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Performance and model of a full-scale up-flow anaerobic sludge blanket (UASB) to treat the pharmaceutical wastewater containing 6-APA and amoxicillin

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ABSTRACT

A full-scale test was conducted with an up-flow anaerobic sludge blanket (UASB) pre-treating pharmaceutical wastewater containing 6-aminopenicillanic acid (6-APA) and amoxicillin. The aim of the study is to investigate the performance of UASB in the condition of a high chemical oxygen demand (COD) loading rate from 12.57 to 21.02 kg m^{-3} d^{-1} and a wide pH from 5.57 to 8.26, in order to provide a reference for treating the similar chemical synthetic pharmaceutical wastewater containing 6-APA and amoxicillin. The results demonstrated that the UASB average percentage reduction in COD, 6-APA and amoxicillin were 52.2%, 26.3% and 21.6%, respectively. In addition, three models, built on the back propagation neural network (BPNN) theory and linear regression techniques were developed for the simulation of the UASB system performance in the biodegradation of pharmaceutical wastewater containing 6-APA and amoxicillin. The average error of COD, 6-APA and amoxicillin were −0.63%, 2.19% and 5.40%, respectively. The results indicated that these models built on the BPNN theory were well-fitted to the detected data, and were able to simulate and predict the removal of COD, 6-APA and amoxicillin by UASB.

1. Introduction

6-Aminopenicillanic acid (6-APA) and amoxicillin are the most common featured pollutants in the fermentation and chemical synthesis-based pharmaceutical wastewater due to the rapid growth and development of pharmaceutical industry [1]. 6-APA, a starting material for preparing commercially important ampicillin and amoxicillin can be derived from either penicillin V or G via enzymatic hydrolysis which also produces phenoxyacetic acid as the side product [2]. Amoxicillin is a broad-spectrum β-lactam antibiotic that belongs to penicillin class organism used as veterinary medicine for treatment of bacterial infections encountered in gastro-intestinal and systemic infections [3]. But the chemical methods for producing 6-APA and amoxicillin are environmentally burdensome and require the use of hazardous chemicals such as pyridine, phosphorous pentachloride and nitrosylchloride [4].

These 6-APA and amoxicillin pharmaceutical wastewaters, arising mainly from equipment cleaning, contain a variety of organic and inorganic constituents including spent solvents, catalysts, reactants and small amounts of intermediate or product, in addition to the usual manufacturing streams such as pump seal waters, waste scrubbers wastewaters, boiler blow down and floor washing [5]. These wastewaters may therefore be high in COD, ammonia–nitrogen (NH_3–N), and total suspended solids (TSS), with a wide range of pH from 1 to 11, changes in production schedules lead to significant variability of the wastewater flow rate, their principal constituents and relative biodegradability [6]. Furthermore, their bacterial toxicity and recalcitrance may also play an important role in decreasing the COD removal efficiency in affected treatment systems [7]. Because of stricter discharge standard (decrease to COD ≤ 120 mg L^{-1} from the previous COD ≤ 300 mg L^{-1}) of water pollutants for pharmaceutical industry [8], an approach towards appropriate technology for the treatment of containing 6-APA and amoxicillin pharmaceutical wastewater has become an imperative task.

Wastewaters produced from 6-APA and amoxicillin pharmaceutical industries pose several challenges for successful treatment [9]. As a modern anaerobic processes used for high rate reactors, the up-flow anaerobic sludge blanket (UASB) is widely used in industrial and domestic waste treatment around the world [10–15]. This mainly due to its simple design, easy construction and maintenance, low operating cost, ability to withstand fluctuations in pH, temperature and influent substrate concentration [16–18]. With these strengths UASB has the potential be applied economically as a pre-treatment system for many industrial effluents, such as paper-pulp liquors [19], spent sulphide liquors [20], fiber-

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Table 1
Performance data of UASB reactors treating of industrial wastewater under various organic and hydraulic loading conditions.

Industrial wastewater	COD loading rate/kgm^{-3} d^{-1}	HRT/h	Influent/mg-COD L^{-1}	% COD removed	Volume/m^3	References
Ethanol–acetone wastewater	2.5	18.0	150,00	80	3000 × 2	Shen and Wang [35], Yuan [25]
Fermentation wastewater	11.8	58	23,450	91	200 × 4	Yuan [25]
Phthalic acid wastewater	3	–	–	–	3000 × 4	Yuan [25]
PTA wastewater	13.1	40.8	–	–	1320	Yuan [25], Ren and Zhao [23]
Poultry manure wastewater	2.5	15.7	5220	53	250	Yetilmezsoy and Sakar [15]
Paper-pulp liquors	4–10	5.5	–	–	600 × 5	Shen and Wang [35], Yuan [25]
Brewery wastewater	4.5	5–6	2000	78	800	Yuan [25]
Citric acid wastewater	10	38–49	10,000	80	380	Shen and Wang [35]
Diastatic fermentation wastewater	4	6	20,000	85	–	Yuan [25]; Ren and Zhao [23]
Concentrated alcohol wastewater	13.6	38	34,060	81	130	Shen and Wang [35]
Pharmaceutical wastewater	13.2	47	25,603	80	1500	Ren and Zhao [23]
Chinese medicine wastewater	5.0	55	16,920	85	750	Ren and Zhao [23]

board manufacturing wastewater [21], and slaughterhouse effluent [22].

Contrasted with this study, previous results regarding the UASB treatability of different industrial wastewaters under various organic and hydraulic loading conditions are summarized in Table 1 [11,23–25]. As seen in Table 1, on one hand, the industrial wastewaters were satisfactorily pre-treated by means of high-rate UASB reactors, on the other hand, the UASB reactors could also become a preferred option for certain pharmaceutical wastewaters due to several operational advantages over other reactor configurations for the treatment of various kinds of liquid wastes [12,13,26].

Though lots of reports about the use of UASB to pre-treat pharmaceutical wastewater, a previous study used a hybrid upflow anaerobic sludge blanket reactor to treat a kind of chemical synthesis-based pharmaceutical was found to be far more effective at a COD loading rate of 8 kg-COD m^{-3} d^{-1} with a COD removal efficiency of 72% [13]. And in another study, pharmaceutical wastewaters was obtained from a local bulk drug pharmaceutical unit, which COD concentration was 13,000–15,000 mg L^{-1}, glucose was the entire feed, COD loading rate range from 2 to 12 kg m^{-3} d^{-1}, the results indicated that ±8% COD was detect to be removed by the UASB [10].

However, publications on the application of UASB in the treatment of pharmaceutical wastewater was operated in lab-scale or bench-scale, scarcely cover the performance of UASB pre-treat pharmaceutical wastewater in full-scale. Furthermore, less study was reported on using UASB for the pre-treat of pharmaceutical wastewater containing 6-APA and amoxicillin in full-scale, especially the performance of UASB to pre-treat pharmaceutical wastewater containing 6-APA and amoxicillin under a high COD loading rate (12.57–21.02 kg m^{-3} d^{-1}), sharply fluctuation of pH (5.57–8.26), and high COD influent concentration (4726–19,951 mg L^{-1}). Therefore, the suitability of using UASB system for the pre-treatment of pharmaceutical wastewater containing 6-APA and amoxicillin is pending to be investigated. In this regard, UASB was employed as a pre-treatment unit to treat wastewater achieved from the United Laboratories Co. Ltd. (Inner Mongolia, China), which runs at unfixed wastewater flow flux of 1169–2805 m^3 d^{-1} for 205 days which the first 96 days were the start-up period.

In addition, the operation of anaerobic reactors needed an accurate mathematical model to offer suggestions and guidance in setting up models. Back propagation neural network (BPNN) can approach any nonlinear systems dynamically, and the network weights can be altered by inputting new training data, then achieving dynamic adjustment of model. Therefore it has a good prospect and profound significance that use back propagation neural network to optimize control parameters of the reactor and propose strategies of reactor in order to perform stably [27]. Three models used to simulate the performance of the UASB pre-treating pharmaceutical wastewater containing 6-APA and amoxicillin were established, based on BPNN and linear regression techniques. What is more, the coat-benefit analysis for the UASB reactor can provide an economical reference for pharmaceutical wastewater treatment.

2. Materials and methods

2.1. Description of the full-scale wastewater plant

The full-scale wastewater treatment plant (WWTP) was designed for biological COD, NH_3–N and another special pollutants removal with a physicochemical–biochemical combination process which located in the northern of China. The flow diagram of the wastewater treatment plant is show in Fig. 1. Four types of wastewater are treated separately throughout the preliminary and primary treatment steps. First, the raw wastewater, result of the treatment of flocculation deposit pool (I) and adjustive pool (I) was fed to the UASB, and the effluent of UASB was enter into the sedimentation tank (I), pre-aeration tank and adjustive pool (II) in sequence. Secondly, the high-strength concentration mixed wastewater of ethanol still age residue, phenyl acetic acid, amoxicillin and 6-APA liquors were fed to tetra tic function device, the effluent COD was less than 3000 mg L^{-1} in spite of influent COD at 240,00 mg L^{-1}. The effluent of 4-function device was entering into adjustive pool (II). Thirdly, after treated in the sedimentation tank, the filter cloth washing wastewater was introduced into the adjustive pool (II). Last, after the low-strength concentration wastewater mixed with liquid glucose, fermentation and refine workshop were introduced to grid screen and water-collecting well, the effluent of which is also enter into the adjustive pool (II). Finally, the mixed effluents from the adjustive pool (II) were treated by the main biological treatment technology: hydrolysis acidification reactor (HAR), cyclic activated sludge system (CASS) and biological contact oxidation tank (BOCT). The activated sludge was settled in sedimentation tank (III) (Fig. 1). And after that, the effluent was discharged into the nearby recipient. This paper only demonstrates the performance of UASB system as a pre-treatment unit.

2.2. Wastewater characteristics

The wastewater containing 6-APA and amoxicillin pre-treated by UASB generated from the processes of product manufacturing and equipment cleaning was mainly specified waste acid water produced when extract penicillin, which containing a variety of organic and inorganic constituents, such as spent solvents, catalysts, reactants and a small amount of intermediates or products. Table 2 summarizes the average conditions adopted during the operation time. It is worthy to point that pharmaceutically active compound; dissolved 6-APA; dissolved amoxicillin and some un-biodegradable organic compounds comprised the influent suspended solids (SS).

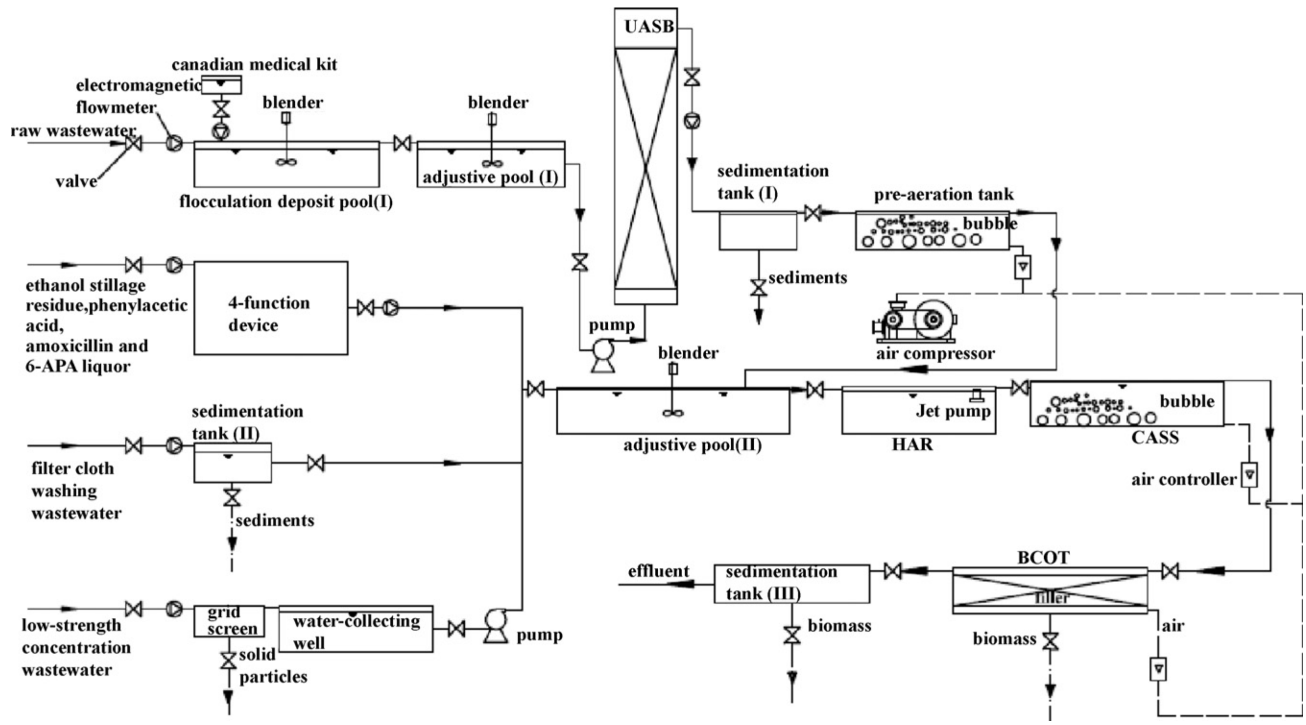

Fig. 1. Process flow diagram of the full-scale WWTP of United Laboratories Co. Ltd.

The operating conditions included 109 days, including three stages. Stage 1 of 97–150 days, stage 3 of 165–205 days and stage 2 of 151–164 days.

2.3. Inoculation sludge characteristics

The UASB reactor was seeded to 35% (v/v) of its total volume with the sludge which taken from a UASB reactor treating the pharmaceutical industry effluent. Total solids (TS) concentration of the seed sludge was approximately 90 g L^{-1} of which 94% was total volatile solids (TVS). After seeding, the TVS concentration within the UASB reactor was 28.83 g L^{-1}.

2.4. Analytical methods

The WWTP was daily sampled during 205 days from March 1st to September 14th, 2008. All measurements were performed under dry weather flow conditions. The effluent was collected at fixed sampling sites between 10 and 11 am everyday for the analysis of COD, 6-APA, amoxicillin, NH_3–N, and pH. Measurements of COD, NH_3–N, SS, TS, TVS, volatile fatty acids (VFAs) and methane were performed according to standard methods [28]. The biogas was recorded by a wet-gas meter. Dissolved oxygen (DO) and pH were monitored daily by a hand-held oxygen meter (COM 381, Shanghai Light Industry Research Institute, China) equipped with a DO probe (COS 381, Shenzhen Futai Instrument Co. Ltd., China) and a portable pH meter (sensION1, HACH), respectively. 6-APA and amoxicillin concentration were measured by high performance liquid chromatography (Prominence LC-20A, SHIMADZM, from Waters; column: C18,60 Å, 4 μm, 3.9 mm × 150 mm; mobile phase: 35% acetonitrile, 2‰ sodium lauryl sulphate, with a flow rate 1.0 ml min^{-1}, 0.01 M H_3PO_4, 0.005 M $K_2H_2PO_4$ and pH 4.6 at 25 °C) [4]. Software MATLAB was used to analyze model numerical solutions.

Table 2
Operating conditions and wastewater characters of the UASB.

Operating conditions	Average value	Fluctuation range
Influent flow ($m^3\ d^{-1}$)	2031.2	1169–2805
Influent COD (mg L^{-1})	7458	4726–19,951
COD loading rate (kg $m^{-3}\ d^{-1}$)	14.6	12.57–21.02
HRT (h)	23.2	16.8–40.3
Influent pH	7.4	5.57–8.26
Influent 6-APA (mg L^{-1})	192	143–315
Influent amoxicillin (mg L^{-1})	92	61–171
NH_3–N (mg L^{-1})	364	156.4–650.2
Suspended solids (mg L^{-1})	765	421–1468

3. Results and discussion

3.1. Acclimation to pharmaceutical wastewater

After seeding the sludge to the UASB, the reactor was initially fed with glucose, after the completion of this period, the glucose based wastewater was gradually replaced by a combination of glucose and pharmaceutical wastewater, and increasing the proportion of the pharmaceutical wastewater in the following stages: 20% (w/v, i.e. wastewater/volume of influent), 40% (w/v), 60% (w/v), 80% (w/v) and finally the reactor was loaded with 100% (w/v) pharmaceutical wastewater (Fig. 2).

As Fig. 2 shown, the completion of the acclimation period was taken 96 days. UASB reactor performed well at the first 10 day at which point 65% COD removal efficiency was achieved. Introducing 20% (w/v), 40% (w/v), 60% (w/v) and 80% (w/v) pharmaceutical wastewater resulted in COD removal efficiency initially from 57% to 58%, 55%, and 51%, respectively. At the end of the feeding period with 100% (w/v) pharmaceutical wastewater, the COD removal efficiency of the UASB reactor decreased to 42%.

3.2. Performance of UASB

3.2.1. COD removal

Fig. 3 showed how these statistics varied over the given 109 days, including influent COD, effluent COD, the % COD removed,

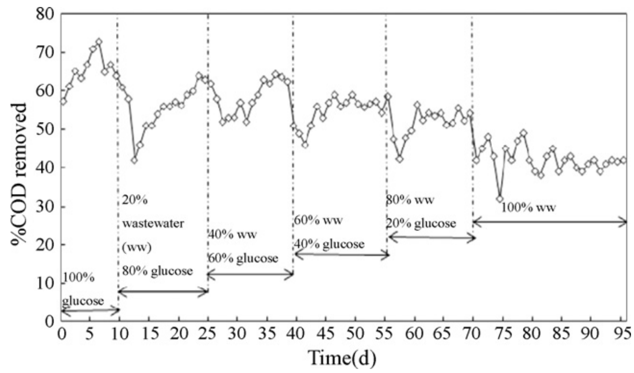

Fig. 2. COD removal efficiency versus time throughout the start-up period.

influent flow, influent pH, effluent pH and COD loading rate. According to the records, UASB influent concentration flocculated substantially from 4726 to 19,951 mg-COD L^{-1} in the stage 1. However, the COD loading rate only had a narrow change of 9.26–14.6 kg m^{-3} d^{-1}. So did the UASB effluent, varied from 2311.1 to 4143.9 mg-COD L^{-1} and % COD removed from 51% to 68%. This indicated that the UASB had a potential for treating high-intensity pharmaceutical wastewater. The reasons that the effluent COD was maintained at a high level at stage 2 were that the influent COD and COD loading rate increased, besides the effect of a shocking COD loading, the inconsistent COD removal was probably owing to the fact that microbial acclimation might not be fully accomplished at that time. Refrigerating units did not work from day 152 to 154. There are a lot of organic residual solvents—butyl, toluene, mycelium and low pH in flocculation deposit pool(I) and adjustive pool(I) in the day 153 due to expanded production of United Laboratories (Inner Mongolia) Co. Ltd. The average values of influent, effluent, % COD removed and COD loading rate were respectively 14780.8 mg-COD L^{-1}, 5098.4 mg-COD L^{-1}, 63.3% and 21.02 kg m^{-3} d^{-1} at stage 2. COD rate removed was high from day 151 to 164 owing to higher influent COD and lower effluent COD. It is worthy to mention that the effluent COD became low from day 165 to 205, and varied from 2071 mg-COD L^{-1} to 4650 mg-COD L^{-1},despite of the UASB influent concentration stabilizing at average 6962 mg-COD L^{-1}. Namely, the full-scale plant has returned to a preferable state only for 14 days. It was noted that, COD loading rates were maintained at a high level at all operation periods. The average values of COD loading rate were 12.57, 21.02 and 13.02 kg m^{-3} d^{-1} for the individual stages. These COD loading rate were significantly higher than reported previously. For example, Sánchez et al. reported values of 0.9–8.1 kg m^{-3} d^{-1} for piggery waste treatment [29]. Oktem et al. reported values of 1.0–9.0 kg m^{-3} d^{-1} for chemical synthesis-based pharmaceutical wastewater treatment [13,30]. The most suitable COD loading rate in this study was 12.6–21.02 kg m^{-3} d^{-1} due to lower effluent of 5098.4 mg-COD L^{-1} and higher % COD removed of 63.3%. Results of this study are in disagreement with a stable COD removal rate reported in the UASB while treating industrial wastewater at a fixed COD loading rate. This inconsistency is presumably attributed to the daily varying wastewater concentrations and COD loading rate in the present study. Only a COD removal efficiency of 65% was achieved in a similar, but one-phase UASBAF reactor while treating chemical synthesis based pharmaceutical wastewater with a COD loading rate 6 kg m^{-3} d^{-1} at an HRT of 2.3 days [31]. Furthermore, the pH of feed to the reactors varied from 5.57 to 8.11, with an average value of 6.5 ($\pm$0.2), while the effluent pH is 7.11–7.68 for all but days 53 and 56 (Fig. 3). Average value of effluent pH was 7.4 ($\pm$0.2), which was lower

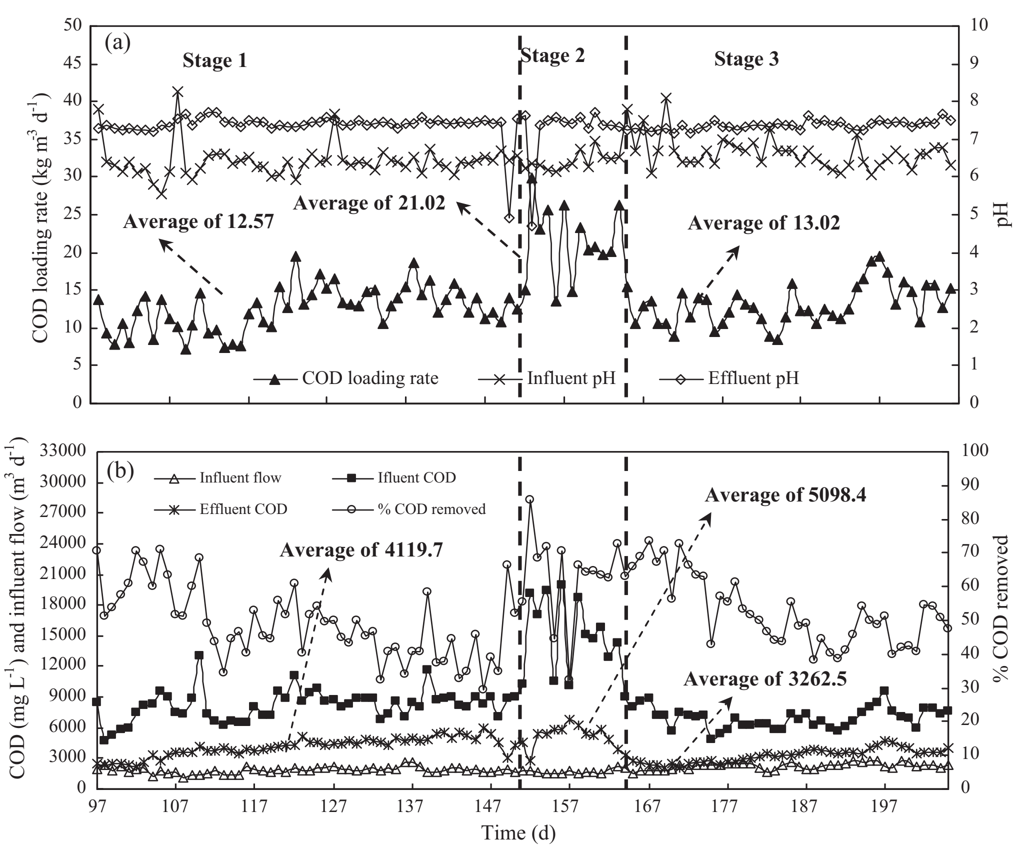

Fig. 3. (a) Variation of COD loading rate and pH in the full-scale UASB during stage 1–3. (b) Variation of influent flux, influent COD, effluent COD and COD removal efficiency in the full-scale UASB during stages 1–3.

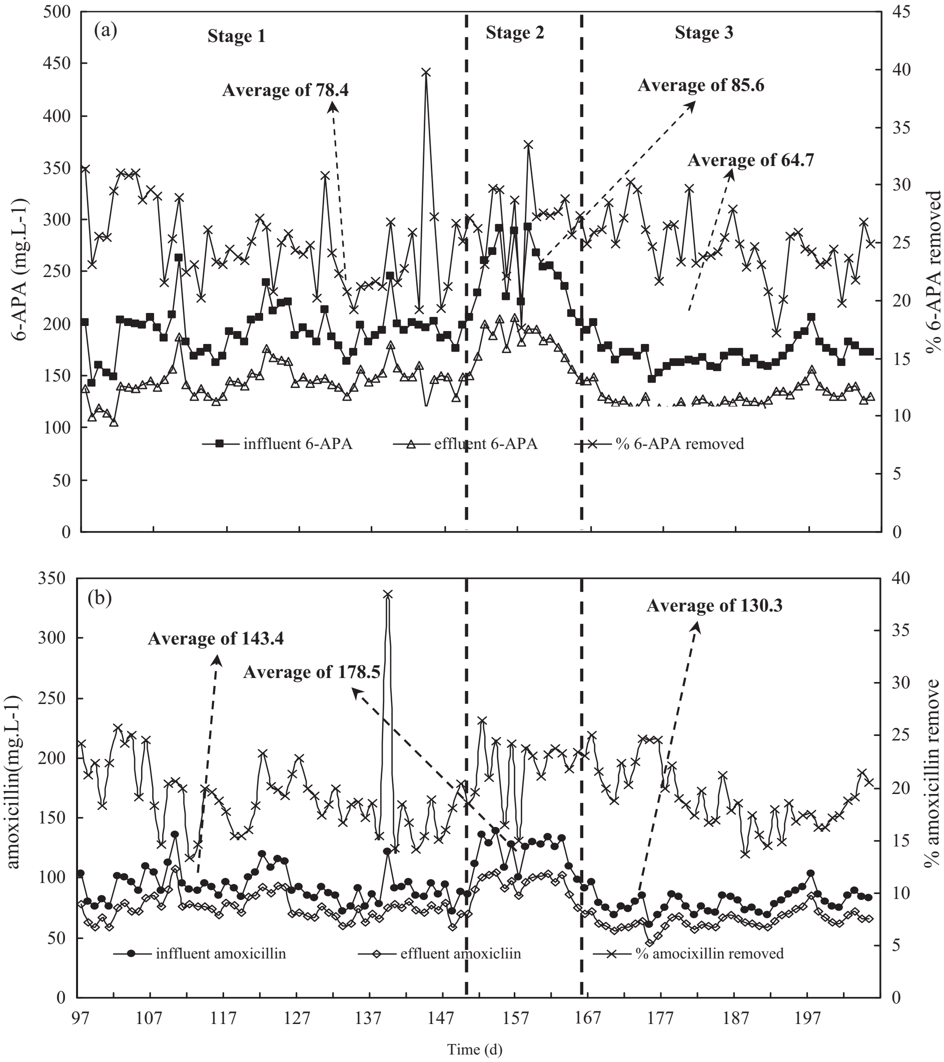

Fig. 4. (a) Variation of influent 6-APA, effluent 6-APA and 6-APA removal efficiency in the full-scale UASB during stage 1–3. (b) Variation of influent amoxicillin, effluent amoxicillin and amoxicillin removal efficiency in the full-scale UASB during stages 1–3.

than 8.1 ± 0.2 of the previous study [15], mainly due to the conversion of VFAs to CH_4 and CO_2 by methanogens. The alkalinity might also be generated as nitrogenous organic compounds contained in the pharmaceutical wastewater, if any, were biodegraded anaerobically.

It is worthy to mention that the analysis of the effluent indicated that the suspended activated sludge, remained 6-APA and amoxicillin, some refractory materials and some unknown intermediate metabolites composed the COD of effluent.

The VFA concentration in effluent, biogas and methane content was detected during this experiment. At stage 1, the VFA concentration was varied from 876 to 1270 mg L^{-1} as COD loading rate ranging from 7.1 to 19.5 kg-COD m^3 d^{-1}. When the COD loading rate was increased suddenly from 12.57 to 21.02 kg-COD m^3 d^{-1} at stage 2, the VFA concentration also increased from 1270 to 2670 mg L^{-1}, indicating that methanogenic inhibition towards toxicity of this pharmaceutical effluents which containing 6-APA and amoxicillin, while at stage 3, when the COD loading rate decreased from 21.02 to 13.02 kg-COD m^3 d^{-1}, the VFA concentration also decreased from 2670 to 1460 mg L^{-1}. This is an indication that the VFA concentration is closely linked with the COD loading rate. On analysis of biogas, we observed a high methane content of 65–68% and 17% for CO_2 was obtained at the experiment. The rest of the biogas was recorded as H_2 with trace amounts of H_2S and unknown gas. The high amounts of methane and hydrogen can prove that the UASB has the potential of the recycling-reusing of the biomass energy.

3.2.2. 6-APA and amoxicillin removal

The influent and effluent 6-APA and amoxicillin, the %6-APA and amoxicillin removed average values of effluent 6-APA and amoxicillin are illustrated in Fig. 4. As recorded, 6-APA and amoxicillin influent concentration flocculated from 143 to 315 mg-6-APA L^{-1}, 61 to 171 mg-amoxicillin L^{-1}, respectively. Though the concentrations of 6-APA and amoxicillin were constantly changing, the effluent concentrations of 6-APA and amoxicillin maintained at a stable level at 160 ± 30 mg-6-APA L^{-1} and 75 ± 29 mg-amoxicillin L^{-1}, respectively. Fig. 4 also demonstrated that, on the 14th day, 43rd day and 56th day, the effluent concentration kept at a stable stage while the influent 6-APA and amoxicillin considerable changed and %6-APA removed appeared peaks, which indicating that UASB reactor not only perform a strong impact load capacity for the COD and NH_3–N, but also have the potential resistance to a shockingly loading to some special form of organic matter, such as 6-APA and amoxicillin in this study. During research, the removal of 6-APA and amoxicillin flocculated were recorded 19–40%, and 13–47%, respectively, with an average removal rate 26.3% for 6-APA and 21.6% for the amoxicillin.

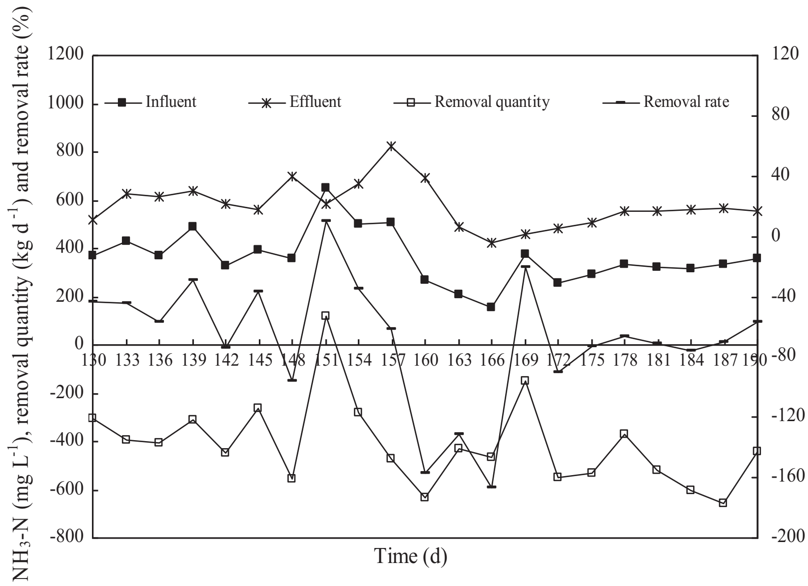

Fig. 5. Influent NH_3–N, effluent NH_3–N, NH_3–N removal quantity and NH_3–N removal efficiency in the full-scale UASB.

As show in Fig. 4, at stage 1, effluent 6-APA varied from 105 to 176 mg-6-APA L^{-1} with an average value at 143.4 mg-6-APA L^{-1} and %6-APA removed from 19% to 37%, corresponding to effluent amoxicillin varied from 59 to 93 mg-amoxicillin L^{-1} with an average value at 78.4 mg-amoxicillin L^{-1} and %amoxicillin removed from 13% to 36%. The performance of UASB at stage 2 (151th–164th day) to reduce 6-APA and amoxicillin consistent with the COD removal, the reduction percentages were higher than the other two stages which reached 33% and 32%, respectively, despite of the concentrations of 6-APA and amoxicillin high in influent and effluent, which reach 178.5 mg-6-APA L^{-1} and 85.6 mg-amoxicillin L^{-1} in effluent. It is worthy to mention that the effluent 6-APA and amoxicillin became low from day 155 to 205, achieved 130.3 mg-6-APA L^{-1} and 64.7 mg-amoxicillin L^{-1}.

3.2.3. NH_3–N removal

The detection of NH_3–N began on the 130st day, and then the measurement of it was made three days a time until the UASB system is running at the end of 190st day, a total of 20 sets of data. The changes of influent, effluent NH_3–N and NH_3–N removal with time are illustrated in Fig. 5 NH_3–N mainly produced from the fermentation process of corn oil. The influent of which sharply fluctuated between 156.4 and 650.2 mg L^{-1}, with the average value of 364 mg L^{-1}. Results showed that the effluent of NH_3–N of the UASB reactor corresponded with the variation in the influent strength. As Fig. 5 show, in most cases the effluent NH_3–N concentration (423.7–821.7 mg L^{-1}) is higher than the influent, with the removal fluctuated from −166.7% to 10.6%. Under acidic conditions, the total organic nitrogen as part of the raw wastewater is broken down because of this outcome. The increase of UASB effluent NH_3–N also provided sufficient nitrogen to the follow-up aerobic operations, thus making up the poverty nitrogen wastewater which had not been treated previously by UASB or the domestic wastewater with low nitrogen. This increasing also avoids re-addition of nitrogen to the water to meet the needs of following aerobic process. This result is consistent with a previous study, which combined UASB-down-flow hanging sponge (DHS) system to treat sewage, finding that the concentration of NH_3–N become increasing in UASB reactor [32], Mahmoud's study illustrated the application of a UASB to treat high-strength sewage had −5% removal of NH_3–N in UASB reactor [14]. However, it is inconsistent with El-Shafai et al. study, they use a UASB-duckweed ponds system to treat domestic wastewater demonstrated that removal efficiencies was 26% during the warm season and 15% during the wintertime [33].

3.3. Cost-benefit analysis

Cost-benefit analysis was done for a UASB reactor on the basis of wastewater generation. The overall costs were comprised by the sum of the capital costs, the operating and maintenance costs [10]. The capital costs of UASB reactor strongly depend on the nature and the concentrations of the pollutants, this UASB reactor capital costs were 157 US$ m^{-3} pharmaceutical wastewater. The estimation of operating and maintenance costs has been made regarding for the full-scale treatment process used for the treatment of this con-

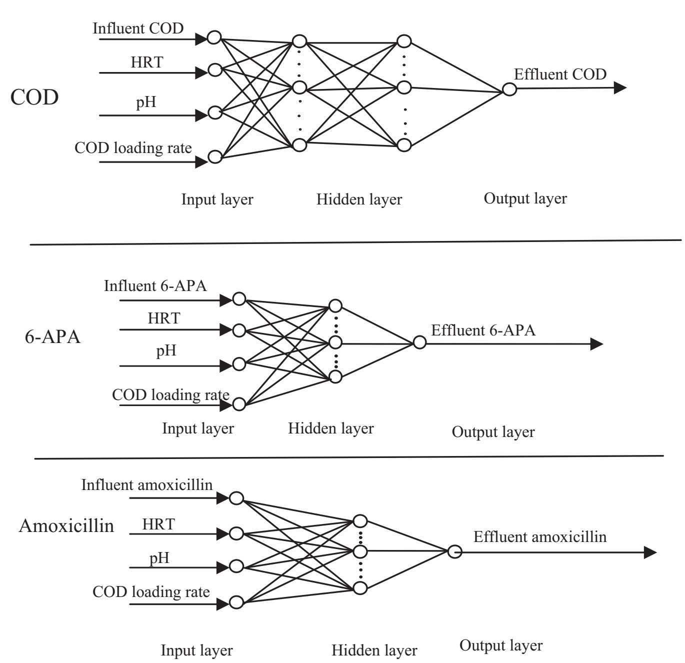

Fig. 6. Topological architecture of the BPNN model.

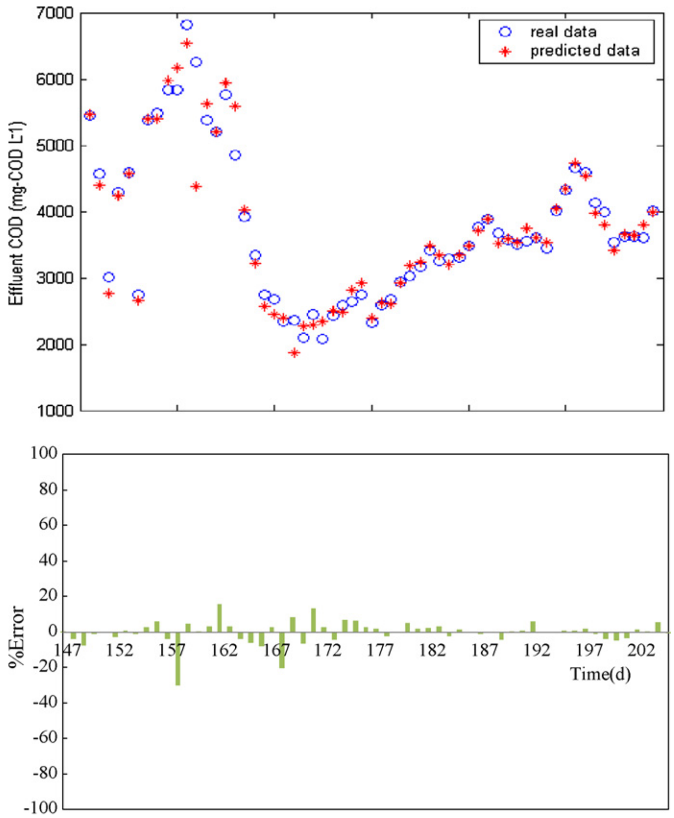

Fig. 7. Comparison of COD simulated results with real data and the error chat.

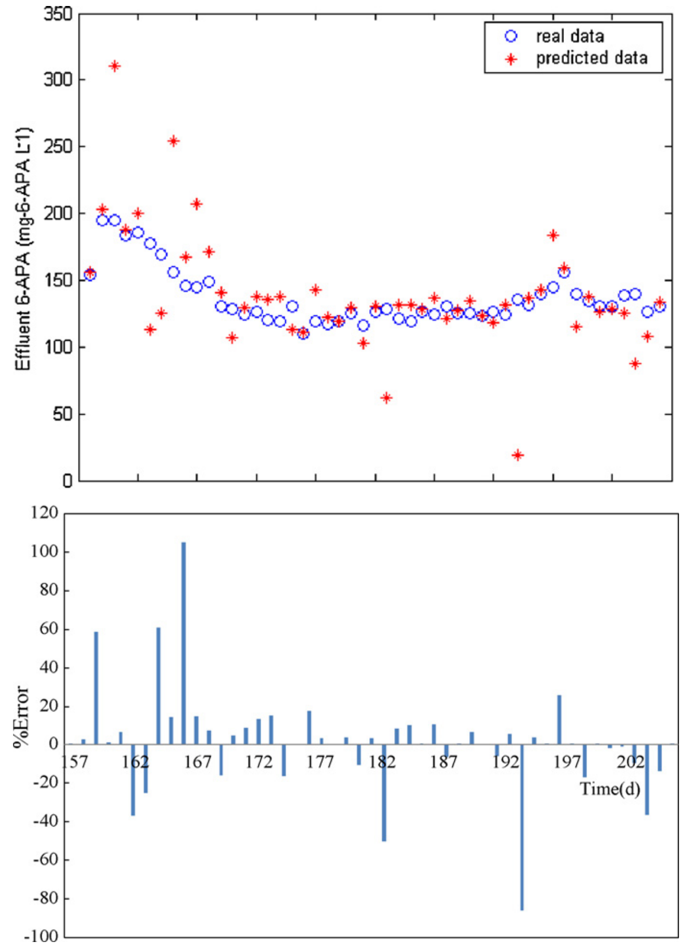

Fig. 8. Comparison of 6-APA simulated results with real data and the error chat.

taining 6-APA and amoxicillin pharmaceutical wastewaters. The operational costs were (US$ 100 m^{-3} pharmaceutical wastewaters): electricity (24.7) and nutrients (11.5). The total estimated cost was 36.2 US$ for treating 100 m^3 bulk pharmaceutical industrial wastewaters.

3.4. Development of a model for the simulation of UASB operation

Three arithmetic models were established by the software program MATLAB to simulate the performance of the UASB in terms of effluent COD, effluent 6-APA and effluent amoxicillin, taking several operating parameters into account—pH, COD loading rate, HRT and influent COD, 6-APA and amoxicillin [12]. Models were based on the BPNN theory and linear regression techniques. The topological architecture of BPNN models were illustrated in Fig. 6, it shows a four-level and two three-level networks. Each network comprises four nodes in input layers, undetermined nodes in hidden layers and one node in the output. Each node is a BP neuron. Influent COD (6-APA, amoxicillin), COD loading rate, HRT and pH of the UASB are the initial variables of input for each network. Effluent COD concentration, effluent 6-APA concentration and effluent amoxicillin concentration are the variables.

Functions and parameters used in models are described as follows: the model for COD, training function, "traingdm" arithmetic; stimulative functions, "tansig", "logsig" (hidden layer) and "purelin" (output layer); study rate (lr), 0.8; other parameters were defaults. Models for 6-APA and amoxicillin, training function, "trainscg" arithmetic; simulative functions, "tansig" (hidden layer) and "purelin" (output layer); study rate (lr), 0.1, other parameters were defaults.

The model program for COD selected the data of 97–146 day of the UASB system as training value, and the other two models were trained using selected parameters from data sets between day 97 and day 156 and were subsequently simulated by using independent data sets between day 157 and day 205. Debugged and perfected through adjusting node numbers of the hidden layers, which represent unobserved-state variables. The results of interactive programming showed that when the nodes of hidden layer were 60 and 4, it was able to well-predict the performances of UASB COD removal (Fig. 7). The numbers of the hidden layers of other two models were 60 and 9, respectively, according to the results of interactive programming in which a satisfactory approximation of the model to the steady-state experimental data between day 157 and day 205 was able to be achieved (Figs. 8 and 9). Overall, ignoring the larger number of outliers caused by several errors (166th day and 192nd day data of simulated effluent 6-APA), these models were well fitted the real data in terms of reactors effluent COD, 6-APA and amoxicillin. The average errors of COD, 6-APA and amoxicillin were −0.63%, 2.19% and 5.40%, respectively, which indicated that the simulation model built on the BPNN theory is a practical and feasible means to simulate and predict the pollutants removal by UASB. These forecast results are consistent with previous study, which established a BPNN model based on the prototype experiment of treating herb wastewater by up-flow Anaerobic Sludge Bed and Anaerobic Filter reactor (UASBAF). At that model 30 representative groups of data were selected for training and 14 groups were for forecasting, 1.89–19.23% errors were obtained eventually [27]. From a previous study, Hanbay et al. based on wavelet packet decomposition, entropy and BPNN developed model to predict WWTP performance. The suitable architecture of the BPNN model was determined after several trial and error steps. According

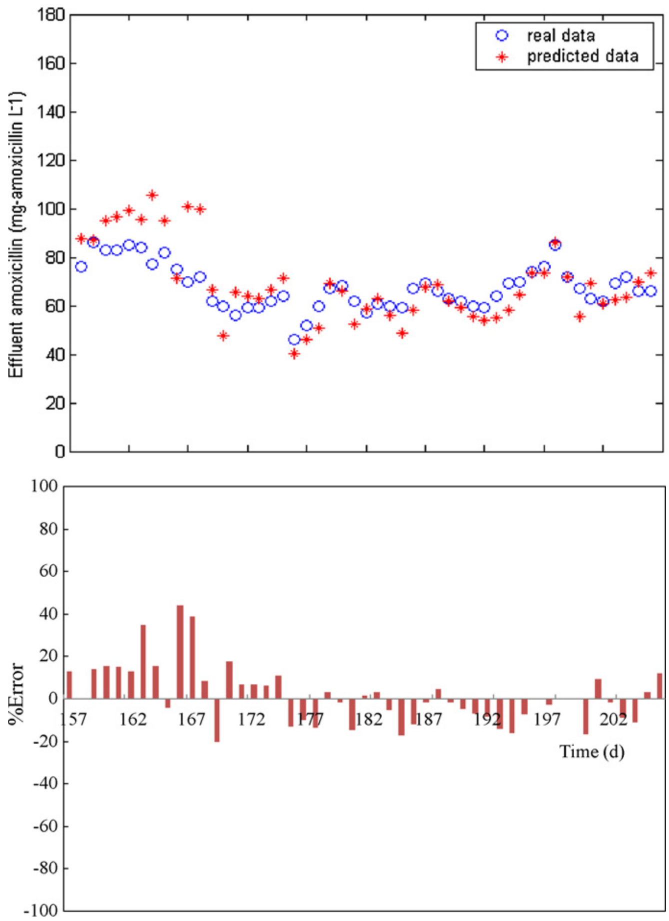

Fig. 9. Comparison of amoxicillin simulated results with real data and the error chat.

to test results, the developed model performance was at desirable level [34].

4. Conclusions

A UASB reactor system was demonstrated on a full-scale for the pre-treatment of pharmaceutical wastewater containing 6-APA and amoxicillin, which comprised a flocculation deposit pool, an adjustive pool, an UASB. The wastewater was high in COD, 6-APA, amoxicillin, varying daily from 4726 to 19,951 mg L^{-1}, from 143 to 315 mg L^{-1} and 61 to 171 mg L^{-1}, respectively, and with a wide range of pH from 5.57 to 8.26. Furthermore the system runs at a high COD loading rate from 12.57 to 21.02 kg m^{-3} d^{-1}. The effluent testing show that the UASB achieved 39–85% COD removal rate, 19–33% 6-APA removal rate and 13–47% amoxicillin removal rate. what is more, pH kept at a narrow range of 7.18–7.72 though influent value was sharply fluctuated, showing that the UASB system performed well in pre-treat pharmaceutical wastewater containing 6-APA and the amoxicillin under a high COD loading rate (12.57–21.02 kg m^{-3} d^{-1}), sharply fluctuation of pH (5.57–8.26), and high COD influent concentration (4726–19,951 mg L^{-1}).

Three models, built on the BPNN theory and linear regression techniques, were developed for the simulation of the UASB system performance in the biodegradation of pharmaceutical wastewater containing 6-APA and amoxicillin. The model system well fitted the detected data, and was able to simulate the removal of COD, 6-APA and amoxicillin. It proved that the simulation model built on the BPNN theory is a feasible and practical means to simulate and predict the organic substance removal by the UASB system.

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