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# Advanced treatment of polysilicon production wastewater using the combination of coagulation, expanded granular sludge bed, anaerobic baffled reactor and biological contact oxidation processes

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**ABSTRACT**

Polysilicon production wastewater (PPW) is characterized by complex composition, high pollution and poor biodegradability. An integrated process comprising of coagulation, expanded granular sludge bed (EGSB), anaerobic baffled reactor (ABR) and biological contact oxidation (BCO) processes was developed at lab scale for treating PPW with an initial chemical oxygen demand (COD) of 3,800–4,350 mg/L, biochemical oxygen demand of 480–620 mg/L, and suspended solids (SS) of 1,350–1,620 mg/L. The optimum conditions for the hybrid system were: 30 mg/L polyaluminum chloride and 1.5 mg/L cationic polyacrylamide for coagulation; the average organic loading rate was 6, 3.5, and 3.5 kg COD/m$^3$ d for EGSB, ABR, and BCO, respectively. Under these conditions, the removal efficiencies of COD and SS were averagely 98% and 98%, respectively, and the quality of final effluent can meet the national discharge standard of China. The coagulation process removed a considerable proportion of SS and most of particulate organics, while the EGSB and ABR played an important role in COD removal. The BCO played a key role in the post-polish of the final effluent. The micro-toxicity of the wastewater was greatly reduced after undergoing the hybrid treatment. This work demonstrates that the hybrid system has the potential to be applied for the advanced treatment of high-strength PPW.

*Keywords:* Wastewater; Fatty acids; Biogas; Biological contact oxidation; Dehydrogenase

## 1. Introduction

Polysilicon is the main component of solar photovoltaic cells [1]. However, the production of polysilicon can produce vast volumes of wastewater with complex composition and high pollution. Polysilicon production wastewater (PPW) is mainly divided into two types: fluoride-containing wastewater and organic wastewater [2]. The fluoride-containing wastewater has a simple composition and can be effectively treated by coagulation–flocculation [3]. The organic wastewater contains high concentrations of polyethylene glycols (PEGs), suspended solids and colloidal substances, characterized by high chemical oxygen demand (COD) content and weak biodegradability [3]. The conventional process for treating PPW is coagulation-hydrolysis acidification-activated sludge, which has disadvantages such as sludge bulking, the requirement of additional carbon source, high treatment costs and strict process control requirements. Thus, PPW treatment has emerged as a major issue affecting the sustainable development of the solar photovoltaic industry.

As a modification of traditional up-flow anaerobic sludge blanket (UASB) reactors, the expanded granular sludge bed (EGSB) reactor offers a potential solution for toxic substances [4]. The system contains expanded granule sludge, and the effluent recycle is used to increase the up-flow velocity and dilute the toxic components in the reactor. Thereupon, EGSB has shown potential applications in industrial wastewater treatment [5,6]. In addition, EGSB has other advantages such as the formation of biomass granules with good settling ability and the improvement of substrate diffusion from the bulk liquid to the liquid/granule interface. EGSB reactor has been successfully applied to treat various kinds of wastewater such as pig manure [7], high-strength nitrate wastewater [8], acid-mine drainage [9], and so on.

The anaerobic baffled reactor (ABR), which has been developed in the 1980s, is a new high-efficiency anaerobic reactor. Compared with conventional anaerobic reactors, ABR has many potential advantages such as longer biomass retention time, lower energy consumption, higher stability, and the ability to separate acidogenesis and methanogenesis longitudinally down the reactor [10,11]. Jiang et al. [10] used a seven-chamber ABR to treat medium-strength synthetic industrial wastewater, and the COD removal reached 90% at an influent COD of 2,000 mg/L. Yang et al. [11] applied a four-chamber ABR to treating alkali-decrement wastewater of polyester fabrics, the COD removal and decolorization ratio could be as high as 79.0% and 87.7%, respectively. Moreover, it was found that the ABR could separate acidogenesis and methanogenesis in longitudinal distribution [11].

The biological contact oxidation (BCO) system was first brought forward at the end of the 19th century. Of the system, microbes are attached to the carriers to form a biofilm, and pollutants in wastewater are decomposed and removed through the thorough contact of biofilm under aerated conditions [12]. BCO is characterized by high efficiency, simple operation and low cost. The integration of BCO and other processes was widely used to treat various wastewaters. For example, bioelectrochemical-BCO and biological floating bed-BCO processes have been tested for treating azo dye and landscape wastewater, respectively [13,14]. An interior micro-electrolysis-Fenton oxidation–coagulation-hydrolysis acidification-BCO system was developed to treat steroid hormones wastewater with an average initial COD of about 15,000 mg/L and pH of 4, in which the COD concentration in the final effluent was reduced to below 90 mg/L [15]. These studies demonstrate that the combination of BCO and other processes is effective for the advanced treatment of wastewater.

The aim of this work was to evaluate the performance of a PPW treatment system consecutively comprising coagulation, EGSB, ABR and BCO. A series of tests were conducted to evaluate the relevant influencing factors involved and to optimize operational parameters. The start-up and operation characteristics of the system were investigated. In addition, the acidification problem during start-up and the solution was explored.

## 2. Materials and methods

### 2.1. Wastewater treatment system

The organic PPW used in this work was obtained from a local polysilicon factory. The wastewater properties are listed in Table 1. The main organic constituent of the wastewater is PEGs. Fig. 1 shows a schematic flow chart of the laboratory-scale PPW treatment system used in this study. First, wastewater was introduced into the coagulation tank; polyaluminum chloride (PAC) and cationic polyacrylamide (CPAM) were added successively to conduct coagulation reactions. Thereafter the supernatant was discharged into the regulating tank, wherein $NH_4Cl$ and $K_2HPO_4$ were added to give a final COD:N:P ratio of 100:10:1. The wastewater was then successively treated by EGSB and ABR. The ABR effluent entered the BCO unit, and the pollutants were further removed by aerobic microbes. Finally, the effluent reached the standard discharge.

### 2.2. Coagulation tests

PPW contains large amounts of PEG granules, silicon powder, silicon carbide particles, etc., resulting in high SS content and high turbidity. Thus, coagulation was firstly conducted for the wastewater. Coagulation conditions were optimized in 250 mL beakers using a programmable jar-test apparatus (Model DC-506, Shanghai Waterworks Company, Shanghai, China). In each case, 150 mL of wastewater was dosed with the desired amount of PAC, stirred at 200 rpm for 2 min. No pH adjustment was conducted. Subsequently, CPAM was added to the solution, followed by a 5 min period of slow agitation (50 rpm) and quiet settling (5 min). The supernatant was taken at 2 cm below the water surface for analysis.

### 2.3. EGSB unit

A laboratory-scale EGSB reactor with an internal diameter of 7 cm and a height of 112 cm was constructed with

Table 1
Characteristics of the wastewater used in the present study

| Parameter | Value |
|---|---|
| pH | 5.5–6.5 |
| COD, mg/L | 3,800–4,350 |
| 5-d biochemical oxygen demand ($BOD_5$), mg/L | 480–620 |
| $NH_3$–N, mg/L | 13–17 |
| Total nitrogen (TN), mg/L | 55–78 |
| Total phosphorus, mg/L | 3.2–4.4 |
| Suspended solids (SS), mg/L | 1,350–1,620 |

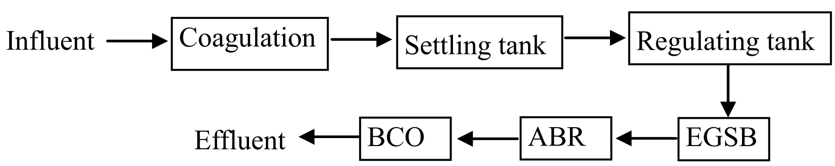


Fig. 1. Schematic flow chart of the PPW treatment system.

Plexiglas for this work and the effective volume of the reactor was 3.8 L. The reactor was operated stably at 35°C ± 2°C throughout the study. A three-phase separator was installed at the top of the reactor to keep the biomass within the reactor and collect gas. The influent rate was controlled by a peristaltic pump. Liquid up-flow velocity ($V_{up}$) was also controlled by inner recirculation with a peristaltic pump. The anaerobic granular sludge inoculated into the EGSB reactor was 6.6 g volatile suspended solids (VSS)/L, taken from a PPW wastewater treatment plant. The sludge retention time (SRT) was between 30 and 45 d. During the initial 30 d, two-time diluted PPW was used to feed the EGSB at a hydraulic retention time (HRT) of 32 h and an average organic loading rate (OLR) of 1 kg COD/m$^3$ d in order to avoid the influence of organic load. After 90 d, original wastewater without dilution was fed to the EGSB, and the OLR was stepwise increased to about 6 kg COD/m$^3$ d by adjusting the HRT. During the acclimatization of seed sludge, sucrose and diammonium hydrogen phosphate were supplemented as nutrients (COD:N:P = 300:5:1) to enhance sludge growth. By adjusting $V_{up}$ and influent flow rate, the effect of OLR on the reactor performance was examined.

### 2.4. ABR unit

A lab-scale ABR (30 × 10 × 15 cm$^3$) was fabricated using transparent plexiglass. The working volume of the reactor was 3.1 L. In this system, a series of vertical baffles system was used to divide the ABR into four compartments with downflow and up-flow chambers. The four chambers had the same structure and dimensions. The lower parts of vertical baffles were bent at 45° to produce an effective mixing between anaerobic granular sludge and the wastewater. In addition, the settling tank was incorporated with the last compartment to reduce sludge in the effluent. Each chamber was equipped with sampling ports for the collection of supernatant, gas and sludge samples. The sidewalls were enclosed within a water jacket to maintain the reactor's inner temperature at 35°C ± 2°C.

The system was inoculated with the same granular sludge as that of EGSB. The inoculation of ABR reactor was carried out by filling with 35% granular sludge and sealed with lids to keep a strictly anaerobic condition. The ABR system was started with three-time diluted PPW for maintaining HRT of 36 h. Then, the OLR was gradually increased by promoting the COD concentration of influent. Finally, the system was integrated with EGSB for the shock test.

### 2.5. BCO unit

The BCO reactor was made of transparent plexiglass, with length, width and height of 30, 15 and 20 cm respectively, and a working volume of 7.2 L. Left upper corner and right bottom corner of the reactor was reserved with an overflowing port so that wastewater can flow in the upper and at the bottom to pass through the whole reactor and can fully contact and react with microbes on the biocarrier. Biocarrier was made of polypropylene fiber, and each piece of the carrier was fixed at carrier holder at certain intervals to form a carrier unit, with carrier amount of 3.0 g/L. This biocarrier has a specific surface area of 1,200 m$^2$/m$^3$, a density of 25 kg/m$^3$ and a porosity of 97%. An aerator was placed at the bottom of the reactor to supply the oxygen, and the dissolved oxygen concentration was controlled to be 2–4 mg/L by adjusting the gas flow.

The return sludge from the secondary sedimentation tank of a PPW wastewater treatment plant was obtained as seeding sludge. After inoculation, the reactor was filled with three-time diluted PPW and aerated for 3 d. After that the system was startup by operated the reactor under batch mode for two weeks. For each day in this period, the reactor was aerated for 20 h, followed by 2 h of settling, and then 50% of the liquid was discharged and new wastewater was added. After the development of biofilm in the biocarrier, the system was operated under continuous-flow conditions.

### 2.6. Analytical methods

Measurement for water quality parameters in the influent and effluent was made according to Standard Methods [16]. In brief, COD was determined with $K_2Cr_2O_7$ and $H_2SO_4$ in a 1:1 ratio by the open reflux method with $AgSO_4$ as a catalyst and $HgSO_4$ to remove $Cl^-$ interference. $BOD_5$ was determined through the oxygen consumption of bacteria breaking down organic matter in the sample over a 5 d period under standardized conditions. $NH_3$–N was determined by Nessler's reagent colorimetry. SS was determined by gravimetric methods. Fluoride ions ($F^-$) were determined using an ion chromatograph (ICS-3000; Dionex, Sunnyvale, CA, USA). Biogas composition was measured using a gas chromatograph (GC17A, Shimadzu, Japan). Volatile fatty acids (VFA) concentration was analyzed by bicarbonate alkalinity according to Anderson and Yang [17].

The wastewater ecotoxicity was determined using an SDI M500 (SDI Co., USA) analyzer based on the inhibition of the bioluminescence of *Photobacterium phosphoreum* [18]. Microtoxicity is expressed as $EC_{50}$ (5 min, 15°C), which is defined as the effective concentration of a solution for a 50% reduction of the luminescence of the bacterium *Photobacterium phosphoreum*.

Microbial dehydrogenase activity (DHA) was determined with 2,3,5-triphenyltetrazolium chloride (TTC) adopting the method described by Yang et al. [11]. The results are expressed as μg triphenyl tetrazolium formazan (TF)/(gVS h).

## 3. Results and discussion

### 3.1. Coagulation optimization

Conventional water clarification processes primarily consist of the destabilization and subsequent removal of colloidal SS materials that are not readily removed by gravity sedimentation alone. Usually, a net negative surface charge causes individual particles to repel each other and remain in suspension. To counteract these repulsive forces, PAC was added to reduce the repulsive force during jar testing.

COD and SS removal performance by various dosages of PAC alone in the presence of 1.5 mg/L CPAM is shown in Fig. 2a. It is found that the removal ratio of both COD and SS increased with an increase in PAC dosage till it reached the highest value, after which the removal efficiency declined with coagulant dosage over the critical value (Fig. 2a). Moreover, COD removal was remarkably lower than that of

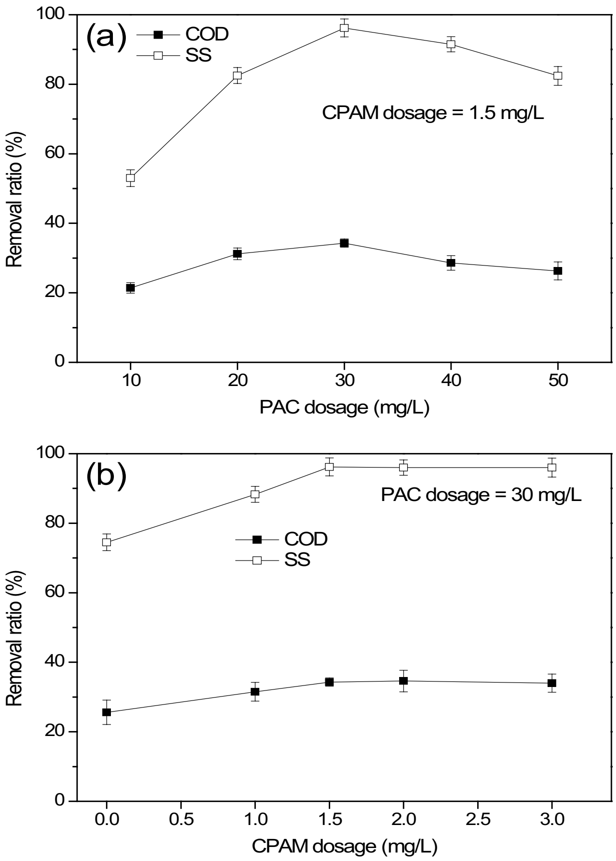


Fig. 2. Effect of (a) PAC dosage and (b) CPAM dosage on COD and SS removal during coagulation tests.

SS. At less than critical coagulant dosage, oppositely charged ions are not enough to neutralize the negative charges of the wastewater. Thus, the performance is improved with increasing PAC dosage. However, the restabilization of the system occurs at over the critical coagulant dosage because of a reversal of the charges caused by the presence of excess counter ions, leading to declined treatment performance at higher coagulant dosages [19]. Hu et al. [20] also observed an optimal dosage for PAC, both higher and lower dosage resulted in a decrease in removal performance. The main aim of coagulation process was to effectively remove SS in this work, thus 30 mg/L was deemed to be the optimum PAC dosage.

Fig. 2b shows COD and SS removal performance by 30 mg/L PAC at various dosages of CPAM. It can be found that adding CPAM can improve treatment efficiency until 1.5 mg/L CPAM, thereafter the performance was changed little with further increasing CPAM (Fig. 2b). Therefore, 1.5 mg/L CPAM was appropriate for this work. Under these conditions, the removal ratios of COD and SS were 34% and 96%, respectively. CPAM was usually used as a coagulant aid for water treatment, because it could accelerate settling speed of colloidal particles for its large molar and electric density [21].

### 3.2. EGSB performance

PPW was treated under the optimized coagulation conditions, and the effluent after settling and adding nutrients was continuously pumped into the EGSB reactor. The EGSB performance results are presented in Table 2 and Fig. 3. The vertical lines in Figs. 3a and b indicate a new HRT was applied to the reactor. During the first 30 d, the start-up stage, the EGSB feed COD fluctuated between 1,320 and 1,530 mg/L at an average OLR of 1 kg COD/m$^3$ d and $V_{up}$ of 1.5 m/h.

In the initial start-up phase (about 10 d), acidification occurred in the EGSB due to VFA accumulation (up to 1.2 g/L) with a pH value as low as 4.5. Moreover, the effluent was turbid with much floating sludge. It was speculated that the activation and growth rate of methanogens in the inoculated sludge was lower than that of acid-producing bacteria, resulting in VFA accumulation. To this end, the following measures were taken: adding lime to the regulating tank for raising the influent pH to around 8.0; increasing the $V_{up}$ to 2.0 m/h; recovering some sludge floc from the effluent. After taking the above measures, the effluent gradually became clear, the pH increased to more than 6.0, and the VFA content dropped to less than 0.4 g/L. the acidification problem was solved after two weeks of adjustment. Once the system stabilized the EGSB achieved a maximum COD removal of up to 50% between days 30 and 90 (Fig. 3a). COD removal gradually increased when OLR was raised from 1 to 4.5 kg COD/m$^3$ d but then slightly decreased with further increase in OLR. Moreover, the system was continuously and stably operated after day 90 at an OLR of about 6 kg COD/m$^3$ d and $V_{up}$ of 1.5 m/h, demonstrating that the EGSB could be operated at higher OLR for long duration. The COD removal remained at around 40% and the effluent COD concentration was averagely 1,600 mg/L during 90–120 d. It can be known that the EGSB reactor was well adapted to the impact of increased OLR, and the biomass amount increased with OLR. The removal ratio of COD increased continuously, and the effluent concentration decreased gradually.

Table 2 represents the EGSB COD removal with corresponding biogas production under different operating conditions. During the initial 30 d of start-up, the biogas obtained was about 2.1 L/d. The average $CH_4$, $CO_2$, $H_2S$, $N_2$, and $O_2$ contents in the biogas were 29%, 15%, 0.4%, 48%, and 7%, respectively. During the first 10 d, a lower $CH_4$ and higher $N_2$ production was observed, indicating the changes in the EGSB operating conditions, namely the abovementioned acidification. A slight difference in biogas composition was observed during the first 30 d and the following 60 d. From 30 to 90 d, the biogas flowrate gradually increased to around 8 L/d with an increase of OLR from 1 to 6 kg COD/m$^3$ d. The average biogas content during 30–90 d was 35%, 17%, 0.6%, 39% and 8% for $CH_4$, $CO_2$, $H_2S$, $N_2$ and $O_2$, respectively. From 91 to 120 d, the average biogas content for $CH_4$, $CO_2$, $N_2$ and $O_2$ was 40%, 18%, 35% and 6%, respectively. Obviously, $CH_4$ yield was improved with the increase of OLR, indicating that methanogens had adapted to the EGSB environment and evolved as dominant populations.

### 3.3. ABR performance

After about two months of the start-up phase, the ABR reactor was integrated into the hybrid system for continuous operation. During the operation of the ABR, the OLR was varied through altering HRT while the influent water quality

Table 2
EGSB COD treatment efficiency and biogas composition under different operating conditions

| Operating time (days) | Operating conditions | | | Biogas flow rate (L/d) | Biogas composition (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | HRT (h) | OLR (kg COD/m$^3$ d) | $V_{up}$ (m/h) | | $CH_4$ | $CO_2$ | $H_2S$ | $N_2$ | $O_2$ |
| 1–10 | 32 | 1 | 1.5 | 1.4 | 28 | 16 | 0.6 | 51 | 3 |
| 11–30 | 32 | 1 | 2 | 2.1 | 31 | 15 | 0.5 | 48 | 6 |
| 31–45 | 32 | 2 | 1.5 | 3.8 | 33 | 16 | 0.4 | 41 | 9 |
| 46–60 | 21 | 3 | 1.5 | 5.9 | 36 | 18 | 0.5 | 38 | 7 |
| 61–75 | 14 | 4.5 | 1.5 | 7.3 | 37 | 17 | 0.4 | 37 | 8 |
| 76–90 | 10 | 6 | 1.5 | 8 | 40 | 18 | 0.5 | 35 | 6 |
| 91–120 | 10 | 6 | 1.5 | 8 | 40 | 18 | 0.5 | 35 | 6 |

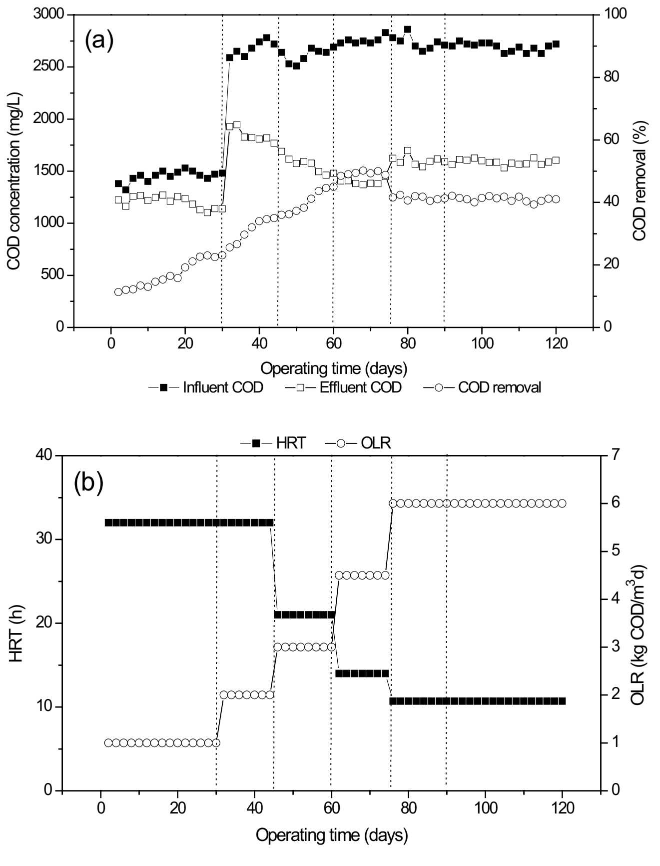


Fig. 3. (a) EGSB COD treatment efficiency and (b) corresponding HRT and OLR.

Table 3
Operational parameters of the ABR

| Operating stage | Duration (d) | HRT (h) | OLR (kg COD/m$^3$ d) |
|---|---|---|---|
| 1st stage | 1–15 | 26 | 1.5 |
| 2nd stage | 16–30 | 15 | 2.5 |
| 3rd stage | 31–45 | 11 | 3.5 |
| 4th stage | 46–60 | 9 | 4.3 |

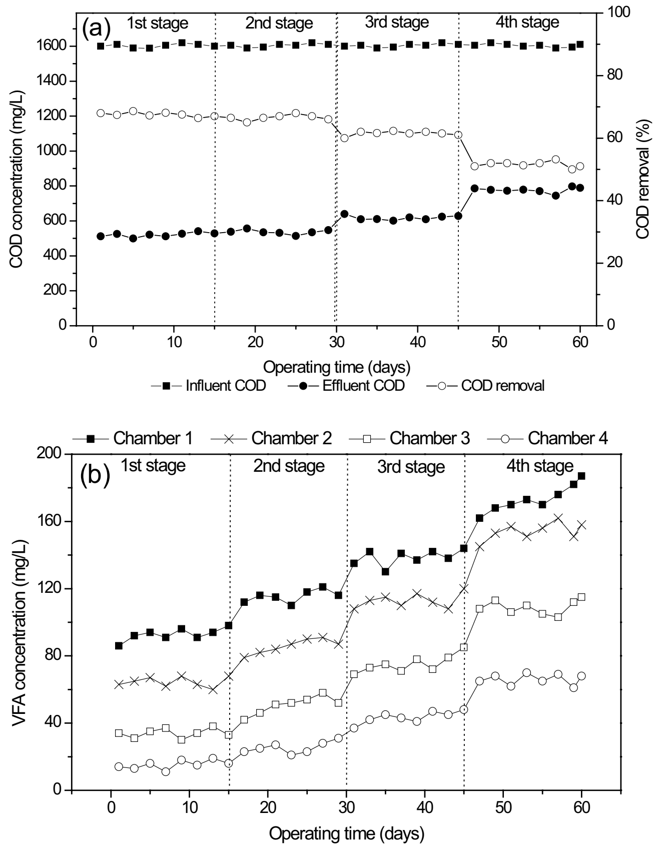


Fig. 4. Profile of COD removal (a) and VFA production (b) in each chamber during the experimental processes of ABR.

was relatively constant (Table 3). During the 1st stage of the formal treatment period (15 d), the OLR of the influent was about 1.5 kg COD/m$^3$ d.

As shown in Fig. 4a, the COD removal efficiency changed with the variations of OLR. During the process of HRT decreased from 26 to 15 h (2nd stage), OLR increased from 1.5 to 2.5 kg COD/m$^3$ d, the average COD removal ratio of the ABR kept stable at around 68% with an effluent COD of about 510 mg/L. This indicates that the ABR had a high shock resistance because the chambers of the ABR were separate and the first chamber bore the main OLR shock [10,11]. It also indicates that the bacteria adapted to the environment of each chamber and the bacteria activities were high. Moreover, this result demonstrates that the treatment performance could not be enhanced through extending HRT from 26 h to higher values. The HRT is positively correlated with COD removal efficiency in anaerobic processes [22]. At higher HRT, the contact time of microbes and substances was longer, which was beneficial for microbes to degrade the organic substances. However, when HRT was greater than a certain level, the microbial activity was suppressed due to the lack of nutrients including carbon sources [22].

As the HRT decreased from 15 to 11 h, the influent OLR was increased from 2.5 to 3.5 kg COD/m$^3$ d and the COD removal efficiency slightly decreased (Fig. 4a). It was because the influent organics did not mix with the bacteria well. The COD concentration and removal efficiency were influenced slightly. The performance of the ABR was not affected greatly. It verified that the ABR was able to resist OLR shock for being operated stably. Then the OLR increased from 3.5 to 4.3 kg COD/m$^3$ d with the decrease of HRT from 11 to 9 h, the effluent COD increased apparently (Fig. 4a). The HRT is one of the important parameters to affect the COD removal efficiency of the ABR and the optimum HRT should be determined based on the operation condition. In this work, the optimum HRT was 11 h (corresponding to an OLR of 3.5 kg COD/m$^3$ d) according to the COD removal efficiency and the investment.

Fig. 4b shows that the concentration of VFA in each chamber varied more complicatedly than COD during the operational condition. It was found that the VFA produced mainly in the 1st and 2nd chambers and then converted to acetate, finally, these acetic acids were generated to methane under the metabolic activity of methanogens in the 3rd and 4th chambers [11]. Moreover, it was observed that VFA concentration was higher at higher HRTs, and the VFA concentration in the 1st chamber increased up to 170 mg/L with an HRT of 9 h. The accumulation of VFA over 150 mg/L was the sign of the instability condition of the ABR system [11].

### 3.4. BCO performance

The effluent quality from the ABR system could not meet the discharge standard. Thus, a post-treatment process was needed. On the basis of the abovementioned results, the ABR was operated at 11 h HRT and the effluent was introduced into the BCO system for final treatment. The BOD$_5$/COD value of ABR effluent was 0.36, indicating that this stream was suitable for aerobic treatment. After the initial start-up period of about 20 d, the BCO was operated for 60 d at HRTs of 32, 26, 20, and 14 h, respectively. Each HRT lasted for 15 d.

The influent and effluent COD concentrations and COD removal during the 60 d operation are presented in Fig. 5. The influent COD concentration was in the range of 601–628 mg/L. When HRT was reduced from 32 to 26 h, the effluent COD increased slightly. This indicates that the BCO had a high anti-shock ability, as the BCO had high biomass density due to the application of biocarriers. The effluent COD increased slightly again when HRT was reduced from 26 to 20 h (Fig. 5). However, the effluent COD increased significantly when HRT was transitioned from 20 to 14 h. At HRT of 32, 26, 20, and 14 h, the average effluent COD values were 67, 75, 86, and 125 mg/L, respectively, corresponding to removal efficiency of 89%, 87%, 86% and 79%, respectively. At 32, 26 and 20 h HRT, the effluent COD met the national discharge standard of China (8978-1996) (Table 4). In consideration of operation costs and treatment efficiency, 20 h HRT was deemed to be suitable for this work.

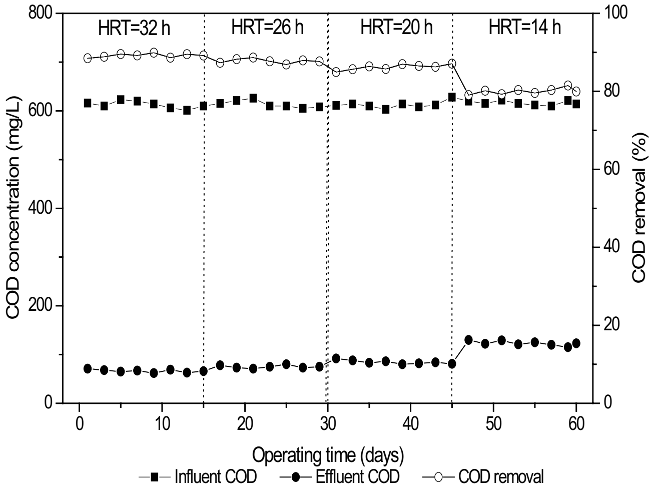

Fig. 5. Influent and effluent COD concentrations and COD removal during the 60 d operation of the BCO system.

Recently, BCO systems have been widely used as a postreatment process for various wastewaters [13,14]. BCO has good flexibility, adaptability and shock resistance. Moreover, BCO systems can be easily modified and connected to other processes for constructing a systematic process.

### 3.5. Evaluation of the hybrid process

As discussed above, the suitable operating conditions for the hybrid system were: 30 mg/L PAC and 1.5 mg/L CPAM for coagulation; HRT = 11 h (OLR = 6 kg COD/m$^3$ d) for EGSB; HRT = 11 h (OLR = 3.5 kg COD/m$^3$ d) for ABR; HRT = 20 h (OLR = 3.5 kg COD/m$^3$ d) for BCO. As can be seen from Table 4, the value of various water-quality parameters in the effluent satisfied the Chinese wastewater discharge standard (GB8978-1996). This shows that the hybrid system is a feasible technology for the treatment of heavily polluted PPW. The coagulation unit undertook a heavy responsibility for SS removal, while COD was mainly removed by the two anaerobic processes (Table 4). More than 50% of COD was removed by the multi-stage anaerobic reactors, and the residual organics was further aerobically degraded by the BCO process. Although the contribution of BCO to COD removal was relatively low, it played an important role in enabling the final effluent to satisfy the required discharge standard.

The concept of integrated physico-chemical–biological treatment has been proven in previous studies for the treatment of various industrial effluents. Liu et al. [22] studied the performance of integrating UASB, sequencing batch reactor (SBR), electrochemical oxidation and biological aerated filter (BAF) to treat leather industry wastewater with an initial COD of 8,300–9,250 mg/L. They found that the

Table 4
Average effluent quality, the total removal efficiency of pollutants, and the contribution of each unit to total removal efficiency in the hybrid system, and the national discharge standard of China (GB8978–1996)

| Parameter | Effluent value | Total removal | Contribution | | | | Discharge standard |
|---|---|---|---|---|---|---|---|
| | | | Coagulation | EGSB | ABR | BCO | |
| pH | 6.7 | – | – | – | – | – | 6–9 |
| COD | 86 | 98% | 35% | 28% | 25% | 12% | ≤100 mg/L |
| SS | 26 | 98% | 97% | 1.3% | 1.0% | 0.7% | ≤50 mg/L |
| TN | 35 | 42% | 13% | 32% | 25% | 30% | ≤50 mg/L |

removal efficiency of various pollutants was higher than 90%, and the ecotoxicity of the wastewater was remarkably reduced after treatment; the quality of the final effluent met the national discharge standard of China set for the leather tanning industry. Zou et al. [23] investigated the feasibility of coagulation–catalytic ozonation–anaerobic SBR–SBR for treating a real sodium dithionite wastewater with an initial COD of 21,760–22,450 mg/L; the results show that the removal efficiencies of COD and SS were averagely 99.3% and 95.6%, respectively, and the quality of final effluent could meet the national discharge standard of China; the coagulation and ASBR processes removed a considerable proportion of organic matter, while the SBR played an important role in post-polish of final effluent. Li et al. [24] used an integrated process comprising of ferrate(VI) oxidation and BAF to treat PPW with an initial COD of 3,630 mg/L, $BOD_5$ of 350 mg/L, and SS of 440 mg/L; the final effluent values of COD and SS were 308 and 35 mg/L, respectively, corresponding to total removal of 91.5% and 92.0%, respectively.

### *3.6. Analysis of acidity and alkalinity of anaerobic processes*

Stream samples were taken from EGSB influent, supernatant of EGSB three-phase separator and upper part of upwelling zones of ABR reactor. The pH, alkalinity and VFA concentration of various zones are listed in Table 5. As shown, the pH values of EGSB and ABR reactors were 6.5–7.4, which were in the suitable range for the growth of anaerobic fermentation bacteria, especially methanogens. In the EGSB reactor, the alkalinity increased from 830 mg/L to 1,220 mg/L. In the ABR reactor, the alkalinity increased slowly after a slight reduction in 1st chamber. The VFA concentration of various zones was below 150 mg/L, suggesting no large accumulation of VFA. The above results demonstrate that the methane production process proceeded smoothly in both EGSB and ABR reactors. The bicarbonate produced in methanogenic reactions could effectively neutralize the VFA formed in hydrolysis/acidification process, thus avoiding apparent pH reduction and destruction of the methane production process.

The pH value decreased slightly in the 1st and 2nd chambers of ABR, whereas increased to higher than 7 in EGSB and 3rd and 4th chambers of ABR (Table 5). It was speculated that the hydrolysis, acidification and methanogenesis proceeded simultaneously in EGSB, and ABR was a multistage anaerobic process. In 1st and 2nd chambers of ABR, the main reactions were hydrolysis and acidification, and low molecular weight fatty acids were the main products, resulting in pH reduction. Moreover, in the 3rd and 4th chambers of ABR, organic acids were further decomposed into $CO_2$, $H_2$ and $CH_4$, causing an increase in solution pH. The change of pH in the ABR reactor created suitable environmental conditions for different microbial communities, which was beneficial for efficient anaerobic reactions.

### *3.7. Microtoxicity changes*

Microtoxicity assessment is a useful technique for the evaluation of water quality changes during wastewater treatment. The changes in the Microtoxicity of raw wastewater and individual effluents are shown in Fig. 6. It can be found that the coagulation process has a small influence on the Microtoxicity. Nevertheless, the Microtoxicity significantly decreased (increase in $EC_{50}$) after EGSB treatment, indicating the efficient removal of toxic substances. The Microtoxicity was further reduced after the subsequent processes. Finally, the $EC_{50}$ value was increased after the hybrid process from 16.3% to 62.6%.

### *3.8. Microbial DHA*

The decomposition of organic substances in the wastewater is catalyzed by microbial enzymes, and the dehydrogenation reaction is the key approach of the active fraction of anaerobic microbes [25]. The DHA of EGSB and ABR reactors are listed in Table 5. It was found that the DHA value decreased along EGSB and the four chambers of ABR. The

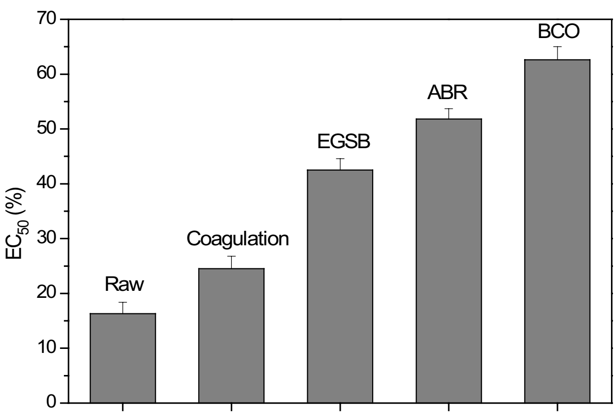


Fig. 6. Ecotoxicity changes in raw wastewater and individual effluents for the hybrid system.

Table 5
Alkalinity, VFA concentration, solution pH and DHA in various zones of the anaerobic system under the optimized conditions

| Parameter | EGSB influent | EGSB | ABR chamber | | | |
|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 |
| Alkalinity (mg/L) | 830 | 1,220 | 1,040 | 1,180 | 1,330 | 1,460 |
| VFA (mg/L) | – | 109 | 138 | 105 | 78 | 42 |
| pH | 6.8 | 7.4 | 6.5 | 6.6 | 6.9 | 7.1 |
| DHA [μgTF/(gVS h)] | – | 162 | 125 | 94 | 73 | 46 |

DHA of 1st chamber was significantly higher than that of the subsequent chambers under the same HRT condition in correspondence with its stronger capability of VFA production. Moreover, the DHA reduced from second to fourth chamber due to the lack of abundant substrate. Hence, the dehydrogenation reaction mainly occurred in the 1st chamber so that most of the substrate was hydrolyzed into VFA. These results suggest that the function of the initial chamber was the process of dehydrogenation and the subsequent chambers were the approach of methane production.

## 4. Conclusions

A novel system coupling coagulation, EGSB, ABR and BCO were proposed for the treatment of PPW, and outstanding performance was achieved. Under the optimized conditions, the quality of the final effluent can satisfy the national discharge standard, and the hybrid process achieved mean removal efficiencies of 98% for COD and 98% for SS. The coagulation process played a crucial role removing SS, while EGSB and ABR reactors showed a significant effect on degrading COD. The BCO process was important in the final effluent polishing. The results show that the hybrid process with efficient and economical advantages is beneficial for treating PPW with high pollution.

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