the samples were mixed and extracted for 15 min in the shaking incubator of the 200 rpm and 25°C. After centrifugation at 2000g for 1 min, the ammonium concentration of the supernatant was assumed to be total ammonium concentration. Ammonium concentration of the liquid sample was immediately analyzed after centrifugation by a distillation method while solid phase

ammonium concentration was determined by subtracting the liquid phase one from the total ammonium extracted. Size distribution of bioceramics and sludge were measured with a Zetamaster Model 5002 (Malvern Instruments, England). Ammonia nitrogen was analyzed by the distillation method. Measurements of other water quality parameters (pH, SS, VSS, and FSS) were followed by the procedures described in the Standard Methods.

4. RESULTS AND DISCUSSION

4.1. Removal efficiency of NH₃-N and NO₃-N

NH₃-N concentration of influent and effluent both in BCSBR and SBR units was measured in a daily basis. Influent ammonia concentration was gradually increased from the initial concentration of 10 mg/L while effluent concentration was affected by the certain level of

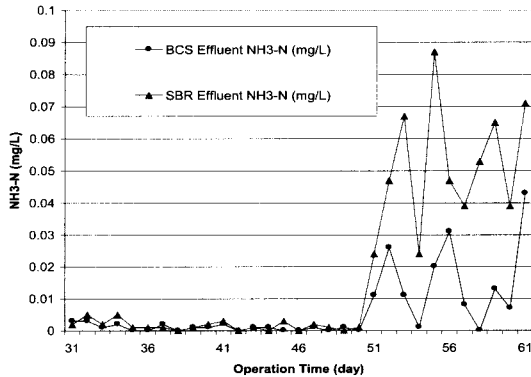


Fig. 3. Changes of NH₃-N Concentration in BCSBR and SBR units.

ammonia loading. Fig. 3 shows the changes of NH₃-N concentration in BCSBR and SBR units. Influent NH₃-N concentration was maintained in the ranges of 10 mg/L. Effluent NH₃-N concentration up to 50 days was almost negligible (less than 0.01 mg/L) in both units. After 50 days of operation, it increased rapidly up to 0.09 mg/L for SBR unit while NH₃-N effluent concentration in BCSBR was consistently lower than that of SBR. Effluent NH₃-N concentration in BCSBR was maintained with the lower concentration than SBR unit regardless of the increase of influent NH₃-N concentration. Removal efficiency of NH₃-N in BCSBR was within the range of 99%.

Fig. 4 shows the changes of nitrate nitrogen (NO₃-N) concentration both in BCSBR and SBR units. Both reactors have shown the similar nitrate concentration in the effluent, indicating that denitrification was almost the same level. After 57th days of operation, BCSBR has shown lower nitrate concentration, which indicates the possible denitrification in the presence of bioceramics. After three-month operation of the BCSBR, it was observed that the morphology of bioceramics has been changed. There was some cavity in the bioceramic balls. The size of the bioceramics decreased after operation. The possible cause of the improved efficiency is due to the biochemisorption of bioceramics in the wastewater treatment process.

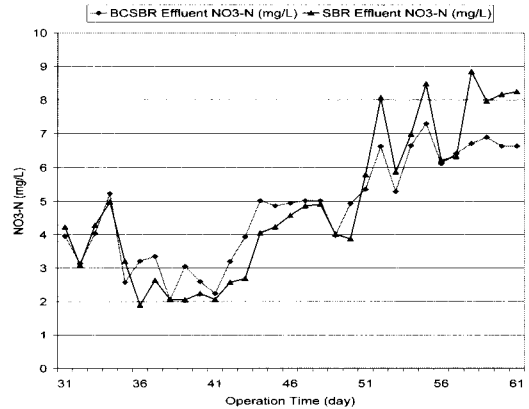


Fig. 4. Changes of NO₃-N in BCSBR and SBR units.

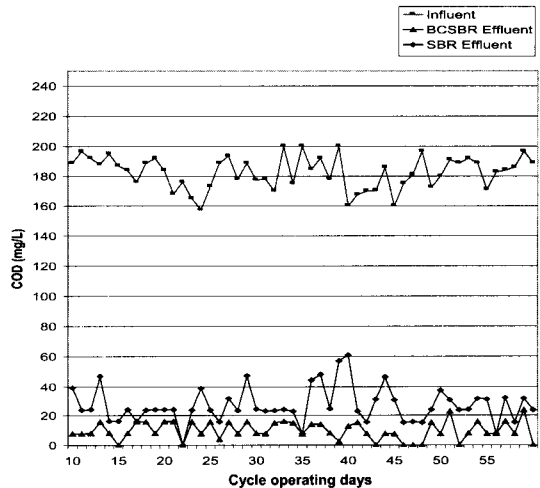


Fig. 5. Influent and effluent COD in BCSBR and SBR units.

4.2. COD removal efficiency

Fig. 5 shows COD monitoring results for both reactors. COD removal was found quite satisfactory for BCSBR with stable effluent quality. The efficiency of removal was significantly consistent in the range of 90-100% for BCSBR. Thus addition of bioceramics improved process performance in the sequencing batch system.

4.3. Effect of shock loading

Shock loading effect by high concentration of NH₃-N was monitored at the last phase of experiment. In the normal loading state, ammonia concentration was

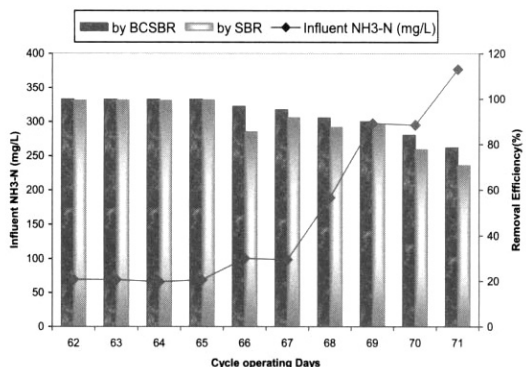


Fig. 6. NH₃-N removal in BCSBR and SBR units with shock loading experiments.

maintained in the range of 70 mg/L. Starting from day 66, the loading of ammonia increased rapidly (from 100 mg/L to 400 mg/L) to compare the removal of ammonia nitrogen in BCSBR and SBR units. Fig. 6 shows the effect of shock loading. Ammonia concentration in the effluent of BCSBR was significantly less than that of SBR effluent. With the increase of influent ammonia concentration, the differences of removal efficiency between the two units were increased. This shows that bioceramics efficiently contribute to tolerating the higher ammonia shock loading.

4.4. Adsorption and desorption

To identify the ammonia sorption and desorption phenomena, 500 mL of distilled water containing 30 mg/L of NH₄-N was taken at different beakers and was placed in multiple stirrer units (Jar tester). The amount of bioceramics taken was 5, 10, 20, and 30 and 40g in different beakers and then the concentrated NH₄-N was estimated in each beaker after stirring. Mixing speed was

Table 5. Experimental results of jar test (Mixing speed = 300rpm, Mixing time = 120sec, Initial Conc. of NH₃-N = 30 mg/L)

Weight of Bioceramics (g)	5	10	20	30	40
Equilibrium conc. of NH ₃ -N (mg/L)	25.3	22.3	16.7	19.0	21.7

30 rpm for 120 seconds of mixing time. Experimental results are summarized in Table 5.

Some researchers had reported (Pak et al., 2002) adsorption phenomena of natural zeolite where they obtained adsorption isotherm with natural zeolite and activated carbon. In their study, it was found that it follows Freundlich isotherm with a K value of 0.5117 with regard to 0.0006 of activated carbon. However, in this study, the adsorption and desorption were not so significant as tabulated in Table 6. Adsorption and desorption results refer to the rejection of any isotherm plotted accordingly. The results did not follow the trend of normal isotherm when plotted graphically. It was reported (H.S.Lee and H.G.Kim, 2003) that the adsorbed amounts of ammonium ion pretreated with sodium chloride were much more than those on samples pretreated hydrogen chloride and sodium hydroxide. Bioceramics used in this study was pretreated with sodium chloride. According to adsorption data as shown in Table 6, the hydrogen chloride-treated bioceramics has the largest surface area. From this fact, it can be concluded that the structure of bioceramic was partially collapsed by a strong acid, hydrogen chloride. It implies that the removal of NH₄-N by bioceramics is not a physical adsorption, but a chemical adsorption, namely an ion-exchange process.

Table 6. Adsorption and desorption of NH₃-N in bioceramics

No. of Jars	1	2	3	4	5	6	7	8	9	10	11
Bioceramics added (g)	0	5	10	20	30	40	60	70	80	90	100
Absorption Equilibrium NH ₃ -N (mg/L)	30.0	29.0	27.96	27.44	26.44	25.12	25.60	25.76	26.86	26.56	26.48
Desorption Equilibrium NH ₃ -N (mg/L)	0	0.138	0.268	0.417	0.640	0.767	0.959	1.03	1.30	1.62	1.67

5. CONCLUSIONS

In this study, parallel set-up of SBR unit with and without bioceramics was operated to investigate the effect of bioceramics in nutrients and COD removals, and the characteristics of sludge. Removal efficiency increased in the Bio-Ceramic SBR due to the biochemisorption characteristics of bioceramics. COD reduction was satisfactory for both cases while BCSBR showed more efficient and consistent removals. Similarly total phosphorous removal efficiency increased up to 65% by the addition of bioceramics. Under shock-loaded condition, the difference of the ammonia nitrogen removal was evident. As a whole, with the addition of bioceramics in SBR unit the following effects were observed:

- Removal of ammonia nitrogen by BCSBR was performed efficiently.
- Ammonia removal under shock loading was superior to SBR.
- Phosphorous and COD removal achieved by BCSBR was in the range of 46 to 65% and 90 to 100% respectively.
- Sludge dewaterability for BCSBR (CST = 15.1s) was higher than that of SBR (CST = 25s).
- Sludge particle diameter in BCSBR ($\Phi = 47.4\mu\text{m}$) was higher than that of SBR ($\Phi = 43.4\mu\text{m}$).
- Removal of $\text{NH}_4\text{-N}$ by bioceramics is not a physical adsorption, but a chemical adsorption, namely an ion-exchange process.

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