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IMPROVEMENT OF BIOFILM ACTIVITIES IN SEQUENCING BATCH REACTOR VIA POLYVINYL ALCOHOL (PVA) GRANULES ADDITION

Nguyen Xuan Lan[a,b], Dang Thi Thanh Huyen[c,*], Pham Thi Thuy[b], Nguyen Manh Khai[b]

[a]*Faculty of Environment, Hanoi University of Natural Resources and Environment, 41A Phu Dien road, Bac Tu Liem district, Hanoi, Vietnam*
[b]*Faculty of Environmental Sciences, University of Science, Vietnam National University, 334 Nguyen Trai road, Thanh Xuan district, Hanoi, Vietnam*
[c]*Faculty of Environmental Engineering, Hanoi University of Civil Engineering, 55 Giai Phong road, Hai Ba Trung district, Hanoi, Vietnam*

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Abstract

Polyvinyl alcohol (PVA) $(C_2H_4O)_n$ is a synthetic polymer material commercially available on an industrial scale. In this study, two formulas were tested for preparing biofilm carriers in spherical shape from PVA/H_3BO_3 (formula 1) and PVA/$NaNO_3$ (formula 2) crosslink bonds without activated sludge entrapment. Formula 2 gave better results with white, round, gel-textured, flexible, and firm carriers. The PVA/$NaNO_3$ granules continued to be used as moving-bed biofilm carriers at a ratio of 10% of the working volume to evaluate the wastewater treatment capacity in the sequencing batch reactor (SBR). After five weeks of operation, the results showed that the PVA/$NaNO_3$ granules turned light yellow due to the presence and development of aerobic biomass. The surface of PVA/$NaNO_3$ granules was plump, elastic, not cracked, and settled well. The amount of biomass attached to the PVA/$NaNO_3$ granules was 0.4 gTSS/g granules. The hydraulic settling velocity of the PVA/$NaNO_3$ granules was 56 mm/s. The wastewater treatment efficiency of the SBR system using moving-bed biofilm activity developed on the PVA/$NaNO_3$ granular carriers was evaluated according to the TSS, COD, and NH_4^+-N parameters at 88%, 90%, and 92%, respectively. The experimental results have demonstrated the potential of developing a new type of biofilm carriers from PVA polymer materials that offer good settling ability and resistance to hydraulic shear force during aeration. Therefore, PVA granules can be easily applied in the column SBR configuration.

Keywords: PVA; granules; biofilm; moving-bed; sequencing batch reactor; SBR; wastewater.

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1. Introduction

Polyvinyl alcohol (PVA) $(C_2H_4O)_n$ is a synthetic polymer material commercially available on an industrial scale and applied as a material for immobilizing microbial biomass. PVA gels suitable for cell immobilization were prepared by repeating freezing and thawing [1–3]. When PVA was dripped and soaked in a saturated boric acid solution, Hashimoto and Furukawa [4] created highly elastic gel granules to immobilize activated sludge in a monodiol crosslink between PVA and boric acid. PVA membranes were also created by irradiation with ultraviolet light and used to entrap enzymes [5]. Shindo used hollow PVA/Canxi alginate gels produced by lyophilized techniques [6] to immobilize yeast.

In wastewater treatment, fluctuations in the flow and quality of the influent make the microbial population diverse and can change significantly during the treatment process. The separation between

*Corresponding author. *E-mail address:* huyendtt@huce.edu.vn (Huyen, D. T. T.)

supernatant and biomass during the sedimentation phase is also challenging. Therefore, the production of a biomass carrier with a polymer gel network such as PVA can improve the efficiency of the biological treatment process such as (i) helping biological treatment systems select and retain bacteria with high biological activity, (ii) having a long biomass retention time in the reactor that increases biomass density, (iii) separating quickly biomass from liquid due to good sedimentation ability.

Many studies have focused on producing spherical PVA granules by monodiol crosslink between PVA and boric acid [4], then improving by hardening with calcium alginate [7] or adding bonding enhancers such as sodium orthophosphate [8], sodium nitrate [9], sodium sulfate [10]. However, most of these granules have a step of immobilizing the sludge in the preparing process, such as activated sludge, anammox sludge, and anaerobic sludge, then used in reactors with fixed or packaged bed media. Due to the PVA being a rather sticky and highly viscous material, it tends to aggregate more when it exists in a moving state due to aeration [3]. The use of PVA gel granules to immobilize highly biologically active bacteria as a commercial carrier capable of long-term transport and storage will also be a challenge in maintaining the viability of the immobilized bacteria. Currently on the market, PVA gel beads that do not immobilize bacteria from Kuraray Co. Ltd. (Osaka, Japan) have proven there commercial value and high application in wastewater treatment as a biomass carrier [11]. These PVA gel beads have diameter of 3-4 mm, a specific gravity of 1.025 g/cm^3, are hydrophilic, and have a porous structure because the solid ratio only accounts for 10% of the volume. This carrier has a 10 to 20 μm pore network that helps bacteria attach up to 1 billion bacteria on each bead [12]. However, importing this carrier will be an economic problem for many wastewater treatment units. Since its introduction in the late 1970s [13], batch biological treatment has had many advantages and applications compared to continuous flow-activated sludge systems. The sequencing batch reactor (SBR) integrates the settling and aeration system, eliminating the sludge recirculation by controlling the sequential timing of the influent feeding, aeration, settling, and decantation phases. In this way, the intermittent flow through the system is controlled by hydraulic retention time (HRT) and separated from sludge retention time (SRT) control, which helps the system to stabilize against fluctuations in the influent while selecting robust bacterial communities with good settling ability and high substrate removal efficiency [14]. The traditional SBR often uses suspended growth-activated sludge for the biological treatment of wastewater. However, when the application requires attached growth microorganisms, the biofilm SBR configuration can be designed and operated to meet the treatment requirements. This is just a technical issue [15, 16]. For example, granular sludge has been a special case of biofilm that could grow as well as be reactivated after long-term storage in the SBR column without the addition of a carrier material [17].

Therefore, in this study, we conducted experiments to produce PVA granules that (i) have good biomass adhesion, withstand hydraulic shear force due to aeration, and settle quickly; (ii) perform wastewater treatment in column SBR configuration as a moving-bed biomass carrier, and (iii) prove the potential to a commercial production scale.

2. Material and Methods

2.1. Chemicals

Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer with the formula $(C_2H_4O)_n$. It is a white, odorless solid powder commonly used as a stabilizer. PVA creates a film with good adhesion and viscosity, making the product flexible and highly tensile. Sodium alginate ($C_6H_7O_6Na$) is a neutral salt in the form of a pale yellow, odorless crystalline powder. It is commonly used in food and cosmetics as a thickener to create a stable product structure. Boric acid (H_3BO_3) is a weak acid in the form of a white, crystalline powder. It is soluble in water and has mild antibacterial properties.

It is commonly used as an antiseptic and natural preservative. Sodium nitrate ($NaNO_3$) is a white, colorless solid with a sweet taste. It is soluble in water and is found most naturally in Chile and Peru. For this reason, it is also known as Peruvian or Chilean saltpeter. It is often used in glass production to increase strength and limit expansion under the influence of temperature. Calcium chloride ($CaCl_2$) is a white crystalline solid with strong hygroscopic properties. It can be used as an additive to reduce the setting and solidification time.

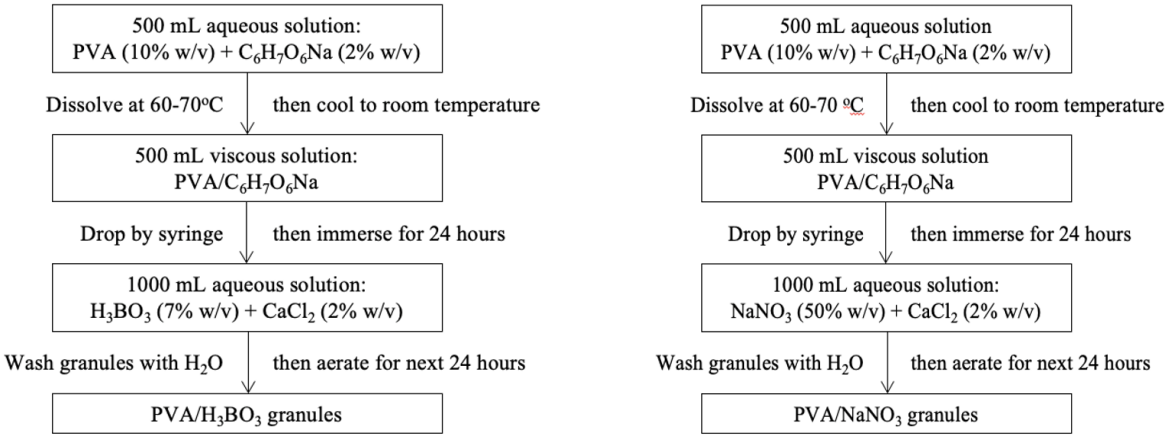
These chemicals are all pure, analytical standards (Analytical Reagent - AR), purchased from Xilong Scientific Co. Ltd. (China) (Table 1).

Table 1. Chemicals used in PVA gel preparation

No	Chemicals	Formulas	CAS No.
1	Polyvinyl alcohol (PVA)	$(C_2H_4O)_n$	9002-89-5
2	Sodium alginate	$C_6H_7O_6Na$	9005-38-3
3	Boric acid	H_3BO_3	10043-35-3
4	Sodium nitrate	$NaNO_3$	7631-99-4
5	Calcium chloride	$CaCl_2$	10043-52-4

2.2. Preparation of PVA granules

The mixture of PVA 10% (w/v) and $C_6H_7O_6Na$ 2% (w/v) solution was prepared in batches by adding water to a glass beaker containing 50 g PVA and 10 g $C_6H_7O_6Na$ up to the 500 mL mark. Next, the mixture was heated and stirred gently on an electric stove at about 60-70 °C for 5 to 10 minutes to dissolve the chemicals. The PVA/$C_6H_7O_6Na$ mixture was then cooled to room temperature (25-35 °C). Prepare 1000 mL of solution A containing saturated H_3BO_3 (7% w/v) and $CaCl_2$ (2% w/v); 1000 mL of solution B containing $NaNO_3$ (50% w/v) and $CaCl_2$ (2% w/v). The PVA/$C_6H_7O_6Na$ mixture was slowly dropped by syringe into solution A (H_3BO_3/$CaCl_2$) and B ($NaNO_3$/$CaCl_2$) to form granules. During the dropping process, solution cup A or B was placed on a magnetic stirrer at a stirring speed of 100 rpm. The spherical PVA gel granules were soaked in the solution cups A and B for 24 hours at room temperature. Then, all the granules were washed several times before being placed in a 2 L container of clean water and continuously aerated for another 24 hours. After aeration,



(a) Formula 1 - PVA/H_3BO_3 (b) Formula 2 - PVA/$NaNO_3$

Figure 1. The procedure of producing PVA granules

the granules that retained their mechanical strength and original shape were filtered and stored at 4 °C in clean water to be used as biofilm carriers in the SBR system, which treats domestic wastewater on a laboratory scale.

The above process was carried out until at least 300 mL of each granule type was obtained. The detailed process is presented in Fig. 1.

2.3. Lab-scale sequencing batch reactor (SBR)

The lab-scale sequencing batch reactor (SBR) system was designed. It used the newly produced PVA granules to evaluate the efficiency of treating domestic wastewater based on the principle of biofilm activity attached to the moving biocarriers, and operating in sequential batches.

The diagram of the SBR system using PVA granular carriers to treat domestic wastewater is shown in Fig. 2.

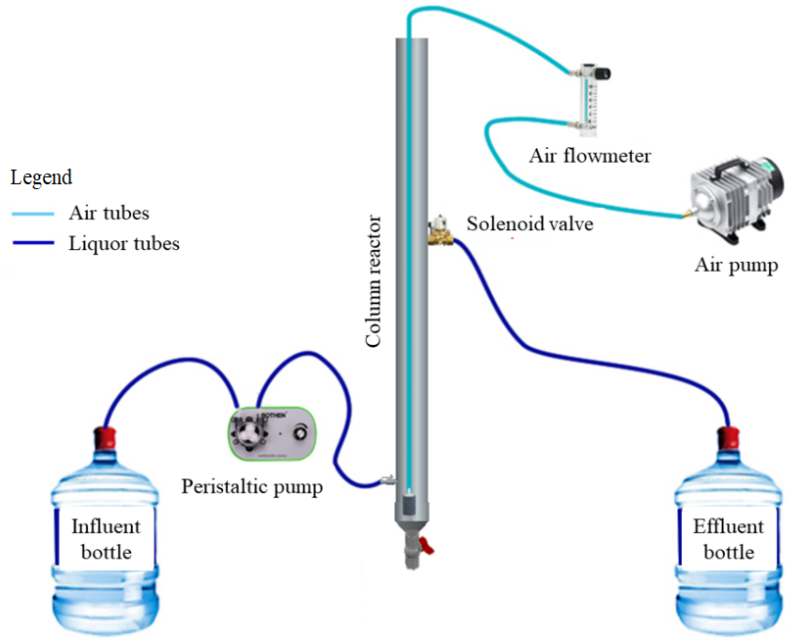


Figure 2. Schematic diagram of the lab-scale sequencing batch reactor (SBR)

The SBR treatment system is column-shaped, made of transparent plastic (Hershey Clear-PVC), with an inner diameter of 76.2 mm (3 inches), an outer diameter of 88.9 mm (3.5 inches), and a height of 1000 mm. 330 mm from the bottom is a drain valve after treatment, opened and closed by a solenoid valve (Uni-D UW-08 1/4), ensuring that the settled volume is 1.5 L. The total working volume of the system is designed to be 3 L, so the volume of water exchanged after each batch is 50%, equivalent to 1.5 L.

The equipment system to operate the SBR column includes peristaltic pump (Grothen G728-1), air blower (Resun ACO-006), air flow meter (LZB-6), pumice stone for air diffuser, influent bottle, effluent bottle, silicone tubing system and valves on the tubes, electrical panel connecting digital timers (03 Timers KG316S) with peristaltic pump, air blower and solenoid valve.

The SBR system was operated in batches. Each batch included influent feeding, aeration, sedimentation, and effluent decanting phases. The PVA granular carriers were introduced into the treatment column, moved freely in the aeration phase due to the up-flow air velocity, and settled freely in the remaining phases. The traditional SBR system uses conventional activated sludge, while the

treatment system in this study applied moving-bed biocarriers. At the effluent drain position inside the SBR column, a mesh plate with a pore mesh diameter of 2mm is fixed to prevent PVA granules washing out from the reaction column, causing pipe blockage and loss of carriers.

2.4. Seeding sludge

The seeding sludge was activated sludge taken from the aerobic tank of the wastewater treatment plant of Vinh Yen City, Vinh Phuc province. For ease of transportation, the mixture of sludge and liquor taken from the aerobic tank at the plant was settled for 30 minutes, decanted, stored in 5L plastic bottles, and transported to the laboratory during the sampling day. Before being poured into the SBR system, the activated sludge was analyzed for several characteristics, with the results being MLSS 26.7 gTSS/L, MLVSS 13.1 gVSS/L, SVI30 78.3 mL/gTSS.

2.5. Domestic wastewater

Domestic wastewater is taken from the drainage pit of Van Chuong residential area, Dong Da district, Hanoi, Vietnam. Table 2 lists the quality parameters of the wastewater.

Table 2. Wastewater characteristics

No	Parameter	Unit	Value	QCVN 14:2008/BTNMT/A
1	pH	-	8.1	5 - 9
2	DO	mg/l	6.8	-
3	Temperature	°C	29	-
4	TSS	mg/l	152	50
5	COD	mg/l	182	-
6	BOD5	mg/l	136	30
7	$NH_4^+ - N$	mg/l	36	5

2.6. SBR operation

First, the SBR system was manually filled with 10% (v/v) PVA gel granules (equivalent to 300 mL granules) and 500 mL of activated sludge as inoculum. When the system was operated with a working volume of 3 L, the MLSS reached 4.45 gTSS/L, and the wastewater volume treated during each batch was 1.5 L.

The SBR system treated wastewater in a sequential batch mode. Each cycle lasted 4 hours, including 4 phases: influent feeding without aeration (60 minutes), aeration (140 minutes), settling (30 minutes), effluent discharge and rest (10 minutes). Three timers on the electrical panel were connected to the peristaltic pump, air pump, and solenoid valve, respectively, to ensure the implementation of these phases in time. When the peristaltic pump was turned on, the wastewater from the influent bottle was pumped into the SBR column from the bottom, passing through the mixed bed of activated sludge and PVA granules to the water level of 3 L within 60 minutes, then the pump closed. Because the volume exchange ratio of the SBR system was 50%, the amount of influent needed to be charged for each cycle was 1.5 L with a flow rate of 25 mL/min. After the influent feeding phase, the air pump was turned on. The airflow into the system through the pumice stone at the bottom of the SBR column was adjusted at 5 L/min by the airflow rotameter, ensuring that the mixture of PVA granules and activated sludge was always in a state of movement in the SBR column. After 140 minutes of aeration, the air pump automatically turned off to switch to the settling phase for 30 minutes. When it was time for the effluent discharge phase, the solenoid valve was turned on to open the discharge valve; thus, the effluent flowed by gravity from the SBR column into the effluent bottle through the

discharge nozzle, then stopped and rested until the peristaltic pump timer switch was turned on to feed the influent for the next cycle. Table 3 shows the operational parameters of the SBR system.

Table 3. Operational parameters of SBR

No	Parameter	Unit	Value
1	Working volume	L	3
2	Volume exchange ratio (VER)	%	50
3	Cycle time	h	4
4	Hydraulic retention time (HRT)	h	8
5	Mix liquor suspended solid (MLSS) for initial startup	g/L	4.45
6	Bed volume of PVA gel granules	% (v/v)	10

After one week of the SBR system start-up, the mixture of PVA granules and activated sludge was manually drained from the bottom of the SBR column, then settled and filtered through a 2 mm sieve to retain the PVA granules. In the next four weeks, the SBR system was operated with only PVA granules as biocarriers to evaluate the wastewater treatment capacity.

2.7. Sample analysis

The morphology of PVA granules was observed using an iPhone 14 camera, an optical microscope (Motic B1-252SP microscope), and a scanning electron microscope (SEM-scanning electron microscope JEOL JSM 6390LV).

Sludge samples and PVA granules were evaluated through characteristics such as MLSS, SVI, settling velocity, and the amount of biomass attached to the PVA granules. The MLSS and SVI parameters were performed using the APHA 2017 standard method (2540G, 2710D) [18]. The settling velocity of PVA granules was performed under static settling conditions in a measuring cylinder containing 1 liter of RO-filtered water. The amount of biomass attached to the PVA granules (g TSS/g PVA-gel) was calculated by taking 10 PVA granules before and after the experiment to determine the attached biomass by the drying and weighing method.

The treatment efficiency of the SBR system was evaluated by analyzing the quality parameters of the wastewater before and after treatment. Samples were collected once a week for five weeks of operation to analyze the COD, NH_4^+-N, and TSS according to the APHA 2017 standard method, respectively 5220D, 4500-NH_3.B&C, and 2540D [18].

3. Result and discussions

3.1. Formation of PVA granules without activated sludge entrapment

Early studies have shown that PVA is a synthetic polymer material that can undergo polymerization with saturated boric acid to form a solid gel and immobilize activated sludge. However, researchers also reported that the PVA gel formed this way had weak binding forces and tended to re-aggregate. Therefore, PVA-boric acid gel was further strengthened by calcium alginate bonding [7]. PVA/sodium alginate mixture and boric acid/calcium chloride mixture were prepared. When the PVA/sodium alginate solution was dropped into a boric acid/calcium chloride solution, PVA would crosslink with boric acid. At the same time, Ca^{2+} ions will be exchanged with Na^+ to form calcium alginate, which helps to solidify the PVA-boric acid granules, increase the density of the gel network, and control the gel pore size.

On the other hand, saturated boric acid is inherently a disinfectant. Its low pH can cause biomass immobilized in the PVA-boric acid gel network to lose activity, even though bacteria in biomass

are surrounded by extracellular polymer substances (EPS) that allow them to withstand changes in culture conditions [19]. Therefore, many studies have used sodium nitrate ($NaNO_3$) [9], sodium sulfate (Na_2SO_4) [10], and sodium hydrogen phosphate (NaH_2PO_4) [20] as an additive for the PVA-boric acid bond. However, most of the efforts to form PVA gel granulation have been studied for immobilizing activated sludge or slow-growing bacteria, such as anammox bacteria [21], in fluidized-bed [22] or packed-bed [23] reactors.

In this study, we intended to produce white PVA granules, which do not immobilize such biomass, to use as a biomass carrier in a moving-bed bioreactor (MBBR) by the mixing force of the up-flow air velocity and have good settling ability in a sequential batch reactor (SBR). Therefore, two formulas for producing PVA granules were experimented: PVA crosslinked with boric acid in formula 1 and PVA crosslinked with sodium nitrate in formula 2. In addition to the different bonds, these two groups of PVA granules were strengthened to prevent aggregation by calcium alginate bonds. PVA granules without activated sludge immobilization were produced by dropping and soaking in the bonding solutions and hardening for 24 hours. The PVA granular strength was verified by continuous aeration for another 24 hours to simulate the moving of the carriers in the MBBR system.

Regarding the process of PVA crosslinked with H_3BO_3 (formula 1), the produced granules were clearer, softer, and more viscous but still retained their round shape after being soaked in the solidifying solution. However, when the PVA/H_3BO_3 granules were put into the aeration tank, they tended to dissolve, clumped together into a mass, and settled at the bottom of the tank. Much foam was released and clumped into a floating mass on the water's surface, as seen via digital images (Fig. 3).

Figure 3. Foam observed due to PVA/H_3BO_3 granules breakage after aeration test

With formula 2 (PVA/$NaNO_3$), the produced granules were opaque white, relatively uniform in shape, firm when pressed, and elastic like rubber granules (see Fig. 4). During and after testing the durability by continuous aeration, the granules showed no signs of breakage, disintegration, or aggregation. They maintained a floating state when aerated and settled quickly when stopping aeration.

As recommended by previous studies, PVA is a sticky and viscous material. This is especially problematic when applying PVA granules with cell immobilization in continuous aerated reactors [24]. The elasticity and strength of PVA granules must resist to the high shear stress encountered in the aeration phase. However, the tendency of PVA granules to agglomerate can make the granular retention difficult or impossible. The chemical ratios used for the PVA granules formulation were 10% (w/v) PVA heated to 70 °C, 2% w/v sodium alginate, 2% w/v calcium chloride, 7% w/v boric acid, 50% w/v sodium nitrate, and a soaking time of up to 24 h to reduce the viscosity of PVA, allowing sufficient time for gel network formation and granules strength. Thus, we believe that the reason type

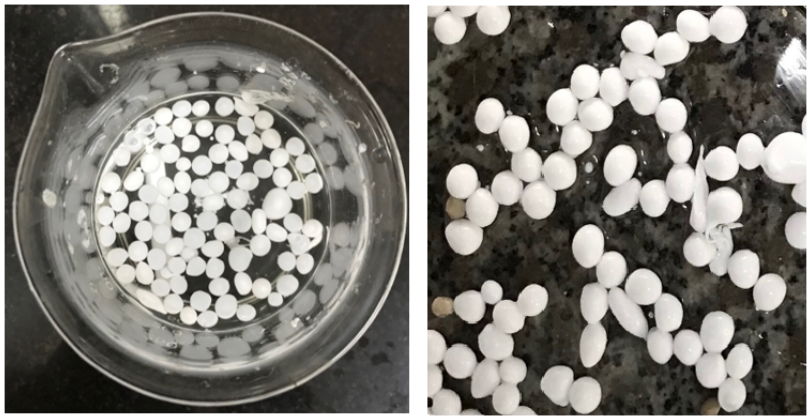
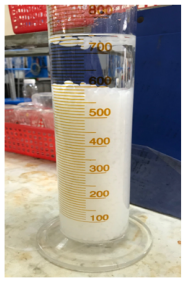


Figure 4. Digital camera images of strong PVA/$NaNO_3$ granules after aeration test

1 granules had weak bonds, quickly broke, and aggregated may be due to the absence of immobilized activated sludge. In other words, the PVA/H_3BO_3 bond was suitable for granulation with activated sludge immobilization. Accordingly, the gel network reaction occurred on the surface of the sludge granules and diffused into the sludge cores over time immersed in boric acid. When no biomass exist, the PVA/H_3BO_3 gel network became loose, soft, and viscous. The product of the PVA/$NaNO_3$ bonding formula was opaque white gel granules, firm but still highly elastic, with dimensions of 4-5 mm and a typical weight of 0.06 g/one granule (Fig. 5). Therefore, the PVA/$NaNO_3$ granules were further experimented in the SBR system as biomass carriers.



(a) PVA/$NaNO_3$ granules

(b) Granule's dimension

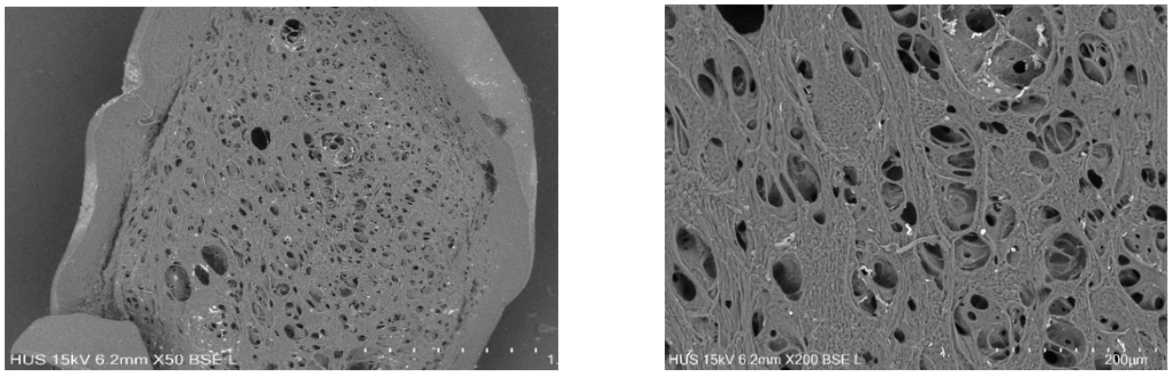
(c) Granule's weight before SBR operation

Figure 5. Digital camera image

3.2. Characteristics of PVA/$NaNO_3$ granules during the SBR operation

Observing the PVA/$NaNO_3$ granules during the aerobic phase in the SBR column, it was found that the granules moved well by the airflow from bottom to top, possibly due to the round shape of the granules that helped them rotate flexibly in the column reactor. Changes in the color and shape of the PVA/$NaNO_3$ granules during the wastewater treatment process were recorded by digital images. After five weeks of operation, most of the PVA/$NaNO_3$ granules gradually changed from white to light yellow. The granules became plump, slightly increasing to 5-5.5 mm diameter, without breaking or hardening. Touching the particles felt firm and elastic like rubber, proving that the particles had good durability and could withstand the hydraulic shear force of the aeration process in the SBR column. The granules also settled entirely in the other phases without aeration, which increased sludge retention time and stabilized biomass growth due to no sludge washout and no need for sludge recirculation.

Scanning electron microscopy (SEM) image analysis (Fig. 6) showed that the fresh PVA/$NaNO_3$ granules had a relatively uniform porous structure allowing bacteria to penetrate and grow proportionally to the ability to conduct oxygen and provide substrates from the wastewater environment. Aerobic bacteria would grow on the outer surface of the granules while slow-growing anaerobic bacteria would be fixed in the core of the granules. The polymer network structure would also help bacteria attach well and reside safely, thereby limiting the impact of biomass peeling due to hydraulic collisions in the SBR column.



(a) ×50 (b) ×200

Figure 6. SEM images of PVA/$NaNO_3$ granules at magnification

Under the optical microscope, the PVA/$NaNO_3$ granules had a rather sharp and seamless outer edge, consistent with the plump surface of the granules when observed by the eye. This may be due to the calcium alginate solidification creating a film for the granule's surface. The uniform circular motion in the SBR column also limited the growth of filamentous bacteria and ensured the solid structure and settling ability of the PVA/$NaNO_3$ granules. Meanwhile, when observed a small piece in the core of the PVA/$NaNO_3$ granules under the microscope, it clearly showed the image of bacteria growing and moving in the porous structure of the PVA/$NaNO_3$ gel network.

Table 4 quantifies the change in PVA/$NaNO_3$ granules via parameters such as biomass attached to PVA/$NaNO_3$ granules and the change in the average settling velocity of PVA/$NaNO_3$ granules.

Table 4. Characteristics PVA/$NaNO_3$ granules

No	Parameter	Unit	Value	
			Before	After
1	Colour	-	White	Yellow
2	Shape	-	Spherical	Spherical and plump
3	Size	mm	4 - 5	5 – 5.5
4	Weight of a typical granule	mg/granule	60	103
5	Hydraulic settling velocity	mm/s	41	56
6	Sludge attached to the PVA granules	gTSS/gPVA granules	-	0.4

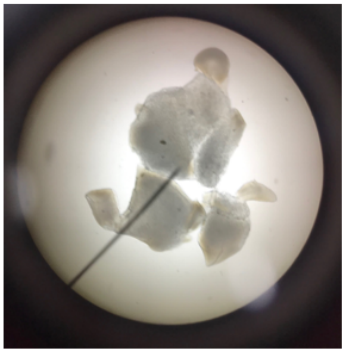
The initial white PVA/$NaNO_3$ granules had a typical mass of 60 mg/one granule. After 1 week of start-up, the mass increased to 67 mg/one granule and reached 103 mg/one granule at the end of operation. The biomass attached to PVA/$NaNO_3$ granules after 5 weeks was 0.4 gTSS/g (PVA/$NaNO_3$ granules) (see Fig. 7). The hydraulic settling velocity of PVA/$NaNO_3$ granules also increased gradually from 41 mm/s of fresh granules to 44 mm/s after one week of start-up. And at the end of

operation, it was 56 mm/s.

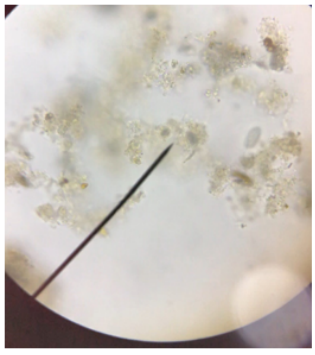
Thus, the formation of gel granules by PVA-$NaNO_3$ bond and solidification by $C_6H_7O_6Ca$ showed suitability for biomass carriers in the column reactors because of the good contact between the spherical granules and the wastewater substrate. Durability under mixing conditions was confirmed because it did not break under operating conditions. This is a potential method for producing polymer-structured biocarriers that are environmentally friendly, inexpensive, and non-toxic to microorganisms.

(a) Original PVA/$NaNO_3$ granules

(b) PVA/$NaNO_3$ granules after 5 weeks in SBR operation



(c) PVA/$NaNO_3$ granules with attached microorganism in microscopy ×20



(d) PVA/$NaNO_3$ granules with attached microorganism in microscopy ×40

Figure 7. Images of PVA/$NaNO_3$ granules under different conditions

To evaluate the potential for commercial production of PVA/$NaNO_3$ granules in this study, we focused on comparing them with PVA gel granules of Kuraray Company (Japan) (Table 5) [12]. The newly produced PVA/$NaNO_3$ granules had the same color, shape, and size but had a mass nearly twice as heavy as Kuraray PVA granules. A PVA/$NaNO_3$ granule weighed 60 mg compared to 38.4 mg of a Kuraray PVA gel granule (Tables 4 and 5). Thus, due to their higher porosity, Kuraray PVA granules are lighter with the same size.

When participating in wastewater treatment as biomass carriers, the PVA/$NaNO_3$ granules were light yellow after 5 weeks in the SBR column. In comparison, Kuraray PVA granules turned black in anaerobic treatment reactors such as UASB [25] and packed-bed system [23] because the attached biomass was anaerobic sludge (Table 6). In aeration reactors with more prolonged operation, the color of the granules will turn dark yellow [12, 26], reflecting the attachment of relatively mature aerobic biomass. The amount of attached biomass on PVA/$NaNO_3$ granules was 0.4 gTSS/g granules, which

Table 5. Characteristics of fresh PVA granules from Kuraray Company (Tokyo, Japan)

No	Parameter	Unit	Value
1	Colour	-	White
2	Shape	-	Spherical
3	Size	mm	3 - 4
4	Weight	g/100 beads	3.84
5	Volume	mL/100 beads	3.9
6	Specific gravity	g/cm^3	1.025
7	Effective surface area	m^2/m^3	~ 2500

was also lower than the amount of biomass attached to Kuraray PVA granules in the aerobic reactor of Yibo Yang et al. (0.41 gVSS/g granules) [26] and the anaerobic UASB reactor of Zang Wenjie et al. (0.93 gVSS/g granules) [25]. The PVA/$NaNO_3$ granules were more solid, and the experimental time was shorter, so the lower amount of attached biomass obtained was utterly reasonable.

Table 6. Characteristics of Kuraray PVA granules after wastewater treatment

No	Parameter	References for Kuraray PVA granules after wastewater treatment			
		[25]	[23]	[26]	[12]
1	Colour	black	black	yellow after 30 days, red brown after 85 days	dark brown color after 60 days
2	Settling velocity	5 cm/s	-	-	-
3	Sludge attached to the PVA granules	0.93 gVSS/g PVA granules	43.3 and 58.4 mg dry biomass/g dried PVA granules	0.41 gVSS/g PVA granules	436 ± 45 mg/L
4	Treatment system	UASB	two packed-bed reactor system	one PVA reactor, two active sludge reactors	integrated system (MBBR, anoxic and oxic)
5	Operation time	117 days	3 months	127 days	more than a year

3.3. Wastewater treatment in the SBR system with PVA/$NaNO_3$ granules

The start-up period of the SBR system was one week with 300 mL of PVA/$NaNO_3$ granules and 500 mL of activated sludge, reaching an initial MLSS concentration of 4.45 gTSS/L. The SBR system performed wastewater treatment in sequencing batches. Each treatment cycle lasted 4 hours, the working volume was 3 L, and the volume exchange rate was 50%. Therefore, the wastewater volume treated in each batch was 1.5 L, the hydraulic retention time (HRT) was 8h, and the system's treatment capacity was 4.5 L/day.

After one week, TSS, COD, and NH_4^+–N removal rates were 68%, 81%, and 76%, respectively. At this point, the wastewater treatment efficiency of the SBR system was still low and unstable, espe-

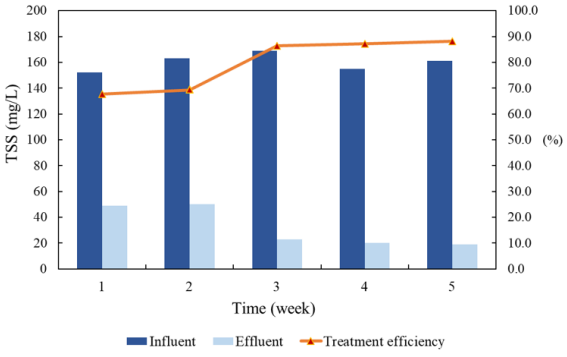
(a) In the start-up period with activated sludge (b) In the treatment period without activated sludge

Figure 8. The PVA/$NaNO_3$ granules SBR operation

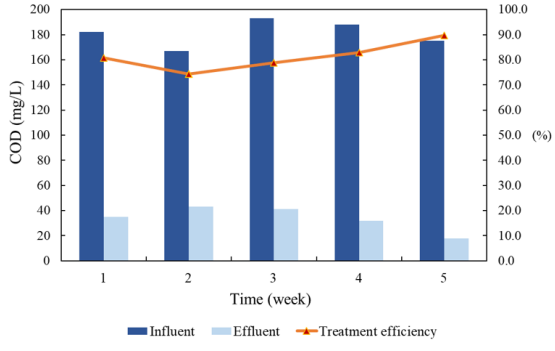
cially the effluent TSS was still high (Fig. 8(a)). However, it was observed that the PVA/$NaNO_3$ granules had begun to turn yellow, showing signs of adhesion and growth of microorganisms. Therefore, the research team decided to separate the sludge from the PVA/$NaNO_3$ granules by sedimentation and filtration to study the treatment efficiency of the SBR system with only PVA/$NaNO_3$ moving-bed carriers (Fig. 8(b)). The purpose was to examine the attachment of biofilm on the PVA/$NaNO_3$ carriers and its wastewater treatment capacity.

During the next four weeks, the SBR system treated wastewater using biofilm activity attached to the moving-bad carriers of PVA/$NaNO_3$ granules, with the time of successive phases and batches unchanged. The PVA/$NaNO_3$ granules were also not removed, supplemented, or circulated, meaning the sludge retention time (SRT) was four weeks.

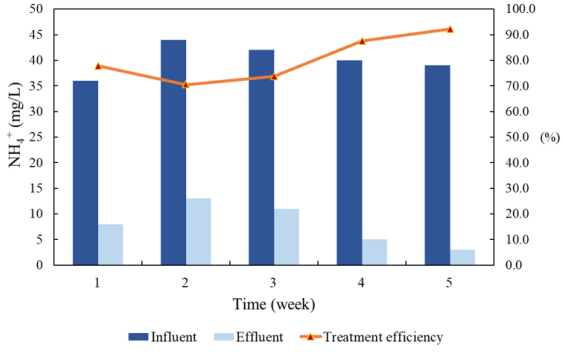
The wastewater treatment efficiency decreased for COD and NH_4^+-N to 74% and 71%, respectively, but remained almost unchanged for TSS treatment efficiency (69%) in the second week (Fig. 9). This was due to the sludge discharge by the end of the first week, which suddenly reduced the number of microorganisms in charge of wastewater treatment. From the second week to the fifth week, the wastewater treatment efficiency gradually increased according to the specific characteristics of each parameter. The TSS parameter increased rapidly in the third week to 86%, then steadily to 87% and 88% in the fourth and fifth weeks. Combined with the observation of the PVA/$NaNO_3$ granules morphology, it can be explained that the third week was the period when solid particles in the wastewater rapidly penetrated the pore network of the PVA/$NaNO_3$ granules, contributing to making the PVA granules heavier and plumper. For COD and NH_4^+-N parameters, the increasing trend of COD treatment efficiency was more linear than that of NH_4^+-N because ammonium oxidizing microorganisms have a slower growth rate than heterotrophic microorganisms consuming organic matter. Therefore, the COD treatment rate gradually increased from 74% in week 2 to 90% in week 5. NH_4^+-N treatment efficiency increased slowly in week 3 (74%), rapidly in week 4, and reached 92% in week 5. At the end of week 5, the concentration values of wastewater quality parameters in terms of TSS, COD, and NH_4^+-N all met column A of QCVN 14:2008/BTNMT, respectively, at 19 mg/L, 18 mg/L, and 3 mg/L.



(a) TSS



(b) COD



(c) $NH_4^+ - N$

Figure 9. Treatment efficiency

Nitin et al. [27] used PVA gel beads from Kuraray Company (Japan), as biomass carriers for treating domestic wastewater with relatively high TSS, COD, and NH_3 removal efficiencies, at 92.3%, 91%, and 90.3%, respectively. However, the treatment system of Nitin et al. was more complex when following the MBBR containing PVA gel beads; there were also an aerotank and a settling system to perform the wastewater treatment. Yibo et al. [26] also operated a wastewater treatment system with a similar configuration to Nitin et al. [27] and achieved efficiencies of 88-94% TSS, 68-93% COD, and 66-99% $NH_4^+ - N$. The concentration values of wastewater quality parameters in Yang's study [28] before and after treatment are similar to the wastewater quality of this study. However, the treatment efficiency of Yang had high fluctuations. It is somewhat lower than this study, which can be explained by the fact that the hydraulic retention time in Wang's system was 2-3 hours, lower than our HRT of 8 hours [29]. Thus, the SBR configuration with the operational parameters set in this study offers the same efficiency as MBBR systems using PVA Kuraray but is more optimal regarding the number of reactors, which means saving space and system construction costs.

4. Conclusions

Polyvinyl alcohol (PVA) $(C_2H_4O)_n$ is a synthetic polymer material commercially available on an industrial scale. In this study, two formulas were tested for preparing biofilm carriers in spherical shape from PVA/H_3BO_3 (formula 1) and PVA/$NaNO_3$ (formula 2) crosslink bonds without activated sludge entrapment. Formula 2 gave better results with white, round, gel-textured, flexible, and firm carriers. The PVA/$NaNO_3$ granules continued to be used as moving-bed biofilm carriers at a ratio of 10% of the working volume to evaluate the wastewater treatment capacity in the sequencing batch

reactor (SBR). After five weeks of operation, the results showed that the PVA/$NaNO_3$ granules turned light yellow due to the presence and development of aerobic biomass. The surface of PVA/$NaNO_3$ granules was plump, elastic, not cracked, and settled well. The amount of biomass attached to the PVA/$NaNO_3$ granules was 0.4 g TSS/g granules. The hydraulic settling velocity of the PVA/$NaNO_3$ granules was 56 mm/s. The wastewater treatment efficiency of the SBR system using moving-bed biofilm activity developed on the PVA/$NaNO_3$ granular carriers was evaluated according to the TSS, COD, and NH_4^+–N parameters at 88%, 90%, and 92%, respectively.

The experimental results of this study have demonstrated the feasibility of developing a formula of producing biomass carriers for wastewater treatment from PVA polymer materials, which can replace those with high prices currently available on the market. With round shape, good settling ability, and resistance to hydraulic shear force during aeration, PVA granules can be easily applied in SBR systems with column reactors, operated in sequencing batches, helping to increase biomass retention time while reducing excess sludge yield and foot-print area, leading to cleaner water quality after treatment.

This study has initially succeeded in testing the formula for producing PVA granules without biomass immobilization. However, it has not yet investigated the peak point of the sludge adhesion to the PVA granules and the optimal operations of the SBR start-up with PVA granules in conditions with and without activated sludge as an inoculum. Therefore, this will be the direction for our subsequent studies.

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