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RECYCLING OYSTER SHELLS AND RED SCORIA STONE FOR BIO-DENITRIFICATION PROCESS IN WASTEWATER TREATMENT

Thi Kim Quyen Vo[1], Ngoc Huy Nguyen[2], Ngoc Hoa Pham[1], Tan Phong Nguyen[1,*]

[1]*Faculty of Biology and Environment, Ho Chi Minh City University of Industry and Trade (HUIT)*

[2]*Faculty of Environment and Natural Resources, Ho Chi Minh City University of Technology (HCMUT), Vietnam National University Ho Chi Minh City*

*Email: *phongnt@huit.edu.vn*

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ABSTRACT

Various media have recently been used to treat nitrogen from wastewater. However, low removal efficiency and operation problems remain challenging when applied at wastewater treatment plants. Natural materials for nitrogen removal have become potential under current sustainable development. Consequently, this study utilized red scoria stone and sulfur-based carriers made from oyster shells for nitrate treatment. Red scoria stones are referred to treat wastewater containing a high C/N (organic carbon/nitrogen) ratio, meanwhile, sulfur-based carriers made from oyster shells are suitable for wastewater containing a low C/N ratio, even with no organic carbon. The nitrate removal rate reached 270 ± 20 g N/m^3.day for packed-bed bioreactor filled with red scoria stone (PBR–stone) and 260 ± 10 g N/m^3.day for packed-bed bioreactor filled with sulfur-based carriers (PBR–carrier). These nitrate removal rates are higher than those of the other media used to treat nitrate from wastewater. Additionally, 88 ± 3% of organic compounds removed in PBR–stone and no external organic carbon added to PBR–carrier are strengths of these media. Recycling these solid wastes creates a new material for wastewater treatment and promotes sustainable development.

Keywords: Red scoria stone, sulfur-based carrier, heterotrophic denitrification, autotrophic denitrification, oyster shell.

1. INTRODUCTION

Nitrogen pollution in water bodies causing adverse effects on the aquatic ecosystem and human health has been a serious environmental issue in recent decades. Consequently, many methods have been invented to eliminate nitrogen compounds in water and wastewater sources. These methods mainly involve physico-chemical processes (e.g., adsorption, separation by membranes, ion exchange, and oxidation), and biological processes (e.g., nitrification, and denitrification). The notable strength of the physico–chemical methods is a rapid nitrogen removal rate, however, nitrogen compounds are incompletely treated but only transferred from one phase to another such as from liquid phase to solid phase for adsorption/ion exchange; or from feed flow to concentrate flow for membrane processes. Moreover, many technical devices and chemicals are required in the operation of physico–chemical processes, thus the capital cost is quite high [1, 2]. Hence, nitrogen removal by biological processes has been widely employed in wastewater treatment plants.

Currently, heterotrophic denitrification has been a favorite among biological processes, in which heterotrophic bacteria simultaneously use organic carbon for metabolisms in microbial cells and for nitrate conversion. Organic compounds donate electrons in heterotrophic denitrification, and nitrate ions accept these electrons to be converted to nitrogen gas, resulting in release from wastewater [3]. The conversion rate of heterotrophic denitrification is stable and high, but this process requires an appropriate organic carbon content. As a result, heterotrophic denitrification cannot be fully effective when the carbon to nitrogen (C/N) ratio in wastewater is lower than 2.86 [4]. Some types of wastewater generated from agriculture, farms, and landfills containing a low carbon content are not suitable for applying heterotrophic denitrification in nitrogen treatment, and external organic compounds can be supplemented to bioreactors [5]. This leads to several disadvantages in operation such as treatment cost increase and by–products formation by organic residuals. The opposite of the heterotrophic denitrification process in terms of electron donors is autotrophic denitrification in which sulfur compounds donate electrons for nitrate conversion. Sulfur compounds including elemental sulfur (S^0) and thiosulfate ($S_2O_3^{2-}$) release electrons to be oxidized to sulfate (SO_4^{2-}), while nitrate ions accept electrons to be reduced to nitrogen gas. These reactions occur with the support of bioenzym derived from autotrophic denitrifiers [6]. Due to no use of organic compounds, the autotrophic denitrification process is fully appropriate for nitrogen elimination in wastewater containing low organic contents. Since alkalinity is consumed in the autotrophic denitrification process, calcium carbonate ($CaCO_3$) is usually associated with sulfur compounds. Many previous studies indicated that some problems can occur when using chemicals in powdered form [7, 8], thus, sulfur–based carriers composed of sulfur compounds and calcium carbonate have been developed.

On the other hand, Vietnam has the advantage of a long coastline, so seafood is very abundant. The oysters are a favorite for Vietnamese and people in the world. Along with a huge consumption of oysters, more and more shells have been discharged and that can cause several environmental pollutions such as obstructing hydraulic flows of surface water bodies and producing unpleasant odors due to biodegradation. Ramakrishna et al. [9] demonstrated that calcium carbonate accounts for 95% of the weight of oyster shells, thus it is noteworthy to use oyster shells for sulfur–based carrier production. Besides, Vietnam also has some inactive volcanoes (e.g., Chu Dang Ya, Thoi Loi, Gieng Tien), so the amount of red scoria stone is quite large and mainly appears in the Central Highlands, and currently, this stone is rarely used in any field. Recycling these solid wastes not only reduces the amount of solid waste released into the environment but also creates a new material for wastewater treatment, which is the main objective of this study.

Several types of bioreactors have been used to stimulate heterotrophic denitrification, typically as anoxic bioreactors, moving–bed bioreactors (MBBRs), packed–bed bioreactors (PBRs), and sequencing batch bioreactors (SBR). Among them, PBRs possess some benefits including low energy consumption, uncomplex device requirements, and easy operation. Microorganisms attach to media layers in PBRs and use substrates (e.g., inorganic or organic carbons, nutrients, sulfur compounds) in wastewater for metabolic processes. Consequently, this study aims to evaluate the denitrification performance occurring in PBRs filled with sulfur-based carriers (autotrophic denitrification) and with red scoria stone (heterotrophic denitrification).

2. MATERIAL

2.1. Sulfur-based carriers and red scoria stones

The previous study by Vo et al. [2] showed the procedure of sulfur-based carriers, in which powdered elemental sulfur (S^0) was mixed with powdered calcium carbonate ($CaCO_3$) with a mass ratio of 1.25:1. Then sodium silicate ($NaSiO_3$) solution was added to stick components together with a mass ratio of solution and mixture of 1:4. However, powdered calcium carbonate was changed to powdered oyster shells in this study. Since Vietnam has large oyster reserves, the shells discharged can cause a polluted environment. Moreover, the oyster shells contain 95% of $CaCO_3$ [9], thus they were reused to make sulfur-based carriers. The oyster shells collected from seafood restaurants were cleaned from residual biomass and sand using a pressure water nozzle, and then crushed to powdered form. The powdered oyster shells were put through a sieve (pore size of 0.1 mm) and mixed with powdered elemental sulfur and sodium silicate solution according to the procedure of Vo et al. [2]. The mixture was shaped by silicone molds with a dimension of 10 × 10 × 10 mm. After being dried at 105 ºC for 10 h, sulfur-based carriers were formed with an average porosity of 60% (Fig. 1).

The natural red scoria stones being popular in Vietnam, especially in the Central Highlands, have been widely used in aquarium cleaning and ornamental planting. The red scoria stones in this study were supplied by a company in District 7, Ho Chi Minh City (Vietnam). The main components of red scoria stones include SiO_2, CaO, MgO, Fe_2O_3, FeO, Al_2O_3, TiO_2, K_2O, Na_2O and a density of 3.3 kg/L (provided by the company). The diameter of the stones fluctuated from 10 to 15 mm (Fig. 1), then were cleaned by a pressure water nozzle before adding to the bioreactor.

2.2. Synthetic wastewater and seed sludge

Synthetic wastewater was made $NaNO_3$ (350 mg/L), $MgCl_2.6H_2O$ (9.50 mg/L), KH_2PO_4 (6.50 mg/L), $FeCl_2.4H_2O$ (2.00 mg/L), $ZnSO_4.7H_2O$ (0.20 mg/L), $MnSO_4.2H_2O$ (0.05 mg/L), and trace element (2.0 mL/L) composed of $CaCl_2.2H_2O$, $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $CuSO_4.5H_2O$, and $(NH_4)_6Mo_7O_{24}.4H_2O$ [2, 10]. This study had two inlets consisting of the first inlet (for the PBR filled with sulfur–based carriers) made from the above components and the second inlet (for the PBR filled with red scoria stones) made from the same components but adding $C_6H_{12}O_6$ (137.5 mg/L) to supply organic carbon for heterotrophic bacteria.

The seed sludge was activated sludge collected from a conventional aerobic bioreactor of a domestic wastewater treatment plant operating in Tan Binh district (Ho Chi Minh City, Vietnam). After being transferred to a laboratory, the activated sludge was settled down within 24 h, then the supernatants and the liquid layer were removed. An average of 1.5 L of seed sludge was added to each PBR. The initial biomass concentration measured was around 4,000 mg VSS/L (VSS: Volatile Suspended Solids).

3. METHODOLOGY

3.1. Experiment design

Two packed–bed bioreactors made from mica plastic (a thickness of 10 mm) were cylindrical with a diameter of 140 mm. The height of each PBR was 470 mm, and the working volume was 5.0 L (Fig. 1). Sulfur–based carriers and red scoria stones were filled in each PBR named PBR–carrier and PBR–stone, respectively. The media accounted for 80% of the working volume of the reactor [2]. Both PBRs were sealed to create anoxic conditions (dissolved oxygen – DO below 0.5 mg O_2/L), and covered by aluminum foils to prevent the growth of photosynthetic microorganisms. Besides, PBRs were placed in the laboratory with an air temperature of 28 – 35 ºC (as the climate in Ho Chi Minh City). The inlets were supplied to PBRs at the bottom, and the upflows were controlled at 1.25 ± 0.2 L/h by wastewater pumps to maintain a hydraulic retention time (HRT) of 4 h. The characteristics of synthetic wastewater are shown in Fig. 1.

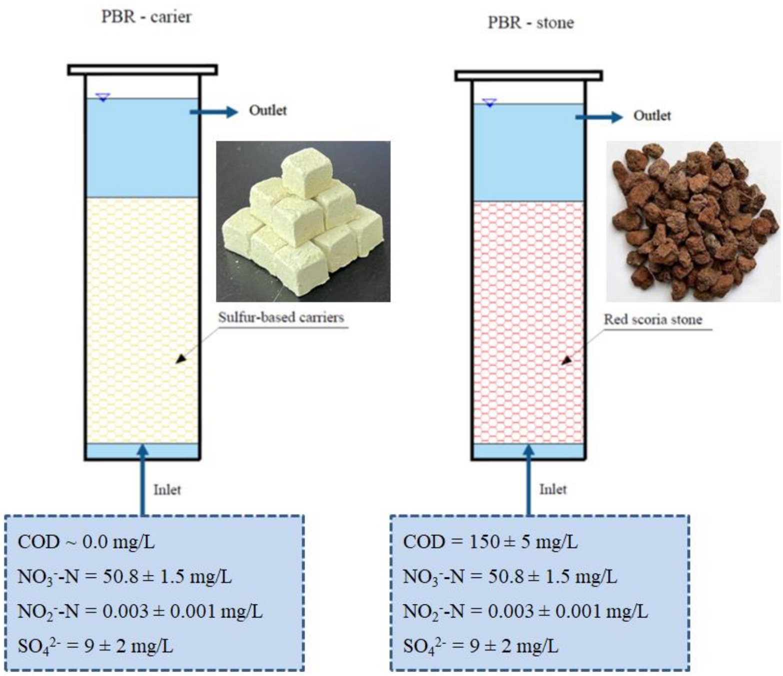

Figure 1 . Packed-bed bioreactors filled with sulfur–based carriers and red scoria stones

3.2. Analytical methods

Water quality parameters were determined with a frequency of 3 – 4 times per week according to APHA [11], such as SMEWW 5220 C for chemical oxygen demand (COD) higher 50 mg/L, SMEWW 4500 NO_2^- B for nitrite (NO_2^-–N), SMEWW 4500 NO_3^- B for nitrate (NO_3^-–N), SMEWW 4500 SO_4^{2-} sulfate concentration, and TCVN 4565-1988 for COD below 50 mg/L. Uv-vis spectrophotometer (Shimadzu, model Z2000, Japan) was used to measure nitrate, nitrite, and sulfate. Additionally, each water sample was analyzed three times. pH and DO values were determined by, respectively, Hanna HI9813–6 and Hanna HI9830–2 electrodes (Nusfalau, Romania).

Loading rate is calculated according to Equation (1):

$$Loading\ rate = \frac{C_{in}}{HRT};\ (kg/m^3/d) \qquad (1)$$

whereas: C_{in} – pollutant concentration in inlet (kg/m^3); HRT – hydraulic retention time (day)

Removal rate is calculated according to Equation (2):

$$Removal\ rate = \frac{C_{in} - C_{out}}{HRT};\ (kg/m^3/d) \qquad (2)$$

whereas: C_{in} – pollutant concentration in inlet (kg/m^3); C_{out} – pollutant concentration in outlet (kg/m^3); HRT – hydraulic retention time (day)

4. RESULTS AND DISCUSSION

4.1. Denitrification performances in PBRs

The inlets were controlled at 50.8 ± 1.5 mg NO_3^-–N/L corresponding to a nitrogen loading rate of 0.30 ± 0.01 kg N/m^3/d, and the nitrate concentration of the two outlets was measured regularly to evaluate the denitrification performance. Since the seed sludge was collected from an aerobic bioreactor, microorganisms need time to adapt to new conditions in PBRs. In details, the nitrate content in the outlet of PBR–stone was 19.3 ± 1.5 mg NO_3^-–N/L in the first 5 days, then gradually reduced within the following days, and was lower than 10.0 mg NO_3^-–N/L after 15 operational days. While, the outlet of PBR–carrier contained 18.6 ± 2.7 mg NO_3^-–N/L in the first 15 days, and it took around 26 days for the nitrate concentration to be less than 10 mg NO_3^-–N/L. In PBR–stone, heterotrophic bacteria attaching to red scoria stones led to biofilm development. Over time, three zones including anaerobic, anoxic, and aerobic are formed in the structure of biofilm [12]. Heterotrophic denitrifiers living in anoxic conditions use organic carbon compounds ($C_6H_{12}O_6$) and nitrate in wastewater for microbial metabolisms and denitrification process. In contrast, no external organic carbon source was added to the inlet of PBR–carrier, thus autotrophic bacteria were dominant in the microbial community. Moreover, autotrophic denitrifiers only use inorganic carbon compounds for metabolisms and elemental sulfur for denitrification process. Owing to the fact that autotrophic denitrifiers have a slow growth rate compared to heterotrophic ones [3], the nitrate conversion in PBR–carrier was carried out more slowly than PBR–stone. The denitrification performance reached stability after 20 days for PBR–stone and 30 days for PBR–carrier. From achieving stabilization onwards, the nitrate content measured in treated wastewater was always lower than 10.0 mg NO_3^-–N/L, such as 7.7 ± 0.8 mg NO_3^-–N/L for PBR–carrier and 6.1 ± 1.2 mg NO_3^-–N/L for PBR–stone. The nitrate removal efficiencies calculated were 80 ± 7% for PBR–carrier and 88 ± 3% for PBR–stone. Besides, the nitrite (NO_2^-–N) content in the two inlets was maintained at 0.003 ± 0.001 mg/L during operational days, and the nitrite content in the two outlets was observed at 0.025 ± 0.011 mg/L. Nitrite is an intermediate in the denitrification process which is converted from nitrate and then converted to nitrogen gas [3]. Thus, the nitrite increase in the outlets demonstrates that the denitrification process occurred in the two PBRs. Additionally, this nitrite concentration (0.025 mg/L) did not inhibit microorganism activities in the two PBRs [13].

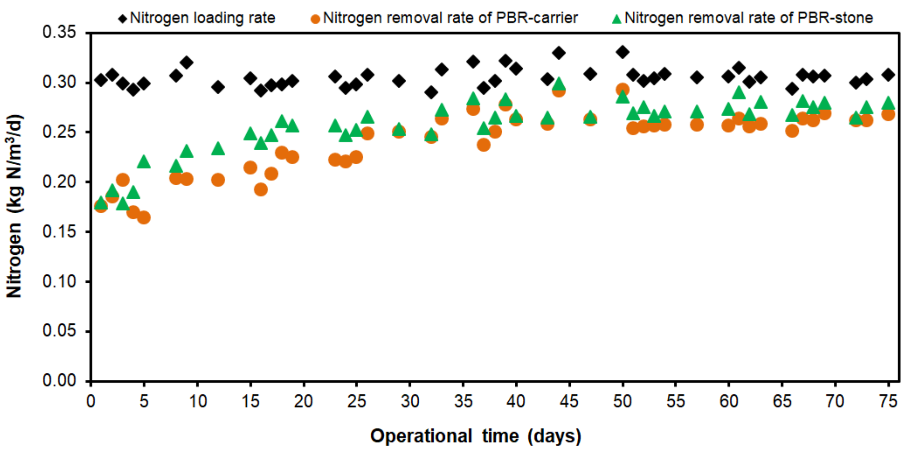

Figure 2 . Variation of nitrogen removal rate in the both packed-bed bioreactors

Obviously, nitrate removal rates of the two PBRs have the same trend with the variation of nitrate concentration. The nitrate removal rate of PBR–stone was low at the beginning (0.18 ± 0.02 kg N/m^3/d) and then increased by 1.5 times after stabilization (Fig. 2). On the other hand, the nitrate removal rate of PBR–carrier was slowly increased and reached the same values as PBR–stone after 30 days. This is explained by the slow growth rate of autotrophic denitrifiers in PBR–carrier, in addition, Zhang et al. [3] also reported that the nitrate conversion by heterotrophic denitrifiers was faster than autotrophic ones. Although the autotrophic denitrification took a longer time to get high efficiency, the nitrate removal rates of the two processes were insignificantly different once both PBRs were in stable operation. Particularly, the nitrate removal rate of PBR-stone was 0.27 ± 0.02 kg $N/m^3/d$, while it was 0.26 ± 0.01 kg $N/m^3/d$ in PBR–carrier ($p > 0.05$, no statistical difference). This indicates that autotrophic denitrification can exhibit the same good performance as heterotrophic processes, it just takes longer for adaptation. Compared to the sulfur-based carriers of Vo et al. [2] made from chemical $CaCO_3$, the nitrate removal rate of sulfur-based carriers made from oyster shells is 1.4–fold lower. However, the carriers made from oyster shells show great environmental significance, reducing manufacturing costs and helping reuse waste (oyster shells).

4.2. Organic removal and sulfate generation

Organic carbon is an indispensable component for microbial metabolisms and synthesis of heterotrophic bacteria, additionally, these bacteria also use organic carbon compounds as electron donors for nitrate conversion. Fu et al. [4] demonstrated that a COD/N ratio of 2.86 is appropriate to achieve a good heterotrophic denitrification performance, thus the COD concentration in the inlet of PBR–stone was controlled at 150 ± 5 mg/L corresponding to a COD/N ratio of 2.9 ± 0.1. The COD content in the outlet was decreased over time, indicating that organic carbon utilization by bacteria in PBR–stone. Data in Fig. 3 showed that around half of COD content (84 ± 7 mg/L) was removed in Days 1 – 15, this is reasonable because bacteria were adapting at that stage thus less organic compounds participated in microbial metabolisms. From Day 20 onwards, the amount of organic compounds used by the microbial community became stable, and the outlet COD concentration was average at 18 ± 5 mg/L, resulting in a removal efficiency of 88 ± 3%. Consequently, using red scoria stones as media for microbial adhesion in bioreactors can treat organic matter and nitrogen in wastewater. Meanwhile, no organic compound was added to the inlet of PBR–carrier to stimulate the growth of autotrophic bacteria. Since the synthetic wastewater was made from tap water, a small amount of organic compounds also exist in tap water, therefore, the COD concentration was measured at 5 ± 3 mg/L. However, COD was not detected in the outlet of PBR–carrier, this can be explained by the existence of some heterotrophic bacteria in the microbial community. Low organic content and anoxic condition demonstrated that nitrate treatment in PBR–carrier was involved in autotrophic denitrifiers.

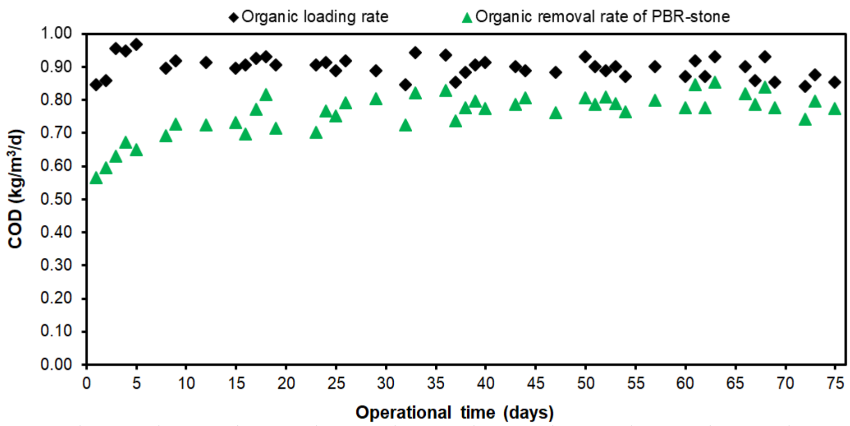

Figure 3 . Variation of organic removal rate in the both packed-bed bioreactors

In the case of sulfate, the SO_4^{2-} content in the inlets was 9 ± 2 mg/L due to components made synthetic wastewater containing SO_4^{2-} ions. Nevertheless, the sulfate content in outlets of the two PBRs was significantly different (Fig. 4). The outlet SO_4^{2-} concentration of PBR–carrier was quite high (252 ± 17 mg/L), this indicated that elemental sulfur (S^0) donated electrons and was oxidized to sulfate (SO_4^{2-}) by autotrophic denitrification process. According to sterio, 7.54 grams of sulfate were generated when one gram of nitrate was converted to nitrogen gas, but the SO_4^{2-}/NO_3^-–N mass ratio was calculated at 5.8 ± 0.4 lower than that of the theoretical ratio. Calcium ions (Ca^{2+}) could cause this lower ratio. Ca^{2+} ions inside sulfur–based carriers precipitated with SO_4^{2-} ions due to $CaSO_4$ formation, leading to a low SO_4^{2-} content in the outlet of PBR–carrier. Vo et al. [2] also indicated this precipitation can reduce the amount of sulfate generation, and the SO_4^{2-}/NO_3^-–N mass ratio was calculated at 6.3 ± 0.1.

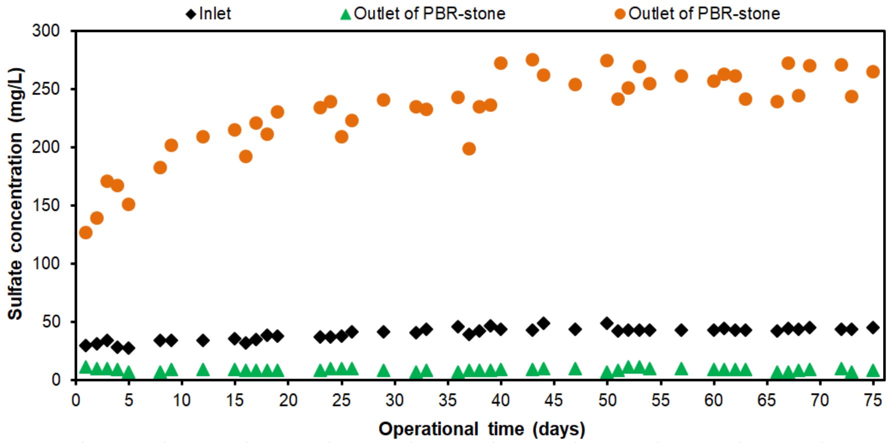

Figure 4 . Variation of sulfate concentration in the both packed-bed bioreactors

4.3. Challenges and future prospects

Heterotrophic and autotrophic denitrification processes exhibit high nitrate removal efficiencies (Table 1). Heterotrophic denitrification is suitable for treating wastewater containing high C/N ratios (at least greater than 2.8). When the organic carbon sources are inadequate, external carbon should be supplied to achieve a good denitrification performance. This leads to some challenges in operation such as increasing costs and forming secondary pollutants. On the contrary to heterotrophic denitrification, autotrophic denitrification is an alternative for treating wastewater containing low C/N ratios or no organic carbon source. Autotrophic denitrifiers utilize inorganic carbon (e.g., CO_2, CO_3^{2-}, HCO_3^-) for their metabolisms. Additionally, the packed-bed bioreactors have been widely applied in nitrate treatment due to some advantages offered such as low energy consumption, uncomplex device requirements, and easy operation. Various media are added to packed-bed bioreactors for bacteria attachment to biofilm forming. Media used can be raw materials (e.g., corn cobs and, red scoria stones) and modified materials (e.g., corn cobs with modified coconut coir and modified macadamia shell biochar, wood chips with hardwood biochar, wood chips with continuous sodium acetate addition, granular activated carbon, a mixture of ceramsite and grainy poly(3-hydroxybutyrate-hydroxyvalerate), and sulfur–based carriers made from oyster shells). Compared to the above media, red scoria stones and sulfur–based carriers made from oyster shells show higher nitrate removal rates (Table 1). These two materials have great potential in nitrate treatment from wastewater. Moreover, the application of natural resources (red scoria stones) or reusing waste (oyster shells) not only removes nitrogen from wastewater but also limits waste discharge into the environment. Howerver, the further evaluation to produce sulfur–based carriers made from oyster shells in large quantities is required such as technical feasibility and economic benefits. Besides, the large-scale supply of red scoria stones is also a challenge.

In addition, a preliminary cost analysis was conducted to compare the economic benefit between sulfur-based carriers made from chemical calcium carbonate and those made from oyster shells. The total cost includes capital (e.g., equipment) and operational (e.g., chemicals, water, energy) expenses. The total cost is calculated at 40.1 million VND for one ton of carrier made from oyster shells and 44.5 million VND for one ton of carrier made from chemical calcium carbonate.

Table 1. Nitrate removal performance of various media in packed-bed bioreactors

Media	Size (mm)	Types of denitrification	Operational conditions	Removal rate ($gN/m^3/d$)	References
Corn cobs	50 – 150	Heterotrophic	C/N = 2.33 : 1 (mol ratio) NO_3^--N = 20 mg/L HRT = 1.5 – 24 hours	9.8 – 24.3	[14]
Corn cobs with modifed coconut coir	50 – 150	Heterotrophic		10.6 – 29.0	
Corn cobs with modifed coconut coir and modifed macadamia shell biochar	50 – 150	Heterotrophic		10.3 – 28.7	
Wood chips	25 × 13 × 5	Heterotrophic		7.1 – 7.8	
Wood chips with hardwood biochar	25 × 13 × 6	Heterotrophic		4.6 – 6.1	
Wood chips with continuous sodium acetate addition		Heterotrophic		10.3 – 120.6	
Granular activated carbon	0.4 – 1.7	Autotrophic	NO_3^--N = 120 – 250 mg/L HRT = 20 – 31 hours Fe(II) = 600 mg/L	70 - 250	[15]
Ceramsite	-	Heterotrophic	NO_3^--N = 14 - 16 mg/L HRT = 12 hours	Not removed	[16]
Mixture of ceramsite and grainy PHBV	-	Heterotrophic		30.5	
Mixture of ceramsite and strip PHBV	-	Heterotrophic		29.9	
Sulfur–based carriers	10 × 10	Autotrophic	NO_3^--N = 50 mg/L HRT = 3 hours	360	[2]
Red scoria stones	10 – 15	Heterotrophic	NO_3^--N = 50.8 ± 1.5 mg/L HRT = 4 hours	270	This study
Sulfur–based carriers made from oyster shells	10 × 10	Autotrophic		260	

5. CONCLUSION

Red scoria stones and sulfur–based carriers made from oyster shells are potential media for nitrate removal from wastewater in packed-bed bioreactors. The nitrate removal rate of both media reaches 270 g $N/m^3/d$. Red scoria stone is appropriate to treat wastewater containing high organic carbon and low nitrogen contents since the stones can stimulate heterotrophic denitrification occurrence. For wastewater containing low or no organic carbon, the application of sulfur–based carriers made from oyster shells is a suitable solution due to no external organic supplement, recycling the solid waste as oyster shells. Besides, using natural material and waste can reduce the cost in wastewater treatment. However, the application of both materials has some challenges as above mentioned, thus further studies need to investigate large-scale applications in real wastewater treatment plants.

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TÓM TẮT

TÁI SỬ DỤNG VỎ HÀU VÀ ĐÁ NHAM THẠCH ĐỎ ĐỂ XỬ LÝ NITƠ TRONG NƯỚC THẢI

Võ Thị Kim Quyên[1], Nguyễn Ngọc Huy[2], Phạm Ngọc Hòa[1], Nguyễn Tấn Phong[1]*

[1]*Khoa Sinh học và Môi trường, Trường Đại học Công Thương Tp. Hồ Chí Minh (HUIT)*

[2]*Khoa Môi trường và Tài nguyên, Trường Đại học Bách Khoa (HCMUT),*

Đại học Quốc gia Tp. Hồ Chí Minh

*Email: *phongnt@huit.edu.vn*

Hiện nay có nhiều loại vật liệu được sử dụng để xử lý nitơ có trong nước thải. Tuy nhiên, hiệu quả xử lý thấp và các vấn đề về vận hành vẫn còn là thách thức khi áp dụng tại các hệ thống xử lý nước thải. Các vật liệu tự nhiên xử lý nitơ trở nên tiềm năng trong quá trình phát triển bền vững hiện nay. Do đó, nghiên cứu này đã sử dụng đá nham thạch đỏ và vật liệu làm từ lưu huỳnh và vỏ hàu để xử lý nitrat. Đá nham thạch đỏ được dùng để xử lý nước thải có tỷ lệ C/N (cacbon hữu cơ/nitơ) cao, trong khi đó, vật liệu làm từ lưu huỳnh và vỏ hàu phù hợp với nước thải có tỷ lệ C/N thấp, ngay cả khi không có cacbon hữu cơ. Tốc độ loại bỏ nitrat đạt 270 ± 20 g N/m^3.ngày đối với bể phản ứng sinh học chứa đá nham thạch đỏ và 260 ± 10 g N/m^3.ngày đối với bể phản ứng sinh học vật liệu làm từ lưu huỳnh và vỏ hàu. Tốc độ loại bỏ nitrat này cao hơn so với vật liệu khác được sử dụng để xử lý nitrat trong nước thải. Ngoài ra, 88 ± 3% hợp chất hữu cơ được loại bỏ trong bể phản ứng sinh học chứa đá nham thạch đỏ và không cần bổ sung cacbon hữu cơ vào bể phản ứng sinh học vật liệu làm từ lưu huỳnh và vỏ hàu là điểm mạnh của các loại vật liệu này. Bên cạnh đó, việc tái chế các chất thải rắn để tạo ra một vật liệu mới ứng dụng trong xử lý nước thải là hoàn toàn phù hợp xu hướng phát triển bền vững hiện nay.

Từ khóa: Đá nham thạch đỏ, vật liệu làm từ lưu huỳnh và vỏ hàu, khử nitơ dị dưỡng, khử nitơ tự dưỡng, vỏ hàu.