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Micro-sized carbon fiber: a new supporting material for microorganisms in the decomposition of nitrogen and phosphorus nutrients in wastewater with high salinity

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Eutrophication, which kills fish, mussels and other animals in aquatic ecosystem, is the response to the excess of nitrogen and phosphorus nutrients. In this study, activated carbon fiber prepared from poly(acrilonitrile) PAN, a carbonaceous material of micro size with high specific area, has been evaluated to be able to create microbiological membranes that could be used in the decomposition of nitrogen and phosphorus compounds in wastewater with salinity up to 30 ppt. Utilization of carbon fiber in the sustainable treatment of highly contaminated aquaculture wastewater with organic and inorganic pollutants was considered as a promising application in Khanh Hoa province, Vietnam, with great treatment capacity, low system's price and implementation's cost.

Keywords: micro-sized carbon fiber, microorganisms, sorption, biofilm, aquaculture, high salinity, wastewater, nitrogen processing, phosphorous processing.

Углеродное микроволокно: новый материал для микробиологических мембран, применимых для разложения азот- и фосфорсодержащих соединений в сточных водах с высокой соленостью

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Эвтрофикация, которая уничтожает рыб, мидий и других животных в водной экосистеме, может быть результатом антропогенных воздействий, приводящих к избытку азот- и фосфорсодержащих питательных веществ. В данном исследовании использовано активированное углеродное волокно, полученное из полиакрилонитрила (ПАН) - материала с микроразмерными фибрами с большой удельной поверхностью, для создания микробиологических мембран, которые показывали способность разлагать соединения азота и фосфора в сточных водах с соленостью до 30 ppt. Как показали испытания этого углеродного волокна в провинции Кханьхоа (Вьетнам), оно перспективно в применении для очистки сильно загрязненных сточных вод аквакультуры органическими и неорганическими соединениями, обладает высокой эффективностью, низкой ценой установки очистительной системы и низкой стоимостью ее эксплуатации.

Ключевые слова: углеродное волокно, микроразмер, сорбция, микроорганизмы, биопленки, аквакультура, высокая минерализация, сточная вода, соединения азота, соединения фосфора.

Introduction

Aquaculture, just behind tourism, is the most important economical branch in Khanh Hoa – a province in the middle of Vietnam. Its benefits are obvious. It improves the quality of farmers' life and it is a nutrient supply to growing high tourism demand for food service. But, simultaneously, aquaculture has negative impact on the surrounding environment in the region. Produced wastewater from farms is mainly discharge into the coastal sea without treatment [1-4]. Untreated wastewater in the huge volume with high content of organic components, nitrogen and phosphorous nutrients leads to serious environmental problems one of which is eutrophication - the explosive growth of algae in the excess of phosphates and dissolved nitrogen compounds.

The concentration of the pollutants can be illustrated according to the total nitrogen (N) and phosphorus (P) criteria. At present, various direct biological methods are being used mainly in the purification of aquaculture wastewater with low salinity [5,6]. The application of technological solutions with low price and transportation cost for using in the treatment of contaminated water with higher salinity in aquaculture areas is vital and practical, but could be a challenge.

Recently, carbon fiber, a fibrous material with a diameter of 5-10 μm, whose main ingredient is carbon atom (> 90%), has been found out to be capable of purifying water effectively with a number of advantages [7-11]: high-rate treatment due to the high activity of microorganisms; successful treatment of Nitrogen and Phosphorus; simplicity of installation, ease of control; absence of harmful chemicals to human being and aquatic fauna. Each carbon fiber contains bulk of smaller fibers with diameter of 5-10 μm: type 1K – 1000 filaments, type 3K – 3000, type 6K – 6000, etc. This type of material could be synthesized from various precursors: petroleum pitch, cellulose resin and polyacrylonitrile (PAN) [12]. In Japan, carbon fibers are installed in ponds, lakes, and coastal sea, to improve water quality of many locations by removing organic contents in the eutrophic natural waters.

In this study, the method of high salinity wastewater treatment applying carbon fiber prepared from PAN is utilized. This is a different method of significant high rated forming microbiological membranes, treatment contaminated wastewater with the listed advantages and low price, suitable for wastewater with considerable salinity, i.e. aquaculture.

Materials and methods

Materials. Activated carbon fiber with high surface area, type 12K – one fiber consists of 12.000 micro-sized fibrils, was purchased from DowAksa, USA. Steel and PVC tubes used for supporting frame were purchased from local stores.

Sampling and analysis. The degree of stability of criteria characterized for the pollution level of aquaculture wastewater allows the experiment to be carried out in a period of three months. Operating parameters of the process: aeration, stirring with the flow in/out, 4-hour hydraulic retention.

The input wastewater samples have been taken from the collection pit before being pumped to the treatment system, the treated wastewater samples – at the designed output after the retention time – 4 hours. The water samples are filled in the 1.5l PET plastic bottles – cryopreserved and taken immediately to the laboratory for the following analysis.

The progress of water treatment is evaluated by the following parameters: BOD5, total N, total P, ammonium, and nitrite, nitrate forms of nitrogen, salinity as well as number of nitrifying bacteria in the water, are also analyzed according to Vietnamese standards (TCVN), SMEWW and HACH.

Treatment Efficiency. Nutritional constituents, characterized by total N and total P prorated according to waste purifying proportion (%), is evaluated according to the following formula:

$$H_X, \% = \frac{(X_i - X_o)}{X_i} \cdot 100,$$

where X_o – the value of the total N (or total P) at the output; X_i – the value of the total N (or total P) at the input of the treatment system.

Results and discussion

Biofilm development. Adhesive micro-sized carbon fibers enable microorganisms to attach to its high area surface by conquering the energy barrier between microorganisms and the surface to form a biofilm. In less than a week of «swimming» in water with high density of nitrifying bacteria, Nitrosomonas, Nitrobacter – about 10^4 cells/mL, thick layers of biofilm have been developed on each bulk of the fibers, which could be observed on the fig. 1. The nature of biofilm can be illustrated from scanning electron micrographs of the carbon fibers after biofilm formation on their surface (fig. 2).

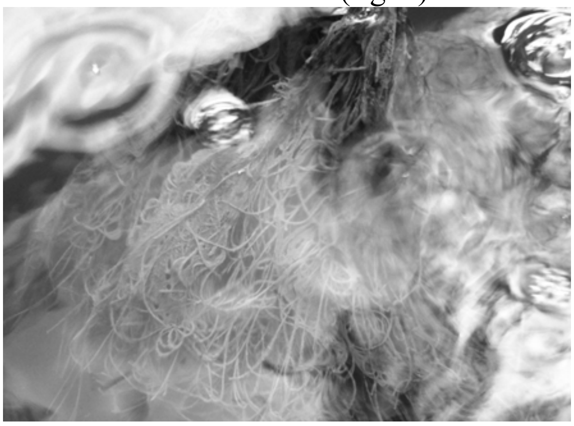

Fig. 1. Biofilms on micro-sized carbon fiber

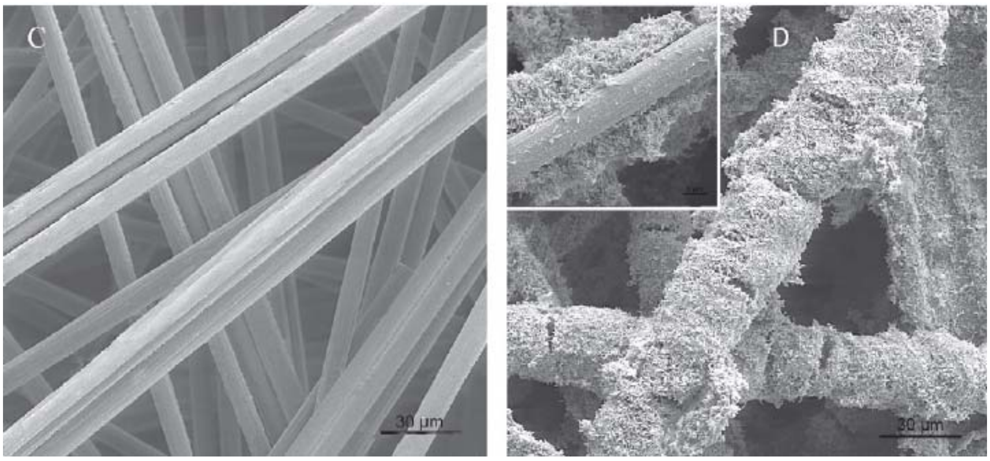

Fig. 2. Scanning electron micrograph of a biofilm: left – before biofilm formation, right – after biofilm formation [13]

Carboxyl and phosphate groups on the cell surface of the bacterium are dissociated in water, made microorganisms negatively charged. The surface of biofilm negatively charged in the water as well. Two negative surfaces form an energy barrier for bacteria to attach the surface. By Brownian motion or movement of various cellular structure, the smaller size bacteria firstly get as close as possible to the carbon fiber surface and contacts reversely. Then extracellular polymeric substances and micro-sized fibers formed by microorganisms go through the energy barrier and adsorb to the surface of supporting fiber, where Van der Waals' force is able to attach the bacteria to the surface [14-17].

Carbon fiber consists almost exclusively of carbon atoms, thus this fiber type is less negatively charged compared to all other synthetic fibers used for biofilm supporting purpose [12]. Therefore the energy barrier between negatively charged bacteria negative surface of carbon fibers is smaller compared to other adsorbing materials. After attachment, Van der Waals' forces are also more intensive between microorganisms and carbon fiber compared to other fibers. Moreover, carbon fibers derived from PAN precursor are turbostratic, thus fibers tend to have high tensile strength.

Biofilm formed on the surface of carbon fibers also provides nutritious substances for microorganism in the aquatic environment. However, until now it has not been reported the reason why carbon fibers are more biocompatible than other synthetic fibers in efficient biofilm development. Important microorganisms used in water treatment, such as nitrifying bacteria to convert ammonium to nitrate and nitrite, are also absorbed to the surface of carbon fibers. Utilization of nitrifying bacteria could be applied in the treatment of heavily polluted water, likewise wastewater from various sources, including aquaculture. Carbon fiber is also safe, toxicity to the human and animal body is not reported. In the consequence, carbon fiber with high adhesive quality and micro size can be a serious candidate for a new supporting material for biofilm development in the aquatic environment.

Wastewater treatment using micro-sized carbon fiber. The input water from tank cultivation aquaculture and water from the treatment system using carbon fiber are characterized by the values in the table 1. Wastewater was pumped directly from collection pit of the breeding farm in Vinh Luong district. Compared to maximum allowed values according to Vietnam's norms, biochemical oxygen demand (BOD5) are all beyond the specified thresholds, which cannot be reused for aquaculture. High ammonia nitrogen level with unpleasant odors is not suitable for the purpose of water supply. BOD5: N proportion is smaller than 20 and BOD5: P – smaller than 100. Consequently, the source is excess of nutritional components – nitrogen and phosphorous compounds, which may lead to serious water eutrophication. The water is also high of salinity, determined by titration with $AgNO_3$ standard solution, which seriously trouble the selection of treatment technology.

Table 1. Efficiency of high salinity wastewater treatment using micro-sized carbon fiber

Characteristic I – input O – output		Series of sampling						Average	Min.	Max.	Efficiency%
		1	2	3	4	5	6				
BOD5 mgO_2/L	I	138	150	125	133	167	169	147	125	169	88.1
	O	22	20	20	18	14	16	17.5	14	22	
Total N mg/L	I	11.6	11.8	13.2	11.9	11.2	12.0	12.4	11.2	13.2	71.1
	O	3.36	3.64	4.20	3.90	3.40	3.10	3.60	3.10	4.20	
Total P mg/L	I	4.03	4.07	4.40	4.30	4.62	4.99	4.40	4.03	4.99	43.2
	O	2.61	2.65	2.67	2.52	2.17	2.39	2.50	2.17	2.67	
N_NH_3	I	7.48	6.70	7.15	6.88	6.47	7.03	6.95	6.47	7.48	81.9

mg/L	O	2.68	1.23	1.30	0.64	0.78	0.92	1.26	0.64	2.68	
pH	I	7.10	7.05	7.00	7.08	6.92	7.07	7.04	6.92	7.10	--
	O	7.60	7.58	7.49	7.34	7.25	7.20	7.41	7.20	7.60	

Evaluated according to the sensory and physical chemistry criteria, the output water from the treatment system using micro-sized carbon fiber was improved considerably: the water was fresh without odors, pollution criteria like BOD5, total N, total P and ammonium nitrogen decreased sharply.

Removal of Nutritive Salts – Nitrogen. Removal of nitrogen compounds is one of key matter in wastewater treatment to prevent eutrophication in the discharged aquatic environment. The reduction of nitrogen substances is due to their process of involving in the constitution of microbiological cells. During the process of anaerobic treatment, the organic nitrogen transforms into ammonia (NH_4OH) under the process of catalytic hydrolysis. Ammonia nitrogen then could be oxidized to nitrate (NO_3^-) through nitrite form (NO_2^-). There are denitrification microorganisms in the biofilm on the surface of carbon fiber, which decompose nitrate nitrogen into nitrogen gas (N_2). Nitrogen then, in the free form of gas, was released into the air (fig 3). Dinitrogen monoxide (N_2O) generation was suppressed by microorganisms on the carbon fiber, which is different from the treatment by activated sludge.

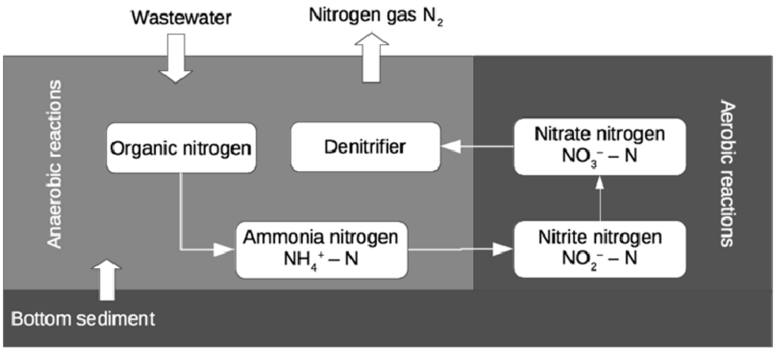

Fig. 3. Nitrogen gas (N_2) generation from nitrogen nutrients in water using carbon

The oxidation of nitrite to nitrate occurs at the high rate, which is proved by the low level of nitrite concentration in water. Constantly, nitrite form does not exceed 0,5mg/l Nitrogen (fig. 4).

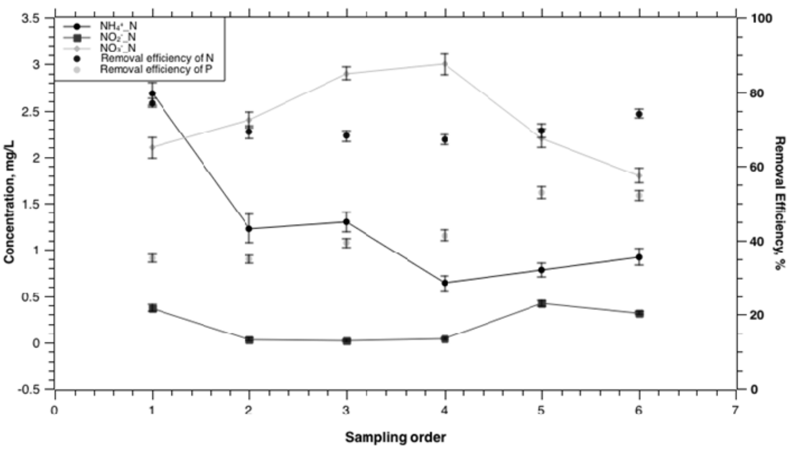

Fig. 4. Variability of nitrogen environmental forms and removal efficiency of nitrogen and phosphorous compounds

The speed of forming nitrate or the degree of ammonia deficiency occurs slowly. This can be explained by the high organic content (high BOD5 value), the low ammonia content, which is unsuitable for autotrophic microorganisms to develop, slowing down the oxidizing process from ammonia to nitrate. The result of determining number of nitrifying bacteria is adequate to these results.

Removal of Nutritive Salts – Phosphorus. Phosphorus is removed from water due to the accumulation of phosphate ion (PO_4^{3-}) as polyphosphoric acid by microbes. Carbon fiber also releases iron ion (Fe^{3+}), which can react with phosphate ion in the water to form insoluble iron phosphate ($FePO_4$). Iron phosphate could be fixed and returned to farmland (fig 5.).

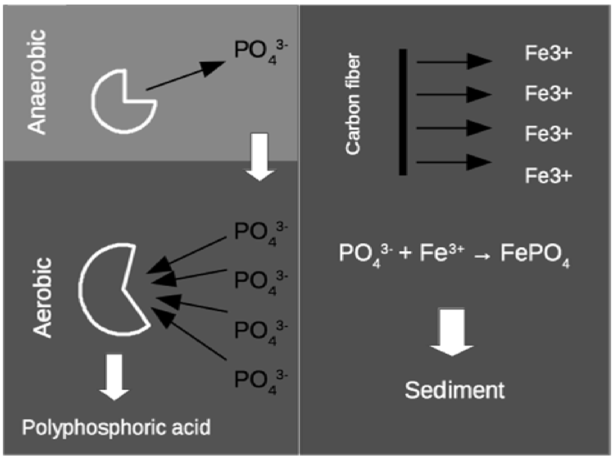

Fig. 5. Phosphorus compounds accumulation by microorganisms on the surface of micro-sized carbon fiber

The single aerobic treatment system using carbon fiber cannot completely remove phosphorus compounds, except for a small amount of 1–2 mgP/L involving in the constitution of microbiological cells (table 1). Thus, phosphorus treatment by the methods of creating microbiological membranes on carbon fiber, and other supporting materials, can only remove phosphorus along with biomass during the process of discharging excessive sludge.

Conclusion

The treatment method of microbiological membrane formation on micro-sized carbon fibers is a high efficient treatment technique, that could be applied in aquaculture with high content of nitrogen and phosphorous compounds to prevent eutrophic water pollution. Nitrogen pollutants are removed through consequence of catalytic reactions, while phosphorous nutrient consumed mainly by microbes as food supply. Carbon fibers were also investigated as high biocompatible and non-toxic supporting material to aquatic fauna and human.

Results of the experiment in this work demonstrate the ability of carbon fiber application in the treatment of aquaculture wastewater with high salinity. This method is also promising in the treatment of various contaminated water sources, such as domestic wastewater, industrial wastewater, contaminated natural water in ponds, lakes, rivers and coastal seas.

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