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Integrated anaerobic/aerobic biodegradation in an internal airlift loop reactor for phenol wastewater treatment

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Abstract−Anaerobic and aerobic biodegradation were integrated in an internal airlift loop reactor (IALR) by adding porous microbial carriers. In this bioreactor, aerobic activated sludge was suspended in the liquid bulk, while the anaerobic microbes were attached within the core of carriers. The integrated IALR was applied to the treatment of synthetic phenol wastewater. After 50 days' acclimation according to co-substance strategy, the influent COD decreased from 3,700 mg/L to 400 mg/L (phenol removal rate was over 99%) with the residence time of 24 h. High performance could be achieved under the operation condition of superficial gas flow rate higher than 0.07 cm/s, temperature beyond 15 °C and the microbial carrier volume fraction larger than 5%. Integration of anaerobic/aerobic biodegradation in IALR enhanced the synergetic effects between aerobic and anaerobic degradation; therefore, it has great potential in the treatment of phenol wastewater and other wastewater containing hard biodegradable organics.

Key words: Anaerobic/Aerobic Biodegradation, Porous Microbial Carriers, Internal Airlift Loop Reactor, Phenol, Wastewater Treatment

INTRODUCTION

In comparison with physical/chemical methods, biological degradation has shown great potential in the treatment of phenolic wastewater due to low cost and being environment-friendly. As the toxicity of phenol [1], the aerobic treatment could succeed only in the case of low concentration [2]. Therefore, the emphasis has been more on anaerobic treatment, which was competent for the degradation of higher concentration phenolic wastewater [3-6]. Anaerobic degradation combined with physical/chemical treatments, *e.g.*, adsorption [7] and advanced oxidation process, or combined with aerobic degradation, has been reported in many previous studies.

Sequential combined anaerobic and aerobic degradation has been widely applied for the treatment of wastewater containing toxic organics, including phenol. Chakraborty and Veeramani [8] reported the aerobic reactor was the most sensitive in terms of phenol shock load in the anaerobic-anoxic-aerobic system. Majumder and Gupta [9] observed that methanol and glucose were good carbon sources for the removal of chlorophenols in sequential upflow anaerobic sludge blanket (UASB) and rotating biological contactor (RBC). Anoxic-aerobic submerged fixed-film reactors were applied for the biological nitrogen and phenol removal [10]. Uygur and Kargi reported the phenol inhibition of biological nutrient removal in a four-step sequencing batch reactor [11].

Recently, several bench scale processes were reported to integrate anaerobic and aerobic environments in one bioreactor [12-14]. In this case, anaerobic and aerobic degradation were simultaneously performed in the different zones of a bioreactor, which enhanced the synergetic effect and promoted the COD removal performance significantly. However, to our knowledge, few works have ever been reported regarding the anaerobic and aerobic process integrated in one bioreactor for the removal of phenol.

In the present study, the anaerobic and aerobic degradation were integrated in an internal airlift loop bioreactor (IALR) for treatment of phenolic wastewater. Our previous study showed the IALR exhibited high performance in aerobic degradation of wastewater due to the high mass transfer rate and abundant contact between biomass and substance [15]. By adding porous polyurethane microbial carriers into the IALR, two distinguished biological zones would be constructed after microbial acclimation, *i.e.*, the aerobic activated sludge suspended in the liquid bulk by air aeration, and the anaerobic microbes attached within the core of porous microbial carriers, so that anaerobic and aerobic degradation were integrated in the IALR. The project of the present study is to explore the treatment performances of synthetic phenol wastewater in the integrated anaerobic/aerobic IALR. The evolution of microorganisms' phenol degradation proficiency and the effects of the operation parameters on the COD/phenol removal were investigated, and the metabolism of phenol in the integrated anaerobic/aerobic IALR was discussed based on the COD/phenol removal data and the morphological observations.

MATERIALS AND METHODS

1. Experimental Set-up

The experimental integrated IALR is shown in Fig. 1. The IALR was made of perspex with volume of 25 L, height of 1,000 mm and diameter of 180 mm. A special designed draft tube with height of 750 mm and diameter of 85 mm was positioned coaxially in the IALR at a distance of 65 mm from the reactor base.

Porous polyurethane microbial carriers (cubic size: 15 mm×15 mm ×15 mm; density: 30 kg/m^3; porosity: 90%; mean pore size: 1.25 mm) were suspended in the IALR with a volume fraction (f_c) of

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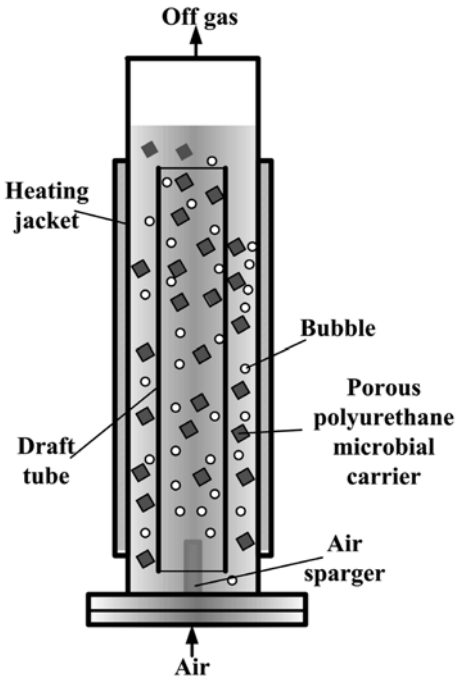


Fig. 1. Schematic diagram of the integrated anaerobic/aerobic internal airlift loop reactor.

Table 1. Composition of synthetic phenol wastewater

	Initial stage	Rising stage	Stable stage
Phenol (g/L)	0-0.21	0.26-1.47	1.47
Glucose (g/L)	0.94	0.19-0.94	0.19
$(NH_4)_2SO_4$ (g/L)	0.24-0.36	0.38-0.87	0.87
Na_2HPO_4 (g/L)	0.05-0.07	0.07-0.17	0.17

10% to conduct the anaerobic condition.

2. Seeded Biomass and Synthetic Phenol Wastewater

For the consideration of investigating the evolution of microorganisms' phenol degradation proficiency, suspended activated sludge from municipal wastewater treatment plant was used as seeded biomass, instead of that from treatment plant of industrial wastewater containing phenol. The initial mixed liquor suspended solids (MLSS) was 4.5 g/L, and the sludge volume index (SVI) was 86 ml/g.

The compositions of synthetic phenol wastewater in different acclimation stages are shown in Table 1. Glucose was added as co-substance to facilitate the seeded sludge adapting to the hydrodynamic circumstance in the IALR and the toxicity of phenol, as well as to accelerate the sludge rejuvenation. The pH of synthetic wastewater was adjusted, ranging 7.5-8.5 with sodium hydroxide and sulfuric acid.

3. Operating Conditions

To promote the growth of anaerobic microorganisms in the core of carriers, the sequence batch reactor (SBR) operation with the period of 24 h was adopted in the experiments, including mixed fill stage (30 min), reaction stage (22 hours), settle stage (30 min), draw stage (30 min) and idle stage (30 min). Air blew into the reactor through a cylindrical air sparger at the superficial air velocity ($\mathbf{u}_G$) of 0.04-0.08 cm/s and the operating temperature was maintained at 20± 2 °C.

4. Analytical Methods

The analyses of COD, phenol and SVI were according to Standard Methods [16]. The pH value was determined with a Cole-Parmer® pH meter (Model 59003-35, Chicago, USA), equipped with a combined electrode (E-201-C-9, Rex, Shanghai, China). Microbial community of the activated sludge was observed by the scanning electron microscopy (SEM) (FEI QuanTA200, USA).

RESULTS AND DISCUSSION

1. Microbial Acclimation

Microbial acclimation according to co-substance strategy could be divided successively into three stages: initial stage, rising stage and stable stage. The COD, phenol concentration and SVI were monitored during the whole procedure.

1-1. Acclimation Stages

The COD variations of the influent and the effluent during microbial acclimation are depicted in Fig. 2.

1-1-1. Initial Stage

In this stage, the influent concentration of phenol was increased gradually from 0 to 0.21 g/L (COD=500 mg/L), while that of glucose was maintained at 0.94 g/L (COD=1,000 mg/L). After 15 days' acclimation, the effluent COD descended below 100 mg/L and became steady, which indicated the sludge gained the preliminary biodegradation proficiency of phenol, denoting the finish of the initial stage.

1-1-2. Rising Stage

In this stage, the influent concentration of phenol was increased rapidly, and that of glucose was decreased gradually. At the end of the 37th day, the influent concentration of phenol was increased to 1.47 g/L (COD=3,500 mg/L) and that of glucose was decreased to 0.19 g/L (COD=200 mg/L). For the consideration that the effluent COD had increased to 800 mg/L, the rising stage was terminated and had to be replaced by a more steady strategy.

1-1-3. Stable Stage

In this stage, to promote the sludge activity, the influent concentration of phenol and glucose was kept at about 1.47 g/L and 0.19

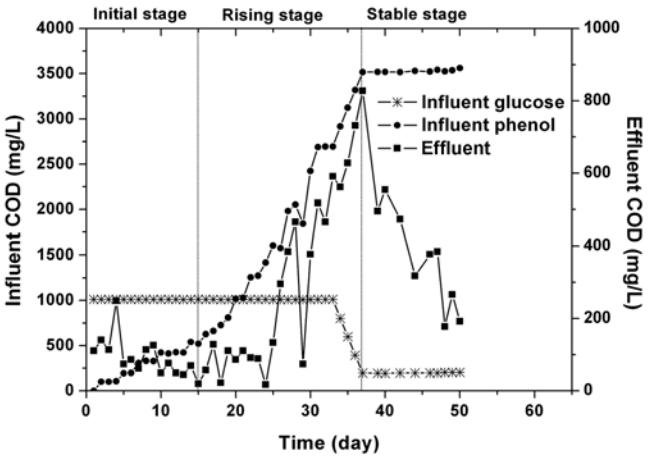


Fig. 2. COD variations of the influent and the effluent during microbial acclimation. The COD of influent consists of phenol and glucose.

g/L, respectively. This stage lasted for 13 days and the operation period was prolonged to 48 h in several batches. At the end of the acclimation stable stage, the effluent COD was maintained below 400 mg/L.

The acclimation process demonstrated that the microorganisms in municipal sludge which was rarely exposed to phenol could gain the biodegradation proficiency of phenol through a relatively short acclimation stage in the integrated aerobic/anaerobic IALR. Although many microbial strains degrading phenol had been cited, most of the aerobic cultures for acclimation were at low concentrations below the toxic limits [17], while the anaerobic acclimation processes required quite a long period for the degradation proficiency [6]. Commonly, the duration of the start-up for anaerobic granules was between 6 weeks and approximately 10 months [18].

1-2. COD Removal Efficiency

COD and phenol variations in each SBR period were monitored after the 10th day. The results of 15th, 30th and 50th day's acclimation are shown in Fig. 3.

The 15th day's data presented the COD removal efficiency in the initial stage. In this stage, the COD was mainly attributed to glucose (COD=1,000 mg/L), so the COD degradation rate reached 7.2 kg COD/m^3/d at the beginning 4 hours and then decreased to 1.44 kg COD/m^3/d, which was dominated by the degradation rate of phenol, with the exhaustion of glucose. The phenomena revealed that the sludge gained little biodegradation proficiency of phenol in the initial stage.

The 30th and 50th days' data presented the COD removal efficiency in the rising and stable stage, respectively. Although the concentration of phenol was increased in these stages, the degradation of phenol was accelerated and the average COD degradation rate approached to 3.36 kg COD/m^3/d on the 50th day, while the phenol removal rate stabilized over 99%. The promotion of COD removal efficiency during the three acclimation stages demonstrated that activated sludge gained biodegradation proficiency for phenol wastewater gradually.

Uygur and Kargi [11] have reported that the COD removal rate was approximately 80% in a four-step sequencing batch reactor with an influent phenol concentration of 0.6 g/L, which was a typical combined anaerobic/aerobic process. Sarfaraz et al. [19] reported removal rate was over 75% at the COD loading of 6.10 kg COD/m^3/d by using granular denitrifying sludge in an anoxic process. In our study, the COD loading reached 3.36 kg COD/m^3/d; therefore, the integrated anaerobic/aerobic IALR exhibited a similar biodegradation proficiency of anaerobic reactors.

1-3. SVI

SVI, which denotes the settling characteristics of the activated sludge, was measured every day and the variations of SVI are presented in Fig. 4.

Along with the increase of influent COD, the frequent fluctuations of SVI reflected the changing of the microbial population proportion and physiological characteristics of the activated sludge. In the initial stage, SVI increased to 120 ml/g in the first 10 days and then decreased in the next 5 days, which indicated that the sludge settling characteristics improved gradually. In the rising stage, along with the increase of phenol concentration, SVI increased to 130 ml/g, which showed the trend of sludge bulking. In the stable stage, after two fluctuations, the decrease of SVI below 110 ml/g again

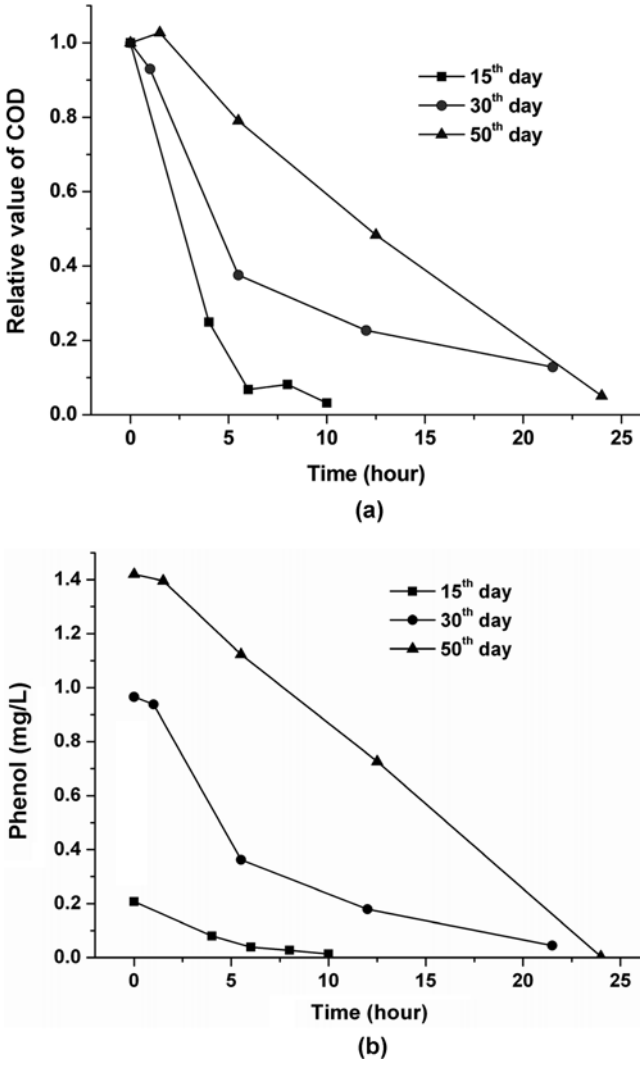


Fig. 3. COD and phenol variations in different stages. (a) COD variations. The influent COD on 15th, 30th and 50th day is 1,630, 3,160 and 3,780 mg/L, respectively. (b) Phenol variations.

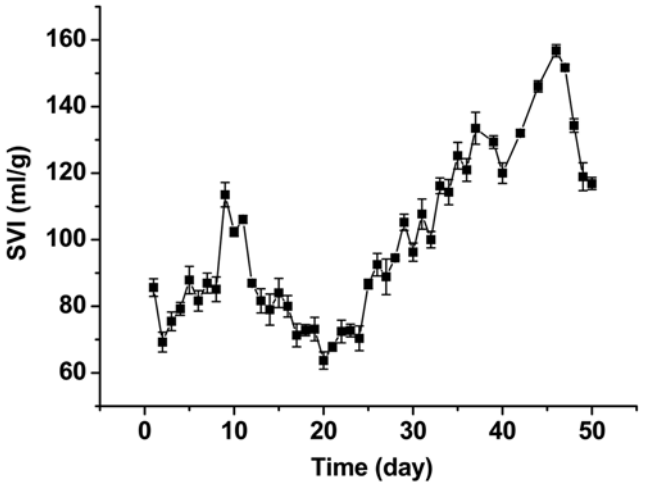


Fig. 4. SVI Variations during microbial acclimation.

revealed the improvement of the sludge settling characteristics at the end of the acclimation.

Wide variation of SVI has been reported. SVI between 12-18 ml/g denoted excellent settling characteristics of anaerobic granules in the anaerobic bioreactors [19,20], while the SVI fluctuated between 75-150 ml/g in the aerobic reactor, in which the suspended activated sludge occupied [21]. In the integrated anaerobic/aerobic IALR, the sludge consisted of aerobic suspended activated sludge in the liquid bulk and anoxic/anaerobic biofilm in the core of microbial carriers, but the SVI was dominated by the suspended activated sludge in the liquid bulk; thus, the SVI was close to that in the aerobic bioreactor.

The experimental results showed that the activated sludge gained biodegradation proficiency of phenol after 50 days' acclimation via the co-substrate strategy. With the comparison of the conventional aerobic or anaerobic wastewater treatment process, there were some special properties exhibited in the acclimation stage of the integrated anaerobic/aerobic IALR. First, the reactor was easy to start. It was a rapid process for the acclimation of sludge in the IALR to gain the biodegradation proficiency, while the aerobic reactor should run under a lower concentration, and it had to spend much longer time for the acclimation of anaerobic sludge. Secondly, as there was no methane generated, the integrated anaerobic/aerobic IALR was convenient in operation and maintenance. Therefore, the integrated anaerobic/aerobic IALR was suitable for the on-site small and decentralized wastewater treatment.

2. Effects of Operation Parameters

To evaluate the effects of operation parameters on the treatment performance, including u_G, temperature and pH, groups of experiments were performed after microbial acclimation. The experiment condition and results are rendered in Tables 2 and 3, respectively. The influent COD contributed by glucose was kept at about 200 mg/L, and the residual was offered by phenol.

Table 2. The experiment condition for parameter studies

Operation parameter	u_G	Temperature	pH
u_G variations (cm/s)	0.02-0.09	0.07	0.07
Temperature variations (°C)	20	15-25	20
pH variations	7.5-8.5	7.5-8.5	6.4-9.0

2-1. The Effects of u_G

Mass transfer and shear stress in the IALR would be enhanced with the raising of the u_G, and as we expected, biodegradation performance was promoted with the growth of the u_G. However, when u_G reached to 0.07 cm/s, at which the abundant gas-liquid-solid mixing and higher liquid recirculation rate was achieved [22], the effluent COD reached a low level and the further increasing of u_G would have little contribution to biodegradation promotion. As higher u_G would lead to higher energy consumption and influence the anaerobic environment within the microbial carriers, u_G was selected as 0.07 cm/s in the following experiments.

2-2. The Effects of Temperature

Temperature has a significant influence on the biological processes and the appropriate range for activated sludge is 15 to 35 °C. The experiment results that the removal rate of COD could approach 90% even at 15 °C exhibited high performance of the integrated anaerobic/aerobic IALR at low temperature.

2-3. The Effects of pH

When pH varied in the range of 6.4-9.0, the effluent COD remained at the low level all along. It could be concluded that the integrated anaerobic/aerobic IALR had excellent shock resistance and a broad operation range. As the anaerobic process was more pH-sensitive, the aerobic process played an important role to stabilize the integrated anaerobic/aerobic degradation, especially the anaerobic degradation.

3. Effects of Microbial Carriers

3-1. Amount of Microbial Carriers

The amount of microbial carriers, which determined the ratio of anaerobic zone in the bioreactor, has important effects on the anaerobic degradation. Fig. 5 shows that the biodegradation rate had a slight growth with the increasing of f_c from 3% to 10%. However, the biodegradation rate in the absence of microbial carriers was decreased obviously, which proved the important role of microbial carriers. According to the experiment data, it seems that 5% microbial carriers in the system could offer enough anaerobic/anoxic zones for the anaerobic treatment and the contribution of more microbial carriers was neglectable for the integration of aerobic and anaerobic degradation. This result was similar to the previous study on terephthalic acid wastewater treatment, in which 5% microbial carriers was occupied [23]. Although more microbial carriers would pro-

Table 3. The effects of operation parameters on COD removal

Operation parameter		Influent COD (mg/L)	Effluent COD (mg/L)	Removal percent (%)	SVI (ml/g)
u_G (cm/s)	0.02	4233	428	90	99
	0.04	4277	266	94	85
	0.07	4284	177	96	79
	0.09	4136	155	96	76
Temperature (°C)	15	4100	443	89	93
	18	4063	384	91	91
	20	4026	142	96	79
	25	3937	74	98	73
pH	8.98	4218	195	95	99
	8.23	4085	177	96	97
	7.45	4210	178	96	75
	6.35	4306	229	95	80

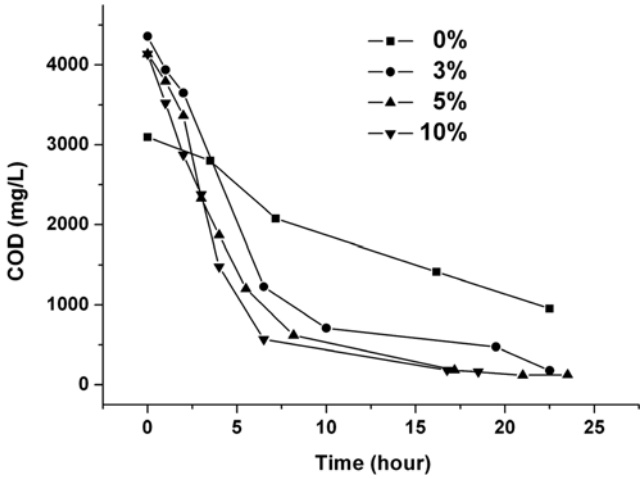


Fig. 5. Effects of carrier volume fraction on COD removal.

vide more aerobic/anoxic/anaerobic zones for biofilm, the phenol concentration was not high enough to maintain the growth for more biomass; thus, more carriers than 5% would not result in much more anaerobic biomass.

3-2. Microbial Observation

To compare the microorganism distribution within and out of the microbial carrier, morphological observations of the activated sludge after acclimation were examined by microscopy.

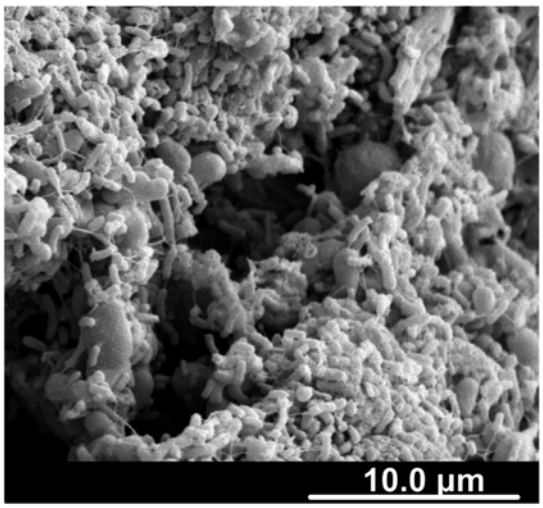
Fig. 6(a) shows that the microbial community in the aerobic zone was mainly composed of coccus and Brevibacterium. Fig. 6(b) reveals the morphology of microbial community immobilized on the microbial carrier's surface was different from that in aerobic zone, *i.e.*, the ratio of Brevibacterium declined and a few spirillums (the typical anaerobes) emerged. Fig. 6(c) shows, within the core of microbial carrier, the proportion of coccus, Brevibacterium and spirillums changed, and the amount of spirillums increased significantly. This phenomenon confirmed the existence of anoxic/anaerobic condition within the core of the porous microbial carrier.

According to the SEM images of the activated sludge, there was no granule in the integrated anaerobic/aerobic IALR and the main morphology was the suspended activated sludge.

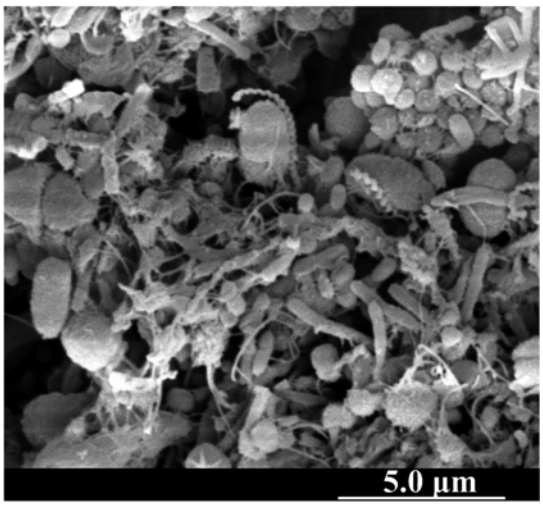
3-3. Discussion on the Effects of Microbial Carriers

The study of microbial carriers affirmed the important role of microbial carriers in the IALR, and the significant advantages of the integrated degradation over the aerobic degradation. As earlier study reported [14], the porous microbial carriers suspended in the bioreactor might function in two ways. On one hand, the anoxic/anaerobic zone within the porous microbial carriers was created due to the oxygen transfer resistance; on the other hand, local microbial enrichment and immobilization, including aerobic and anaerobic microorganism, were enhanced [24,25].

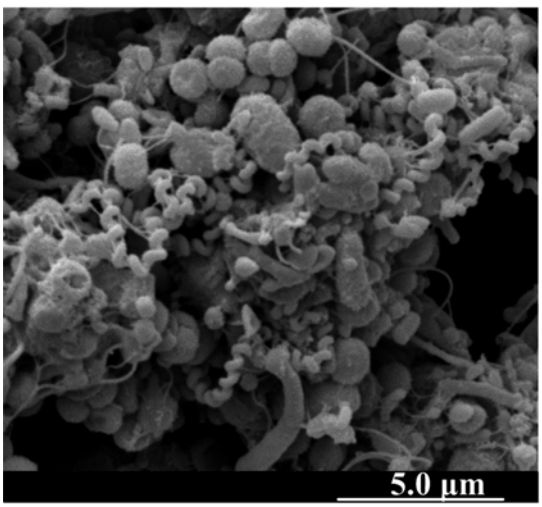
The metabolism of hard biodegradable organics in the integrated anaerobic/aerobic IALR could be described by a four-step mechanism. In the first step, the hard biodegradable organics diffused into the core of carrier from liquid bulk due to the concentration gradient; in the second step, the hard biodegradable organics were degraded by anaerobic hydrolization and acidification processing and converted into biodegradable organics, such as volatile fatty acids; in the third step, the biodegradable intermediate products diffused



(a)



(b)



(c)

Fig. 6. SEM images of the sludge. (a) SEM images of the suspended activated sludge in liquid bulk. (b) SEM images of the sludge immobilized on the microbial carrier's surface. (c) SEM images of the sludge immobilized within the core of microbial carrier.

to the liquid bulk from carrier; finally, the biodegradable intermediate products were degraded by aerobic microorganisms, in the liquid bulk immediately. The synergetic effects between aerobic and anaerobic degradation were remarkably enhanced in the integrated IALR [26,27]. The anaerobic degradation, which converted the hard biodegradable organics to a substance that could be consumed by the aerobic microorganism, facilitated the aerobic process; at the same time, the continuous consumption of anaerobic product by aerobic metabolism, enhanced the anaerobic hydrolyzation and acidification against the negative effects of the accumulation of the anaerobic products. In this way, the treatment period was shortened and the treatment efficiency was promoted.

CONCLUSIONS

Anaerobic and aerobic biodegradation were integrated in one IALR, by adding porous microbial carriers. Microbial acclimation in the integrated IALR showed a shorter phase for the biodegradation proficiency of phenol than the aerobic or anaerobic system. After 50 days' acclimation, the integrated IALR could degrade the influent COD from 3,700 mg/L to 400 mg/L (phenol removal rate was over 99%) with a residence time of 24 h. The high performance could be attributed to the enhanced synergetic effects between aerobic and anaerobic degradation integrated in the IALR. Organics undergoing anaerobic degradation within the porous carriers became biodegradable intermediates and diffused into the liquid bulk, where the intermediates were quickly degraded via aerobic biodegradation. In this way, the anaerobic degradation facilitated the aerobic process; at the same time, the continuous consumption of anaerobic product by aerobic metabolism, enhanced the anaerobic hydrolyzation and acidification against the negative effects of the accumulation of the anaerobic products. What's more, the local microbial enrichment and immobilization were also enhanced in/on the carriers, which also promoted the activity of the microorganisms and the biodegradation rate.

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