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Efficiency of porous burnt-coke carrier on treatment of potato starch wastewater with an anaerobic–aerobic bioreactor

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ABSTRACT

In the towns and countryside in the west of China, potato starch wastewater is an important source of water pollution as it is organic wastewater which is produced in high concentrations. The anaerobic–aerobic integrative baffled bioreactor is a new type of mobile equipment which is effective in the treatment of potato starch wastewater. In order to increase the efficiency of the anaerobic–aerobic integrative baffled bioreactor, porous burnt-coke particles, a waste product of heavy industry, were used as carriers in the aerobic pond to support the growth of microorganisms. Using this technique, the maximum reduction in chemical oxygen demand (COD) achieved was 98.7%, and the COD value in the effluent was less than 200 mg/L under the following operational conditions: pH 5.0–8.5 at 25–35 °C. The ammonium nitrogen (NH_3–N) concentration in the wastewater was 10 mg/L and the use of burnt-coke removed 82.3% of this contaminant.

1. Introduction

Surface water pollution is a serious problem for many developing countries because industrial and domestic wastewater containing excessive concentrations of nitrogen- and phosphorous-containing organic pollutants is discharged into natural waters such as rivers and lakes [1]. This problem is greater in the water resources of towns and cities due to the higher concentrations of organic materials and ammonia discharged in the wastewater. The high COD (chemical oxygen demand) results in the consumption of the majority of dissolved oxygen (DO) thus converting the water into an anoxic or even an anaerobic state, which is fatal to many aquatic species. Moreover, ammonia is toxic to aquatic organisms, especially the higher forms, such as fish, even at low concentrations of 0.5 mg/L [2]. Therefore, the treatment and reutilization of industrial and domestic wastewater is of prime importance and many types of technologies have been developed to address the problem of wastewater treatment. During recent decades, the development of an anaerobic method for treating wastewater technique has progressed rapidly and can now be considered to be a promising biological technique for the treatment of wastewater. This is due to its various advantages, such as being nontoxic, economic, simple, and applicable to a wide variety of wastewaters [3–5].

Potato is one of the world's most important staple food crops and numerous potato and starch products are used in industrial production. Water pollution caused by starch production has been reported to be a serious problem in many Asian countries, particularly in China [6], Thailand [7,8] and India [9,10]. In the west of China, where there is a lack of water resources, potato starch wastewater is an important source of water pollution as it contains a high concentration of organic contaminants. Because most starch processing factories are located in towns and the countryside dispersedly, it is very difficult to collect and treat all wastewater together. Therefore, the design and manufacture of mobile equipment for the treatment of the potato starch wastewater is extremely urgent in this part of China.

In order to treat the potato starch wastewater which contains starch, saccharides, protein and other soluble substances, we designed a simple piece of equipment known as the "anaerobic–aerobic integrative baffled bioreactor for the treatment of high concentration starch wastewater". The advantages of this bioreactor include rapid biodegradation, low yields of sludge, and excellent process stability. It was found that the treatment efficiency was increased if the carrier was used in an aerobic pond. The efficiency of a burnt-coke carrier in the treatment of potato starch wastewater is discussed in details in this paper.

2. Materials and methods

2.1. Experimental apparatus

The anaerobic–aerobic integrative baffled bioreactor, a novel type of bioreactor, has been designed and manufactured by our group. A schematic diagram of the equipment is shown in Fig. 1. The

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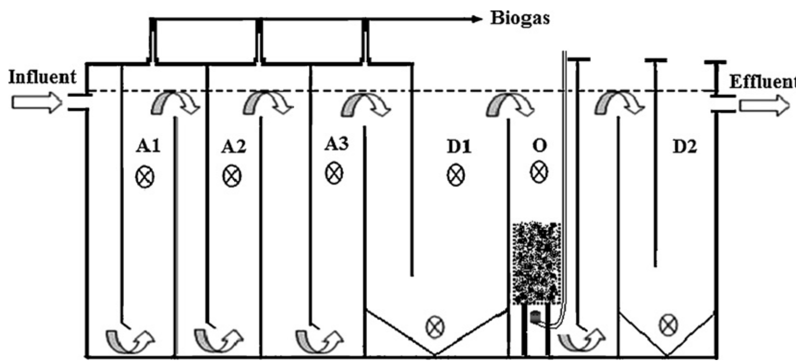

Fig. 1. Treatment process of wastewater using the integrative baffled reactor. : low sample outlet; A: anaerobic pond; O: aerobic pond; D: deposition pond.

anaerobic–aerobic integrative baffled bioreactor is made of Plexiglas, and includes three anaerobic ponds (A1, A2, and A3), two depositions (D1, D2) and one aerobic pond (O). Its dimensions are approximately 72 cm in length, 20 cm in width and 36 cm in depth. A1, A2, and A3 are same dimensions, which are approximately 7.6 cm in length, 20 cm in width and 36 cm in depth. D1's dimensions are approximately 9.2 cm in length, 20 cm in width, and 36 cm in depth. O's dimensions are approximately 7.8 cm in length, 20 cm in width, and 36 cm in depth. D2's dimensions are approximately 7.7 cm in length, 20 cm in width, and 36 cm in depth. The total volume is 48 L and the total effective volume is 37.5 L. The bioreactor is rectangular and is subdivided equally into down-flow and up-flow sections by a series of 5-mm thick vertical high/low baffles. Due to the 45 $^{\circ}$ turnout angle, the baffles cause the wastewater to rise and then flow downwards into the reactor.

2.2. Experimental set-up and operational conditions of reactors

The bioreactor system is operated by a fill-and-draw mode for 2 weeks to enable the inoculated activated sludge to be completely retained within the porous carrier particles; the system is then switched to continuous operation.

Experimental raw wastewater was obtained from a Potato Starch Mill in Tianshui, China. The characteristics of the raw potato starch wastewater were as follows: COD (mg/L) = 1100–4500; ammonium nitrogen (mg/L) = 8.9–48.5; pH 5.0–8.5. Moreover, trace elements such as Fe, Co, Ni, and Zn were added to the raw wastewater before it was treated in the bioreactor.

The main factors which influenced the biotreatment of the wastewater included temperature, pH and dissolved oxygen (DO) in the aerobic pond. The COD values of the potato starch wastewater inflow ranged from 1100 to 4500 mg/L while the pH was between 5.0 and 8.5. The temperature was controlled between 25 and 35 °C. The pH value in pond A1 and pond A2 were the same and were maintained at between 5.0 and 8.5, while that in pond A3 was controlled at between 6.5 and 7.8. A suitable concentration of dissolved oxygen (DO) (about 3.0 mg/L) is required in order to ensure maximum efficiency of the biofilm in the aerobic pond.

2.3. Analysis and methods

The parameters studied included chemical oxygen demand (COD), ammonium nitrogen (NH_3–N) concentration, the nature of the microorganisms, concentration of dissolved oxygen (DO) and pH. Samples were withdrawn for analyses at regular intervals from the inflow and from different ponds at each stage.

COD was measured colorimetrically using the dichromate reflux method [11]. The appropriate amount of sample was introduced into commercially available digestion solution in the range 0–180 mg/L containing potassium dichromate, sulfuric acid and mercuric sulfate and the mixture was then incubated for 10 min at 165 °C in a COD reactor. COD concentration was measured colorimetrically at 610 nm using a 5B-3 COD Rapid Detector (Lanzhou Lianhua Sci. Co., China). The concentration of NH_3–N was monitored by the Nesslerization method according to the Standard Method for the Examination of Water and Wastewater. The pH value was monitored with pHS-3C precision pH meter (Shanghai Cany Precision Instrument Co., Ltd, China).

The surface of carrier and species of microorganism in the anaerobic ponds (A1, A2, and A3) and those attached to the carrier in the aerobic pond were analyzed by a JSM-5600 LV scanning electron microscope (JEOL, Japan). A sample of the microorganism mat was excised from the wall of each anaerobic pond (A1, A2, and A3) and placed in three separate bottles. A sample of the microorganisms attached to the carriers was also withdrawn from the aerobic pond (O) and placed in bottles. After drying for 10 h under vacuum at 40 °C, these samples were fixed in 0.1 mol/L phosphate buffer solution (pH 7.3) containing 2.5% glutaraldehyde for 12 h at 4 °C. After fixation, samples were rinsed three times in 0.1 mol/L of phosphate buffer solution (pH 7.3) and dehydrated gradually by successive immersions in ethanol solutions of increasing concentration (30, 50, 70, 80, 90, and 95%). The samples were then washed three times in 100% ethanol. The drying process was then completed by incubating the samples for 2 h at 40 °C. The particles were then coated with gold powder and attached to the microscope support with silver glue. SEM photographs were taken at 25 and 20 kV.

3. Results and discussion

Irregularly shaped porous burnt-coke particles with a size distribution of between 1 and 2 cm, and a 50% packing ratio were used as the carrier in the aerobic pond to support the growth of microorganisms. The surface area of particles in aerobic tank is near 0.57 m^2. It was found that the higher the biomass concentration in the carrier the more organic matter was removed. Microorganisms in the aerobic room are included by the main bacteria particles, such as bacteria, glucose cocci, fungi, protozoa, micro-algae. These bacteria through the metabolic role are further degradation of organic matter in water. This bioreactor was found to be effective for reducing the COD and removing NH_3–N in high-strength starch wastewater.

As single-phase anaerobic reactor wastewater treatment showed some disadvantages. The multi-phase reactor anaerobic system had been applied in wastewater treatment for dealing with high concentrations of organic wastewater, acid production and the production of methane from the two reactors [12,13]. In this bioreactor, we have chosen three anaerobic ponds and one aerobic pond. The anaerobic reaction process is more complicated than that of aerobic reaction. According to the major components of starch wastewater and various components of anaerobic biodegradation of the way, the system was divided into three-phase anaerobic biodegradation. The first phase (A1) and second phase reactor (A2) were designed for the hydrolysis. A1 is main reactor for carbohydrates and most of the main protein. A2 is used to hydrolysis a mutual relationship between the oxygen-based protein and organic acids, and also for middle methanation reaction. A3 is mainly responsible for the production methane. D1 is designed to sediment. One of its roles is to separate anaerobic and aerobic room, and to ensure that the anaerobic conditions in anaerobic room. Moreover, this device is integrated, simple structure, easy movement, and suitable for small workshops.

3.1. Inflow and effluent COD concentrations and the removal rate of COD

The aerobic pond was filled with carriers composed of burnt-coke materials. The COD in the inflow and effluent are shown in Fig. 2a and it can be seen that the COD of the effluents ranged from 90.2 to 531.2 mg/L, and that these were relatively stable even when the COD of the inflow varied greatly (from 1614 to 4892 mg/L). Meanwhile, it was found that 90.0% of effluent COD values were below 200 mg/L. The variation in the removal rate of COD plotted against time is shown in Fig. 2b. The results reveal that COD was reduced by 88.4–98.7%. Obviously, during a period of more than three months of steady-state operation, the effluent COD values remained relatively stable and the maximum removal rate of COD reached 98.7%.

3.2. Effect of HRT on COD and COD reduction efficiency

Hydraulic retention time (HRT) is an important parameter for any bioreactor used to treat wastewater. Fig. 3 shows the effect

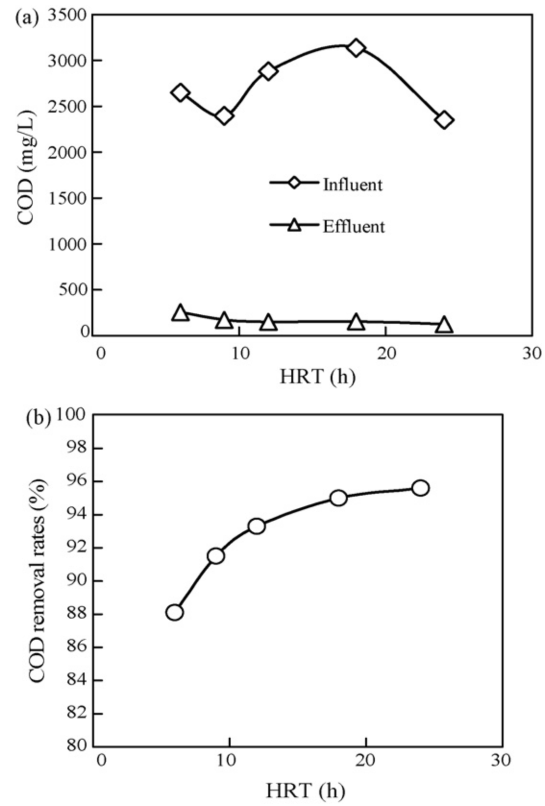

Fig. 3. The relationship between COD with HRT. (a) Inflow and effluent COD versus HRT and (b) the removal rates of COD versus HRT.

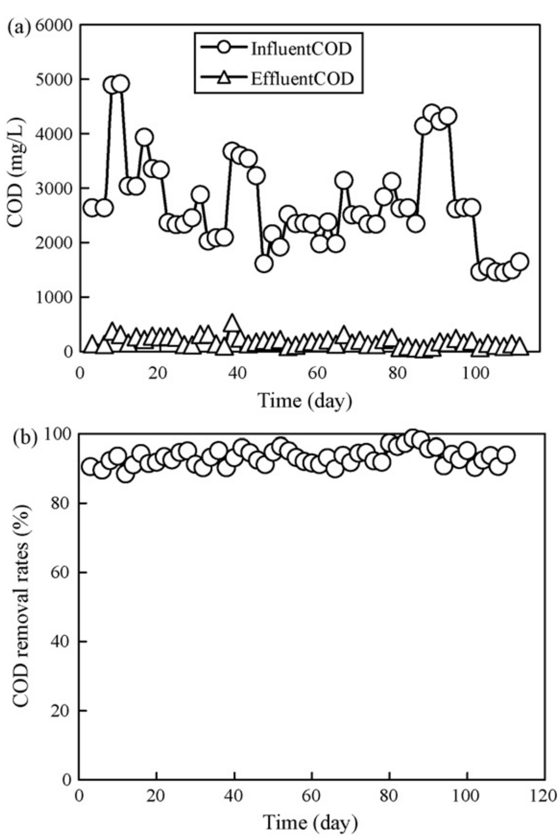

Fig. 2. Relationship between COD and time. (a) Inflow and effluent COD versus time and (b) the removal rate of COD versus time.

of hydraulic retention time on the COD and on the percentage reduction of COD. To investigate the influence of HRT on the efficiency of COD reduction, the HRT was varied from 6 to 24 h after three months of steady-state operation. The results showed that the removal rate of COD first increased sharply with the increasing of HRT and then increased more steadily. By increasing the HRT from 6 to 24 h, the COD of the effluent gradually reduced from 257 to 124.4 mg/L, and the total removal rate of COD increased from 88.1 to 95.6%. The COD concentration of effluent was less than 200 mg/L and the maximum removal efficiency of COD was more than 93.3% if the HRT was more than 12 h. Therefore, the optimal HRT was 12–24 h to produce effluent water that was of a quality suitable for discharge. Considering the total volume and effective volume of the bioreactor, the COD removal rate is 1.14×10^5 mg $L^{-1}/(D\,m^2)$ for the total volume and 1.47×10^5 mg $L^{-1}/(D\,m^2)$ for effective volume of the bioreactor, respectively.

3.3. Average daily COD and the removal rate of COD in different ponds

During a period of steady-state operation, daily COD concentrations in the different ponds were monitored and are presented in Fig. 4a. It showed that the mean daily raw water (inflow) COD concentration was 2711.5 mg/L and the mean COD concentrations in the three anaerobic ponds (A1, A2, and A3) was 759.8, 523.4, and 361.2 mg/L, respectively, while the COD concentration in the aerobic effluent was 184.6 mg/L.

The removal rates of COD in different ponds are shown in Fig. 4b. During a period of steady-state operation, the average removal rate of COD per day in the A1 pond was 72.0%. The total removal rates of COD in A1 and A2 ponds were above 81.0%. The total removal rates of COD in all the anaerobic ponds

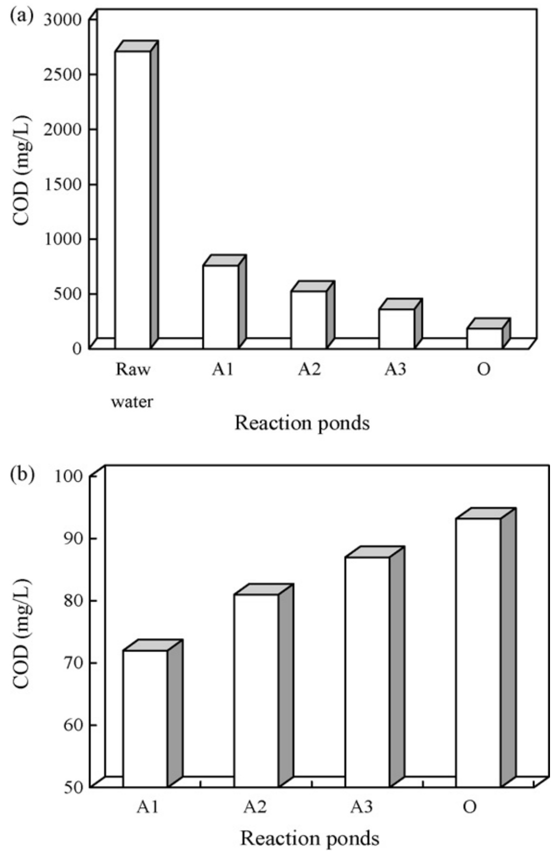

Fig. 4. Histogram of daily COD and the removal rate of COD in different ponds. (a) Average COD concentration and (b) daily removal rate of COD.

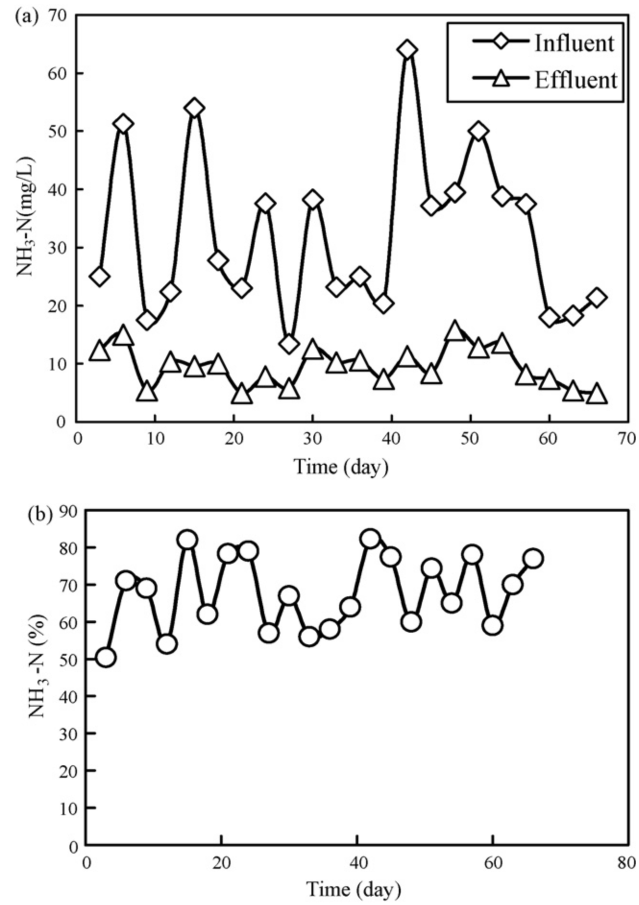

Fig. 5. NH_3–N concentration and NH_3–N removal rates plotted against time (a) NH_3–N concentrations in inflow and effluent versus time and (b) removal rates of NH_3–N versus time.

reached 87.0%, while the total removal rate of COD in the complete anaerobic–aerobic bioreactor was still above 93.2%. The results indicated that the efficiency of treatment was ideal in the bioreactor. The water quality of the effluent attained discharge standard.

After adding burnt-coke to the aerobic pond, the maximum removal rate of COD was 98.7%, while it was 96.0% in the absence of the burnt-coke [14]. It shows that the efficiency of the reactor is considerably improved in the presence of burnt-coke particles acting as carriers. The reason is that burnt-coke carriers provide a much larger surface area for the attachment of a biofilm which then leads to an increase in biomass concentration. Latex has also been used to fill the aerobic pond. The removal rate of COD was found to be 98.0% [15], which is similar to that achieved using burnt-coke. However, since burnt-coke is a waste product of industry, it is cheaper than latex. Also, in comparison with latex, both the internal and external surfaces of burnt-coke carriers are more coarse and porous, which enables a greater concentration of microorganisms to attach to its surfaces.

Dissolved oxygen (DO) is an important parameter for any bioreactor used to treat organic wastewater [16]. Therefore, dissolved oxygen had been also measured during the experiment. It was found that COD removal rate increased from 78.5 to 95.5% if DO was increased from 0.66 to 5.78 mg/L. COD removal rates were less than 92.6% if DO was lower than 3 mg/L. As the supply of oxygen causes to consume excessive energy, and speeds microbial metabolism too, which cause inadequate supply of nutrients to their own microbial oxidation. Therefore, in this experiment, the treatment plant aerobic room of dissolved oxygen concentration to 3 mg/L suitable.

3.4. *Efficiency of ammonium nitrogen removal*

Inflow and effluent NH_3–N concentrations were measured and shown in Fig. 5a. The NH_3–N concentration in the inflow varied from 13.4 to 64.0 mg/L with an average value of 32.0 mg/L and that in the effluent ranged from 5.0 to 15.8 mg/L with an average value of 9.6 mg/L. The variation in the removal rate of NH_3–N has been plotted against time in Fig. 5b. The removal rate of NH_3–N fluctuated from 50.4 to 82.3%, while the average removal rate was 64.0%. The NH_3–N concentration in the effluent decreased slightly as that in the inflow decreased, while the efficiency with which NH_3–N was removed increased slightly. The NH_3–N concentration in the effluent was maintained under 10 mg/L. These results indicated that this bioreactor was relatively ideal for the removal of NH_3–N from starch wastewater.

3.5. *SEM observation*

Typical SEM (scanning electronic microscopy) images of porous burnt-coke carriers at different stages during the treatment of potato starch wastewater are shown in Fig. 6. The coarse, porous nature of the burnt-coke carriers can be clearly seen. The diameter of the pores was about 3–30 cm (Fig. 6a) and many microorganisms can be seen attached to the pores in the burnt-coke surface in the aerobic pond (Fig. 6b). The microorganisms grew in the pores and fissures of the carrier surface, and were mainly composed of orb-formed bacteria, bacillus and slice bacteria. The microorganism congeries in the anaerobic ponds (A1, A2, and A3) are shown

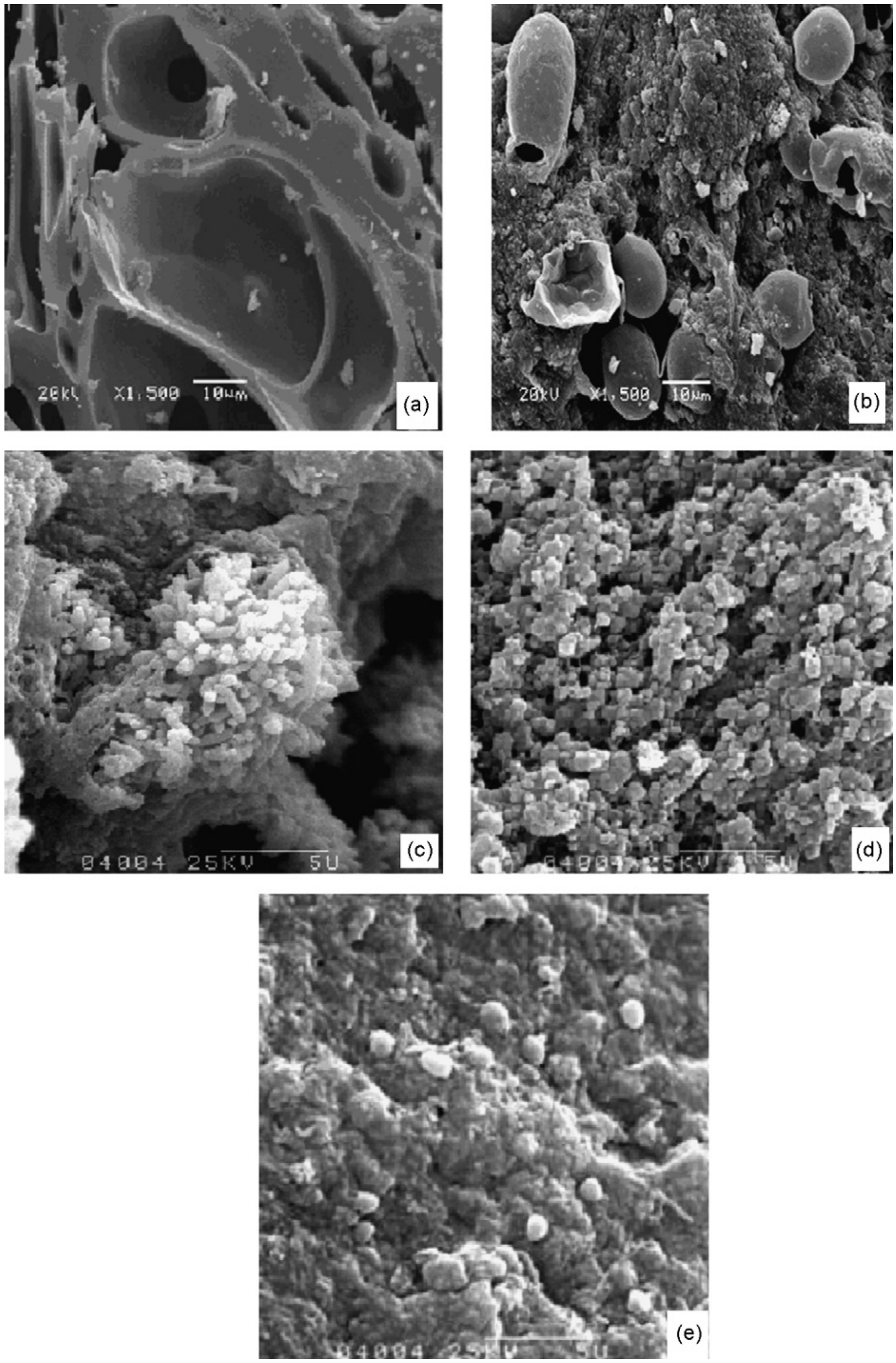

Fig. 6. Scanning electron microscopy (SEM) photographs of the microorganisms forming the biofilm in the bioreactor. (a) The surface of the carrier before attachment of microorganisms; (b) the same surface of the carrier after the attachment of microorganisms; (c) microorganisms present in A1; (d) microorganisms present in A2; and (e) microorganisms present in A3.

in Fig. 6c–e. The difference in the biofilm morphology in the different anaerobic ponds is obvious. In anaerobic pond A1 (Fig. 6c), the microorganism congeries is arranged in a regimented form, which included orb-formed and slice bacteria. In A2 (Fig. 6d), the microorganism congeries was presented in piece form and the distribution of the congeries was more uniform than that in A1. In A3 (Fig. 6e), the microorganism congeries grew prolifically, and orb-formed bacteria were present on the surface. In both aerobic and anaerobic ponds, the shape and structure of the microorganism not only protects the individual microorganisms, but also improves the adsorbent and oxidization capability of the whole biofilm with regard to the organic matter in the water, which in turn leads to the effective treatment of starch wastewater in the bioreactor.

4. Conclusion

A new type of anaerobic–aerobic reactor configuration, the anaerobic–aerobic integrative baffled bioreactor packed with porous burnt-coke was proposed for the treatment of potato starch processing wastewaters. The treatment of high concentration potato starch wastewater using the anaerobic–aerobic integrative baffled bioreactor at 25–35 °C, with a dissolved oxygen

(DO) concentration in the liquid phase of about 3 mg/L and pH 5.0–8.5, reduced the COD concentration of the effluent to less than 200 mg/L and increased the maximum removal rate COD to 98.7%. The NH_3–N concentration of the effluent was maintained at 10 mg/L, which demonstrated that effluent water of discharge standard could be achieved.

This configuration is an effective solution to the treatment of wastewater for most small- and medium-sized starch plants in China which possess little economic capacity to invest in environmental controls. The use of burnt-coke particles to fill the aerobic pond and support the growth of microorganisms is appropriate since burnt-coke is itself a type of waste residue produced by industrial processes. The surfaces of burnt-coke carriers are coarse and porous, particularly the inner surfaces which contain large numbers of pores, and this makes them an ideal environment for the attachment of high concentrations of microorganisms.

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