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Investigation of a sewage-integrated technology combining an expanded granular sludge bed (EGSB) and an electrochemical reactor in a pilot-scale plant

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ABSTRACT

A sewage-integrated treatment system (SITS) for the treatment of municipal wastewater, consisting of an expanded granular sludge bed (EGSB) reactor to remove soluble organic matter and an electrochemical (EC) reactor to oxidize the NH_3–N, was evaluated. The performance of the EGSB reactor was monitored for 12 months in a pilot-scale plant. Iron shavings were added to the EGSB reactor on the sixtieth day to improve the removal efficiency of the chemical oxygen demand (COD), suspended solids (SS) and total phosphorus (TP). After the iron shavings were added, the effluent COD, SS and TP decreased from 104 to 46 mg L^{-1}, 21 to 8.6 mg L^{-1} and 3.62 to 1.36 mg L^{-1}, respectively. Moreover, in the EC reactor, which was equipped with IrO_2/Ti anodes, the NH_3–N and total nitrogen (TN) concentrations decreased from 25 to 12 mg L^{-1} and 29 to 15 mg L^{-1}, respectively. The NH_3–N was directly oxidized to N_2, resulting in no secondary pollution. The results demonstrated the possibility of removing carbon and nutrients in a SITS with high efficiency. The system runs efficiently and with a flexible operation, making it suitable for low-strength wastewater. The results and parameters presented here can provide references for the practical project.

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1. Introduction

The anaerobic method is a sustainable technology for municipal wastewater treatment because of its simple design, its use of non-sophisticated equipment, and the low operating and capital costs. In addition, anaerobic treatment is quieter than aerobic treatment and does not require aeration. Anaerobic treatment plants have a limited space requirement and can be planned at locations within or just outside a city. Anaerobic technologies have been successfully used to treat a number of wastewater types, including low-strength wastewater [1,2], which is representative of most municipal wastewater. Sunny et al. [1] reported that over 70% chemical oxygen demand (COD) was removed, and the effluent COD was approximately 50 mg L^{-1} using anaerobic technology. It was also reported that a COD removal efficiency exceeding 80% was obtained in an EGSB reactor operated at 20 C°, with an influent COD between 630 and 715 mg L^{-1} [2]. Mario et al. [3] mentioned that the potential of the anaerobic technology could be further explored in the treatment of dilute wastewaters.

Municipal wastewater has a low organic content, with a COD in the range of 250–1000 mg L^{-1}. In southern China, such as in Shanghai, the COD concentration is lower than 250 mg L^{-1} [4]. The expanded granular sludge bed (EGSB) system, suggested as an improvement to the conventional up-flow anaerobic sludge bed (UASB) system, offers a potential solution for low concentration municipal wastewater [3]. The EGSB is expanded and the hydraulic mixing is intensified to improve the wastewater–biomass contact. For the treatment of low strength wastewaters at ambient temperature, the EGSB reactor has proven to be an attractive technique. In this reactor, a high up-flow velocity (V_{up} > 4 m h^{-1}) [2] is achieved by recirculating the effluent or by using a tall reactor. The excellent performance of the EGSB reactor in treating low-strength wastewaters can be attributed to the reactor's large mixing intensity and the efficient wastewater–biomass contact induced by the high up-flow velocity [5–7], which enables greater mixing when the loading rates are low. However, the EGSB reactor would cause the washout of fine biomass after prolonged treatment at low loading rates [8]. Therefore, EGSB and EGSB-based reactors have been widely applied in anaerobic treatment. Unfortunately, the EGSB reactor removed only 60–80% of the COD, making the compliance of effluents with environmental discharge standards difficult. The main reason for this low COD removal was that certain sulfates, which cause a sulfur redox reaction to occur [9], affect the removal of COD from wastewater. Under anaerobic conditions, sulfate-reducing bacteria (SRB), which are similar to methanogens, deoxidize sulfate into sulfide. During the COD measurement, sulfide as the organic pollutants would be oxidized, which could increase the value of the COD. In addition, the hydrogen sulfide has a strong

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odor and is poisonous. It has been reported that these effects can be controlled by ferric iron dosing [10–13], which minimize the adverse effects by forming FeS. In this study, iron shavings, which are by-products from the iron and steel industries, were added into the EGSB reactor to inhibit the effect of SRB on the COD removal. The iron shavings contain iron (>95%), carbon (0.35–0.42%), silica (0.20–0.45%), chromium (1.35–1.65%) and a few other trace elements (e.g., Mo, S, P, Ni, each <0.03%) [14]. The iron shavings were selected because of the abundant local supply and relative low cost (approximately \$0.25 kg^{-1}). The iron shavings have an internal electrolysis between zero-valence iron and carbon. In this process, the SRB are inhibited by iron [12], and the sulfide is precipitated by forming iron sulfide. In addition, the PO_4^{3-} and suspended solids (SS) are precipitated by $Fe(OH)_2$. The reactions are as follows:

$$\text{Anode}: \quad Fe \Rightarrow Fe^{2+} + 2e^-$$

$$\text{Cathode}: \quad 2H^+ + 2e^- \Rightarrow 2[H] \Rightarrow H_2$$
$$Fe^{2+} + S^{2-} \Rightarrow FeS \downarrow$$

The EGSB reactor is effective in removing soluble pollutants, but inorganic compounds, such as NH_3–N and PO_4^{3-}, are only removed from the wastewater stream to a limited extent [1]. In particular, the concentration of NH_3–N is greater than the effluent criteria for surface discharge (<25 mg L^{-1}) [15]. As an essential nutrient, ammonia nitrogen enhances the growth of algae in the surface water, causing eutrophication and other environmental concerns. Therefore, additional treatment is required when nutrient removal is necessary. Combined with proper post-treatment, anaerobic treatment provides a sustainable and appropriate method to provide a good quality effluent from municipal wastewater, not only for developing countries, but also for advanced countries. Therefore, integration of the EGSB reactor and nutrient removal will be a powerful alternative for municipal wastewater treatment.

The conventional methods for eliminating ammonia from wastewater, such as biological treatment, air stripping and ion exchange [16,17], have several constraints, including their inability to reduce ammonia to much lower levels, pollutant transfer into other media, higher cost, and sensitivity to temperature. The results of a previous study showed that NH_3–N and total nitrogen (TN) were removed effectively from wastewater by electrochemical process and the NH_3–N could be oxidized into N_2 directly [18–21]. The EC method offers a number of advantages, including simple design, flexible operation, higher efficiency and a wide, suitable temperature range. Moreover, the EC method is well-known for its ability to efficiently remove NH_3–N from wastewater. Similarly the use of the EC method has been reported to have potential use to reduce the ammonia concentration in wastewater or landfill leachate because of its operational simplicity [18–20,22–24]. Therefore, integration of nutrient removal in an anaerobic process could be a powerful alternative to anaerobic treatment for municipal wastewater treatment. In this study, the proposed strategy consists of an EGSB reactor to remove soluble organic pollutants, suspended solids (SS) and PO_4^{3-}, followed by an EC reactor to eliminate the NH_3–N. The overall treatment is referred to as a sewage-integrated treatment system (SITS).

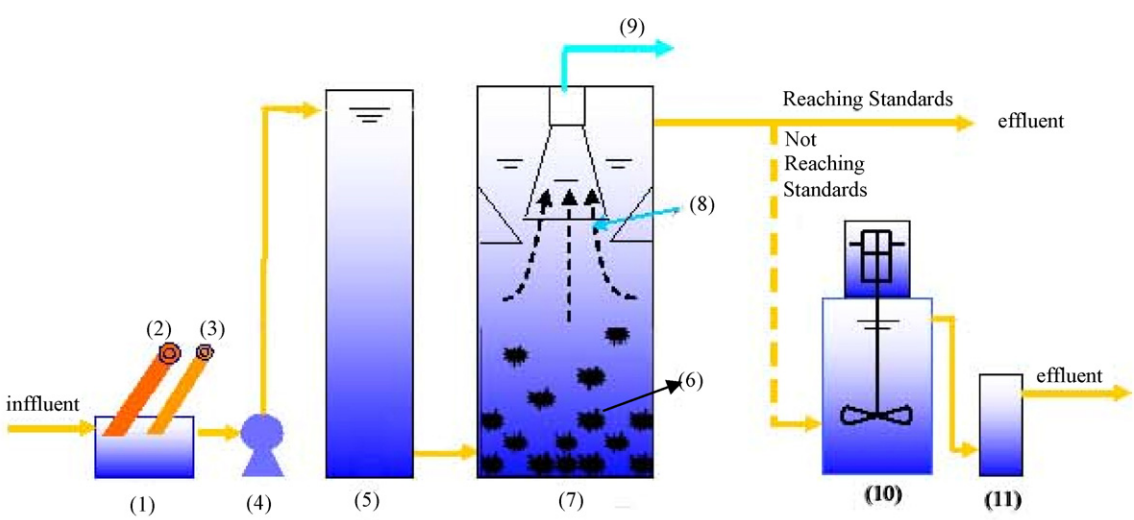
Until recently, the EC method has been only used as an advanced treatment to remove the pollutants that the conventional technologies cannot efficiently remove because the cost of an electro-oxidation pre-treatment, which is used to treat wastewater, is much higher than that of conventional method. Therefore, the use of electro-oxidation as a post-treatment process can lower the cost and improve the quality of the effluent. In this study, the EC method is used as a post-treatment process to remove the NH_3–N, which could not be removed in the EGSB reactor.

There is little information in the literature about the EGSB-EC treatment of municipal wastewater, particularly eliminating carbon and nitrogen simultaneously using SITS in a pilot-scale process. The objective of this study was to perform a technical evaluation and design a flexible concept of the use of the EGSB-EC system in a pilot-scale test, which would make it possible to efficiently dispose municipal wastewater, especially for developing countries with warm climates. At the same time, specific parameters, including pH, HRT (hydraulic retention time) and COD removal efficiency in the EGSB reactor, and HRT, current density, and the type of electrode in the EC reactor, provide references for the practical project.

2. Materials and methods

2.1. Setup of pilot plant

The setup of the pilot plant was designed based on the characteristics of the wastewater and the experimental results obtained in the laboratory [4,18]. Fig. 1 shows the overall schematic diagram of



(1) water-collecting well, (2)coarse screen, (3) fine rack, (4) water pump, (5) regulating reservoir, (6) iron shavings, (7) EGSB reactor, (8) biogas, (9) outlet of biogas, (10) regulating tank of electrochemical system, (11) electrochemical reactor

Fig. 1. Schematic diagram of the sewage integrated treatment system (SITS).

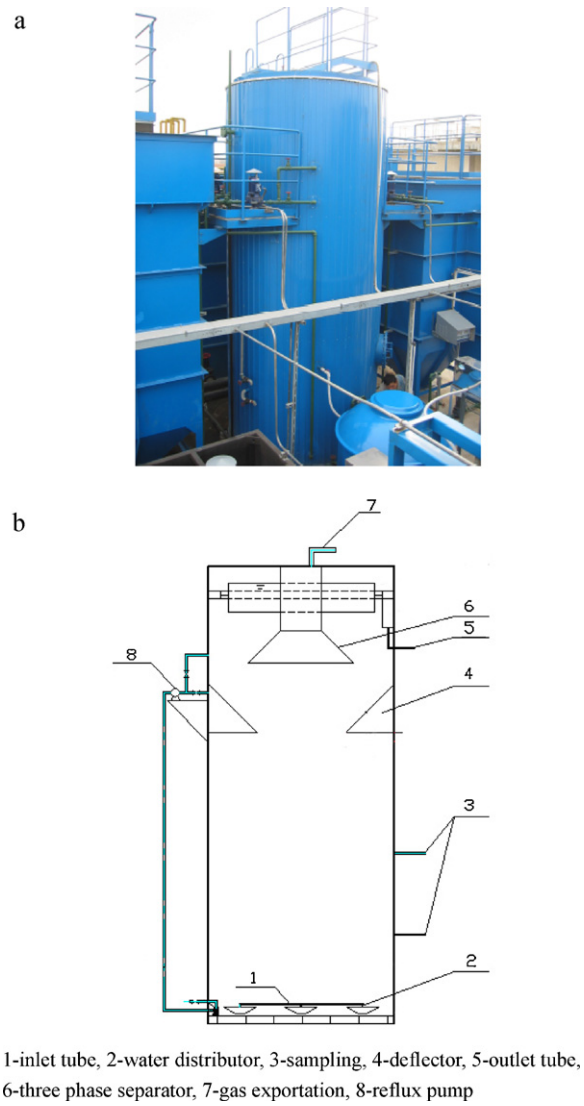


Fig. 2. Diagram of EGSB reactor in pilot plant: (a) the schematic of EGSB reactor (b) cutaway drawing of EGSB.

the SITS. The combined municipal wastewater in the grit chamber flowed into the water-collecting well (1) and through the coarse screen (2) and fine rack (3) to remove the particles and was then pumped into the regulating reservoir (5) to adjust the quality and quantity of wastewater. Next, the wastewater was pumped into the EGSB reactor (7) containing iron shavings (6). In the reactor, the biodegradable organic matters were decomposed, and the biogas was released through exportation (9). The EGSB reactor effluent was monitored every 2 days. If the ammonia concentration was over the second level of discharge criteria (<25 mg L^{-1}) [15], the effluent was pumped into the EC system (10) and (11) to remove the ammonia. If the ammonia concentration was below the second level of discharge criteria, the effluent was directly discharged into the municipal drain network. The EC system was operated intermittently with changes in the ammonia concentration.

2.1.1. EGSB reactor unit

The wastewater was pumped continuously from the regulating reservoir into the EGSB reactor, which had a height of 5.6 m, an internal diameter of 2.3 m, an effective volume of 12.5 m^3, and an overall volume of 23 m^3. The structure was made of carbon steel and the outside layer was a heat preservation layer made of mineral wool. Fig. 2 shows the diagram of the EGSB reactor in the pilot plant. Fig. 2(a) contains the schematic of the EGSB reactor. The reactor was completely closed to prevent air introduction and to guarantee anaerobic conditions for the process. Fig. 2(b) is a cutaway drawing of the EGSB reactor. The wastewater was pumped through the inlet tube (1) and was arranged by the water distributor (2). In the top of the reactor, the water, biogas and sludge were separated by a deflector (4) and three-phase separator (6). The sludge was kept in the reactor by the deflector (4). The biogas was released through the three-phase separator (6) by gas exportation (7) on top of the EGSB reactor. Biogas was bubbled into a 10% lime solution to remove CO_2 and H_2S. The effluent water flowed to the next process through an outlet tube (5). Samples were collected from points (3) located 1 m and 2 m from the bottom. The reflux was pumped by the reflux pump (8) to the bottom of the reactor to maintain a higher up-flow velocity.

The iron shavings were added in the EGSB reactor on the sixtieth day. The iron shavings have a fairly large surface area (approximately 0.2–0.3 m^2 kg^{-1}) and excellent mechanical and hydraulic characteristics. The amount of iron shavings was calculated according to the concentration of SO_4^{2-} and S^{2-} in the influent and effluent and the running time. Approximately 142 kg of iron shavings was added on the sixtieth day during the operational period.

2.1.2. Electrochemical system

Pilot-scale experiments were conducted in the cylindrical EC system shown in Fig. 3(a) and (b), which was designed based on the experimental results achieved in the laboratory and consisted of an EC reactor (1) and a regulation pool (2). The quadrate regulation pool (2) was designed with a size of 1.60 m × 1.60 m × 1.20 m, as shown in Fig. 3(a). It was made of stainless steel, and the surface was protected from corrosion by oil paint. Fig. 3(b) shows the schematic of the EC reactor in the pilot plant. The diameter was 0.25 m, and the height was 0.90 m. The total volume was 16 L. A direct current power source supplied a voltage of 3.0–6.5 V at a constant current (10–38 A). The current density was 55.3 A m^{-2}. The electrolysis cell was equipped with four IrO_2/Ti anodes and five stainless steel cathodes, with a size of 790 mm × 100 mm × 1 mm and a surface area of 7.9 × 10^4 mm^2; the distance between the anode and the cathode was 6 mm. The HRT in the electrolysis cell ranged from 5 min to 30 min, depending on the ammonia concentration.

2.2. Municipal wastewater

The pilot-scale setup was situated in a municipal treatment plant with a capacity of 1,700,000 m^3 d^{-1} in Shanghai, China. This wastewater treatment plant treated its sewage using enhanced flocculation. The influent wastewater used for the pilot-scale plant was the effluent from a grit chamber of the wastewater treatment plant. Table 1 contains the characteristics of the municipal wastew-

Table 1
Characteristics of municipal wastewater in pilot-scale plant.

Parameter	Unit	Range of change	Average value
COD	mg L^{-1}	186–317	231
BOD_5	mg L^{-1}	67.3–120.6	88
SS	mg L^{-1}	60.0–140.0	86.2
NH_3–N	mg L^{-1}	16.4–32.6	25.0
TN	mg L^{-1}	22–41	29
PO_4–P	mg L^{-1}	1.3–2.7	2.2
TP	mg L^{-1}	2.0–4.9	3.6
Alkalinity	mg$CaCO_3$ L^{-1}	213.3–286.1	236.1
VFA	mgCH_3COOH L^{-1}	6.5–39.7	23.5
Turbidity	NTU	85–298	165
Colority	times	16–50	30
pH	/	7.3–8.3	7.6
SO_4^{2-}	mg L^{-1}	86.8–289.7	152.5
S^{2-}	mg L^{-1}	2.8–12.3	8.9

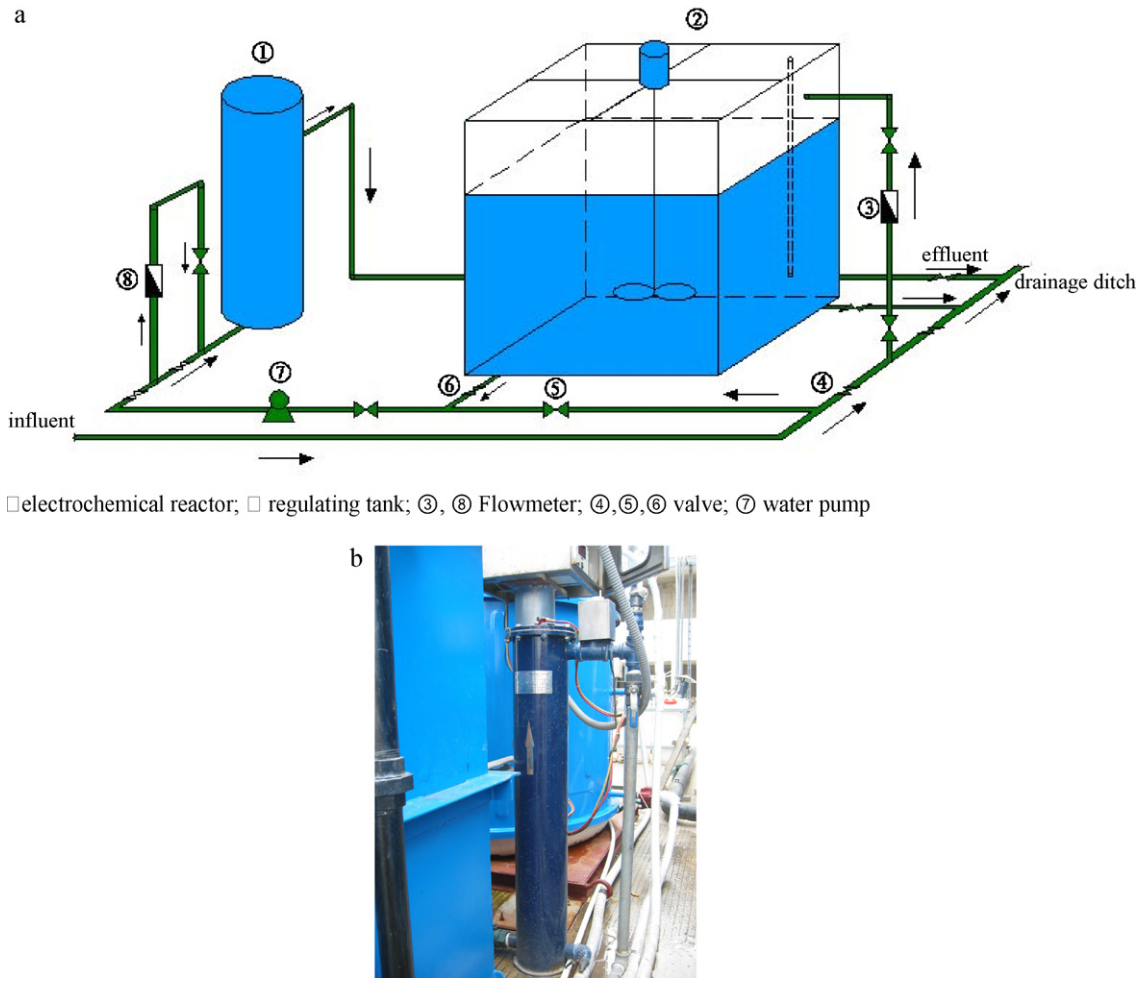


Fig. 3. Schematic diagram of electrochemical system: (a) schematic diagram of electrochemical system and (b) outline of electrochemical reactor in pilot plant.

ater, which includes domestic and industrial wastewater. Table 1 shows that the COD concentration was lower, ranging from 186 to 317 mg L^{-1} with an average of 231 mg L^{-1}. The corresponding value of NH_3–N ranged from 16.4 to 32.6 mg L^{-1}, with an average of 25 mg L^{-1}.

2.3. Analysis

The influent and effluent concentrations of ammonia, TN, TP, COD, SS, alkalinity and S^{2-} were measured according to the Standard Methods for the Examination of Water and Wastewater [25]. SO_4^{2-} was measured by a gravimetric method [25]. The initial pH was determined with a pH meter (PHS-2C, Tianda Company, Shanghai, China).

2.4. Acclimatization stage

The seed anaerobic sludge in this EGSB reactor came from a traditional anaerobic digester in the Songjiang sewage treatment plant (Shanghai, China). The initial sludge concentration was 65.4 g L^{-1} MLSS and 33.4 g L^{-1} VSS with a SVI of 43. When the reactor was completely filled, approximately 1 m^3 d^{-1} of raw wastewater was added until the effluent pH, COD and alkalinity were in equilibrium and within the optimal range of operation with the aim of acclimatizing the biomass to the substrate. Steady-state conditions of the anaerobic reactor were obtained two and one-half months after the start-up.

The HRT of the bioreactor was gradually reduced from 8 h to 6 h, 5 h, 4.5 h, and 4 h. During the experiment, the organic loading rate (OLR) ranged from 0.19 to 1.01 kg (m^3 d)$^{-1}$.

3. Results and discussion

The course of the pilot-scale operation was nearly 1 year. The start-up time was over two and one-half months. More than 5 months was spent to investigate the operation of the EGSB reactor. Finally, the EGSB and EC reactors ran under the optimal conditions for approximately 4 months. In this paper, the performance of the EGSB and EC reactors is studied in detail.

3.1. EGSB reactor performance

3.1.1. Sludge characteristics

Table 2 presents the change in MLSS and VSS concentration, SVI, and VSS/SS in the reactor at heights of 1 m and 2 m from the bottom during the operational period. The sludge concentration at a height of 1 m started high and then decreased slowly with time, and the sludge concentration at a height of 2 m started lower and increased with time. Throughout the study, the excess sludge was not discharged, except for sampling. The sludge was satisfactorily retained in the reactor, and sludge washout did not occur, even in the high liquid up-flow velocities. The ratio of volatile suspended solids to total suspended solids (VSS/SS) was approximately 0.52 ± 0.6, although the MLSS and MLVSS changed with time, which demon-

Table 2
Characteristics of granular sludge during operational period.

Character		MLSS ($g\,L^{-1}$)	MLVSS ($g\,L^{-1}$)	VSS/SS	SVI ($mL\,g^{-1}$)
Time for sample	Height from bottom				
Initial	1 m	68.0	35.2	0.52	45
	2 m	19.2	10.2	0.53	45
15th day	1 m	74.4	40.7	0.55	46
	2 m	7.2	3.5	0.49	45
42 day	1 m	22.4	11.5	0.51	30
	2 m	21.8	11.4	0.52	28
72 day	1 m	32.2	17.0	0.53	26
	2 m	22.5	11.3	0.50	26
100 day	1 m	40.3	23.3	0.58	24
	2 m	22.3	11.9	0.53	29
135 day	1 m	31.3	14.5	0.46	31
	2 m	22.3	10.9	0.48	27

strated that the activity and stability of the sludge had improved. The biomass did not grow rapidly; rather, the amount of biomass decreased because of the low strength of wastewater. There was no large granular sludge during the running period. However, the small biomass did not have an obvious effect on the COD removal efficiency. Sunny et al. [1] also found that the granular sludge disappeared slowly during the operation of a UASB reactor but had no impact on the COD removal efficiency. The results were similar to those observed in this study.

The SVI, as an index of the sludge settling ability, ranged from 24 to 45 $mL\,g^{-1}$ TSS at heights of 1 m and 2 m from the bottom, which indicated excellent settling ability. Although the SVI decreased with time, the sludge had a better settling ability. The SVI also demonstrated that the small amount of biomass had no obvious effect on the characteristics of the sludge.

3.1.2. COD removal in the EGSB reactor

In the pilot-scale plant, the concentration of sulfate was high, with an average value of 152.5 $mg\,L^{-1}$. The sulfate was reduced into sulfide by sulfate-reducing bacteria (SRB) under anaerobic conditions, which would affect the removal of COD and also produce an H_2S odor. In this study, the scrap shavings were added to the EGSB reactor, to inhibit the SRB [12], causing the sulfide to be precipitated by forming iron sulfide. In addition, the PO_4^{3-} and SS would be precipitated by $Fe(OH)_2$.

During the operation, the iron shavings were added in the sixtieth day, as shown in Fig. 4. Fig. 4 also shows the COD concentration in the influent and effluent of the EGSB reactor. The influent COD concentration varied from 186 to 317 $mg\,L^{-1}$, and the COD in the effluent changed significantly after the iron shavings were added. Before iron shavings were added, the COD concentration in the effluent ranged from 76 to 123 $mg\,L^{-1}$, with an average of 104 $mg\,L^{-1}$. The average removal efficiency was approximately 59%. However, the COD concentration in the effluent was higher than the second level of discharge criteria [15]. After the iron shavings were added, the average COD concentration in the effluent decreased from 104 to 46 $mg\,L^{-1}$, and the removal efficiency increased to 81.5%. Fig. 4 demonstrates that the COD concentration in the effluent was more stable and maintaining a value of 46 $mg\,L^{-1}$, which was little affected by fluctuations of the influent. These results demonstrated that the iron shavings had important effects in decreasing the COD concentration. Similar results were found by Peng et al. [12].

The COD was measured by the standard $K_2Cr_2O_7$ method [25]. During this process, the sulfide is be oxidized by $K_2Cr_2O_7$ which increases the COD value and does not reflect the real concentration. In this study, before the iron shavings were added, the COD value increase caused by sulfide was nearly 60 $mg\,L^{-1}$, which was larger than the 55.7% average COD in the effluent. The iron shavings, which contain carbon, zero-valence iron and other matters, have an internal electrolysis between that of zero-valence iron and carbon. In this process, the iron was eroded to form Fe^{2+}. In addition, hydrolytic acidification, the first step during the process of anaerobic degradation of organic matters, would increase the acidity. The acidic conditions would accelerate the corrosion of iron, and the sulfide would be precipitated by the formation of iron sulfide (FeS) [26]. The results shown in Fig. 5 suggest that the concentration of sulfide decreased with the addition of iron shavings. All of the results demonstrated that the reduction of sulfate by SRB results in the formation of hydrogen sulfide, which subsequently reacts with ferrous iron to form a precipitate of ferrous sulfides under anaerobic conditions [26]. Navnit reported similar findings in a study on the use of iron salts to control dissolved sulfide in trunk sewers [11].

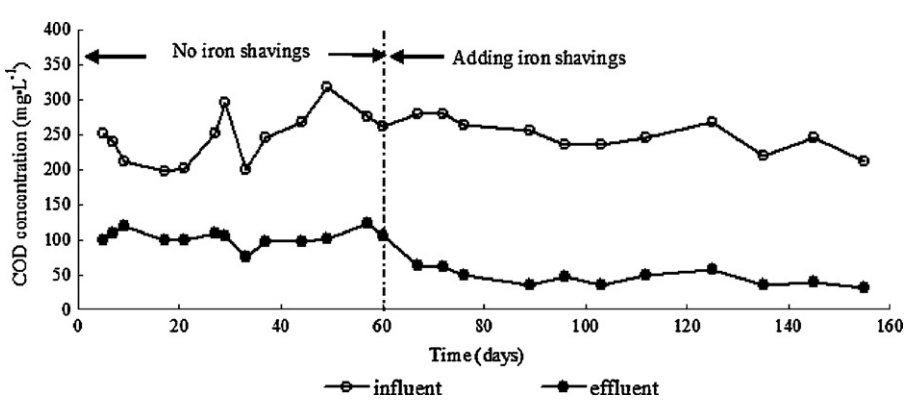


Fig. 4. COD variation of influent and effluent in the EGSB reactor during operational period.

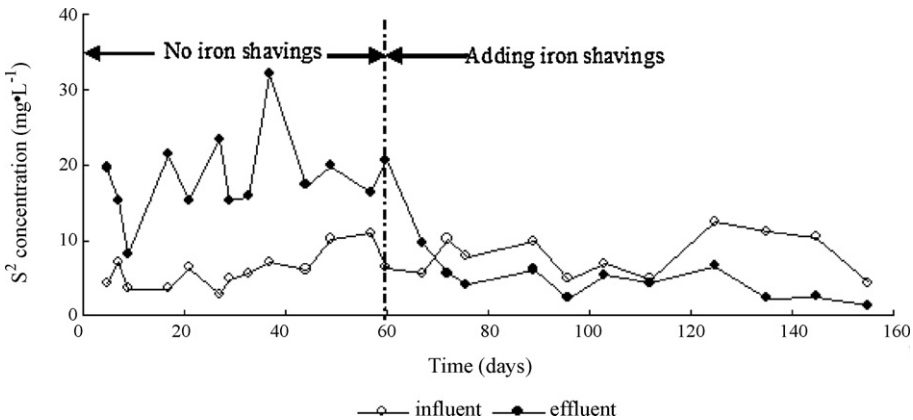


Fig. 5. Sulfide variations of influent and effluent in the EGSB reactor during operational period.

Fig. 5 presents the sulfide variations of the influent and effluent in the EGSB reactor. It demonstrates that the concentration of sulfide was higher before the addition of iron shavings, although the concentration of the influent was lower. The concentration of the effluent ranged from 8 to 32 mg L^{-1} with an average value was 18 mg L^{-1}, while the value of the influent was only 5 mg L^{-1}. The reason for this difference is that the sulfate in the wastewater was reduced to sulfide by SRB under the anaerobic conditions, resulting in a higher effluent sulfide concentration than influent concentration [10]. After the iron shavings were added, the average concentration of sulfide in the effluent decreased to 3.6 mg L^{-1} because the sulfide was precipitated by forming iron sulfide. These results demonstrated that the iron shavings decreased the COD value by controlling the sulfide concentration in the effluent.

The SS concentration in the effluent and influent are presented in Fig. 6. It shows that the SS were removed efficiently in the EGSB reactor. Before the iron shavings were added, the average SS in the influent was 87 mg L^{-1} (62–132 mg L^{-1}) and that in the effluent was 21 mg L^{-1} (16–33 mg L^{-1}), a removal efficiency of 75.8%. After the iron shavings were added, the average SS in the effluent was only 8.6 mg L^{-1}, which satisfied the first level A of discharge criteria (<10 mg L^{-1}) [15], although that of the influent fluctuated between 31 and 115 mg L^{-1}; the removal efficiency was 89%. This indicated that the $Fe(OH)_2$, formed by Fe^{2+} and H_2O, could absorb and precipitate the SS [27].

If the settlement of sludge is poor, the loss of biomass is generally inevitable with the high up-flow velocity in the EGSB reactor. The loss of biomass would strongly affect the COD removal efficiency. However, the SVI ranged from 24 to 45 mL g^{-1} in the EGSB reactor, as shown in Table 2, and the settling ability was better. Although the up-flow velocity ranged from 3.8 to 5.2 m h^{-1} with a reflux ratio ranging from 1:1 to 6:1, sludge washout was not observed during the operational period because of the sophisticated gas–solid–liquid separation used in the EGSB reactor.

As expected, little or no biogas production was observed during the pilot test because the biogas produced during the anaerobic treatment of municipal wastewater at low COD concentrations in the influent was dissolved in the effluent, which implies that anaerobic treatment of low concentration wastewater could not be used as an energy recovery process.

3.1.3. *The changes in pH and alkalinity in EGSB reactor*

The pH is a key factor in the anaerobic reactor. During the process, most bacteria, such as hydrolytic bacteria and acid-forming bacteria, can grow well in a pH range of 5.0–8.5. However, methanogens are more sensitive to changes of pH and have stronger activity in a pH range of 6.5–7.8, which is the pH range of an anaerobic reactor [28].

The pH is controlled by a buffer system in the anaerobic reactor. In the anaerobic process, VFA can heavily affect the pH if the buffer system cannot control it well enough. Therefore, adjusting the alkalinity is an effective method to maintain the pH. The alkalinity and pH variations in the EGSB reactor effluent and influent are presented in Fig. 7. As shown in Fig. 7(a), at any point, the pH in the system was in a favorable range (7.0–7.8) for SRB. The average value was 7.4. The results showed that the pH in the EGSB reactor was suitable for methanogens, demonstrating that the operation in the EGSB reactor was better and the VFA did not accumulate. The average concentration of VFA was 15.6 mg L^{-1}, which is also consistent with these results.

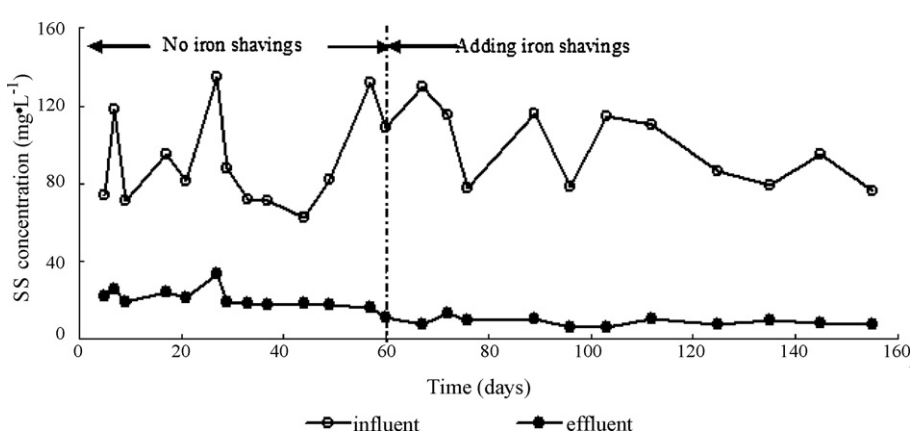


Fig. 6. SS variations of influent and effluent in the EGSB reactor during operational period.

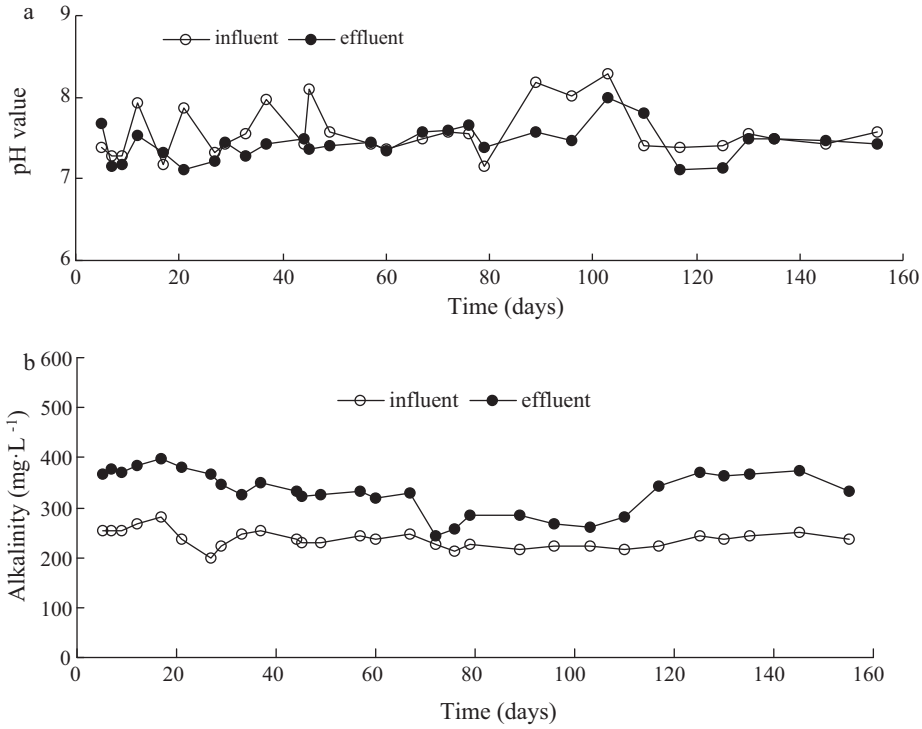


Fig. 7. Variations of pH (a) and alkalinity (b) of influent and effluent in EGSB reactor with time.

As shown in Fig. 7(b), the average alkalinity of the influent was 236 mg L^{-1}, but that of the effluent was 333 mg L^{-1}. There are two primary reasons for this increase. First, the bicarbonates were produced in the methanogenesis reaction, as shown in Eq. (1). Second, the reduction of sulfate and the degradation of nitrogen compounds also produced bicarbonates and increased the alkalinity, as shown in Eqs. (2) and (3):

$$CH_3COO^- + H_2O \rightarrow HCO_3^- + CH_4 \quad (1)$$

$$CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^- \quad (2)$$

$$RCHNH_2COOH + 3H_2O \rightarrow RCOOH + 2H_2 + NH_4^+ + HCO_3^- \quad (3)$$

During the field operation, alkaline compounds, such as $NaCO_3$, $NaHCO_3$, NaOH, and $Ca(OH)_2$, can be added to the anaerobic reactor to control the pH, but this increases the operational cost. However, in the EGSB reactor, the influent can be diluted by the refluxing of the effluent, which can control the pH, eliminating the need for alkaline materials to be added to the reactor. This pH control is one of the advantages of the EGSB reactor.

In the influent, the ratio of the alkalinity to the COD was 1.02, which is close to the value recommended by some experts [29,30]. The ratios of N to COD and P to COD were 0.126 and 0.0156, respectively, which are higher than those of a previous study (0.018 and 0.0028, respectively) [29]. The reason for this increase is the low concentration of COD in this study. The optimal ratios maintained the satisfactory performance of the EGSB reactor.

3.1.4. The removal of N and P in the EGSB reactor

Fig. 8 shows the changes of ammonia and phosphorus concentrations in the reactor. Fig. 8(a) shows the concentration of ammonia in the effluent and influent. The ammonia concentration of the influent ranged from 16.4 to 32.6 mg L^{-1} during the operational period. The concentration of ammonia in the effluent was higher than that of the influent because some organic nitrogen (from amino acids, proteins, and other materials) was transformed into ammonia under the anaerobic conditions. The average NH_3–N concentrations of the influent and effluent were 24.8 and 26.3 mg L^{-1}, respectively, which are greater than the second level of discharge criteria (<25 mg L^{-1}) [15].

Fig. 8(b) shows the concentration of TP in the effluent and influent. The TP concentration of the influent was approximately 3.6 mg L^{-1} during the operational period, while the concentration of the effluent changed greatly after the addition of iron shavings. Before the iron shavings were added, the TP concentration of the effluent ranged from 2.48 to 4.7 mg L^{-1}, with an average value of 3.62 mg L^{-1}. However, after the iron shavings were added, the average TP concentration decreased to 1.36 mg L^{-1}, a 62.4% removal efficiency. Fe^{2+}, formed in the internal electrolysis of the iron shavings, precipitated phosphate as insoluble ferric hydroxyl-phosphate complexes [31,32]. There are varying stoichiometric ratios between phosphorus and iron. de Haas et al. proposed a formula for ferric hydroxyl-phosphate complexes under P-limiting conditions, ranging from $Fe_3(X^{2+})PO_4(OH)_8$ to $Fe_{2.33}(X^{2+})_{2.5}PO_4(OH)_9$, where X^{2+} is a divalent cation (e.g., Mg^{2+} or Ca^{2+}) [33].

3.2. Electrochemical treatment

The EGSB reactor did not remove the NH_3–N from the wastewater, as shown in Fig. 8(a). Therefore, it was necessary to remove NH_3–N in a post-treatment process. EC oxidation can be effectively employed to eliminate NH_3–N from wastewater [18–20,22–24]. Liu reported that NH_3–N was directly oxidized to N_2 by the anode or indirectly oxidized by OH produced in the anode and cathode [18]. Li found that approximately 88% of the degraded ammonia could be detected as N_2 in the produced gas [19].

First, the effectiveness of EC oxidation to remove NH_3–N after the EGSB reactor was evaluated using a pilot-scale test, using the optimal electrode and retention times determined in former articles [18–20,34]. The electrolysis cell was equipped with four IrO_2/Ti anodes and five stainless steel cathodes. The HRT in the electrolysis

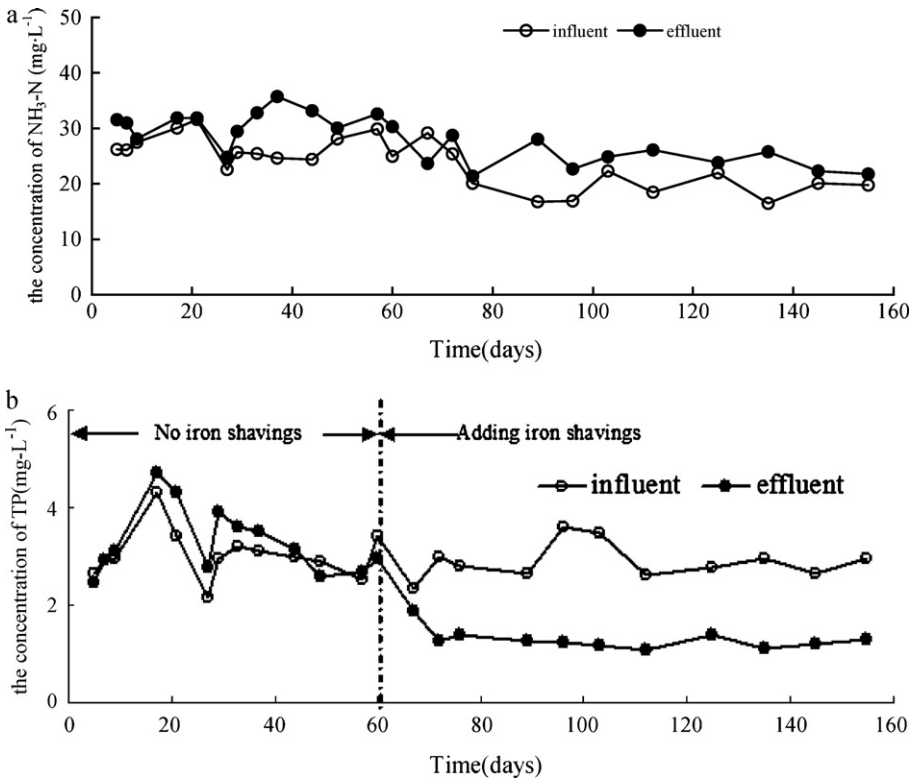


Fig. 8. Variations of NH_3–N (a) and TP (b) of influent and effluent with time.

cell ranged from 5 min to 30 min depending on the concentration of ammonia.

The average concentrations of NH_3–N, NO_3^-–N, NO_2^-–N and TN in the effluent of the EGSB reactor and after EC oxidation, together with the COD, Cl^-, SO_4^{2-} and PO_4^{3-} concentrations, are presented in Table 3. It shows that the effluent of the EGSB reactor, which was the electrolyte, contained a higher concentration of NH_3–N (25 mg L^{-1}) and also a higher concentration of Cl^- (390 mg L^{-1}) and SO_4^{2-} (16.7 mg L^{-1}).

Table 3 shows that the concentration of NH_3–N was reduced to 12 mg L^{-1} by the EC treatment. In addition, the concentration of TN was 15 mg L^{-1}, which complies with the first level B of discharge criteria (<15 mg L^{-1}) [15]. The removal efficiencies of NH_3–N and TN were 52% and 48.2%, respectively. Table 3 also demonstrates that the NO_3^-–N and NO_2^-–N concentrations in the effluent decreased slightly after the EC treatment. The results indicated that the reduced NH_3–N was completely removed as N_2 from the water and did not transform into any other compounds, which is consistent with the results of Li and Liu [19,20]. Furthermore, the COD was removed by the EC treatment, and the average concentration decreased from 46 to 31 mg L^{-1}, as shown in Table 3. Nearly 32.6% of the COD was removed in the experiments, indicating that electrolytic degradation of the organics present in effluents also occurred during the electrolytic experiments.

During the operational period, the concentration of NH_3–N in the effluent ranged from 16.4 to 32.6 mg L^{-1}, and 30% of the concentrations were greater than the second level of discharge criteria (<25 mg L^{-1}) [15]. Therefore, there were two options to treat the effluent from the EGSB reactor, as shown in Fig. 1. If the concentration of NH_3–N in the effluent exceeded the second level of discharge criteria [15], the effluent was collected into the regulating tank, and the NH_3–N was removed by the EC reactor. If the concentration did not exceed the discharge criteria, the effluent was discharged directly into a drainage ditch. Remarkably, the EC reactor could be operated intermittently, depending on the ammonia concentration. Moreover, the results of a batch test illustrated that the ammonia concentration decreased rapidly and linearly with time [19]. Therefore, the HRT in electrochemical reactor ranged from 5 min to 30 min.

The energy consumption necessary to electro-oxidize the NH_3–N to 12 mg L^{-1} at the pilot-scale ranged from 15.34 to 92.43 kWh g^{-1}-NH_3–N. This is a high cost, especially with the HRT of 30 min. However, only about 30% of the influent, which an average NH_3–N concentration of 28 mg L^{-1}, had to be treated in the EC reactor to meet the second level of discharge criteria (<25 mg L^{-1}). Therefore, the average consumption was approximately 3.54 kWh g^{-1}-NH_3–N.

In addition, the evaluation of a batch EC reactor in the lab showed that the NH_3–N removal efficiency was much higher (average of 90%) and could reduce the ammonia nitrogen almost to zero. These large differences may be caused by the following factors. First, there were many other pollutants in the real wastewater of the pilot-scale plant, which could affect the removal of NH_3–N. Second, the treated wastewater with such a low ammonia concentration (<0.5 mg N L^{-1}) meets strict requirements for ammonia in critical receiving water bodies, such as Dianchi Lake in Yunnan Province, China, but in general, there was no need to reduce the NH_3–N to a very low concentration.

The results of the long-term pilot plant operation testified that NH_3–N could be removed efficiently with short a HRT and could remedy the defect of the EGSB reactor for higher NH_3–N concentrations. EC oxidation is an effective method for the additional removal of ammonia nitrogen from the effluent of anaerobic reactors treating municipal wastewater. Moreover, compared with the conventional methods for ammonia removal from municipal wastewater, the EC reactor has a simple design, a fast ammonia removal rate, reliable treatment efficiency, creates no bio-solids, uses non-sophisticated equipment, and has flexible operation. This

Table 3
Average concentration of NH_3–N, TN, NO_3^-–N, NO_2^-–N and COD in influent and effluent of electrochemical treatment.

	pH	TN (mg L^{-1})	NH_3–N (mg L^{-1})	NO_3^-–N (mg L^{-1})	NO_2^-–N (mg L^{-1})	Cl^- (mg L^{-1})	SO_4^{2-} (mg L^{-1})	PO_4^{3-} (mg P L^{-1})	COD (mg L^{-1})
Influent	7.92	29	25	1.69	0.436	390	16.7	1.02	46
Enfluent	7.13	15	12	1.80	0.092	–	–	–	31

flexible operation makes it suitable for continuous flow or intermittent flow, depending on the concentration of NH_3–N in the effluent from the EGSB reactor.

It has been reported that disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetonitriles (HANs) would be produced during EC treatment [35]. DBPs were not investigated in this study but will be studied in future experiments.

4. Conclusions

In this study, a SITS for the treatment of municipal wastewater, consisting of an EGSB reactor to remove soluble organic matters, followed by an EC reactor to oxidize the NH_3–N, was proposed. Based on the results of long-term pilot-scale plant, the following conclusions were drawn.

(1) The performance of the EGSB reactor, in which iron shavings were added to improve the removal efficiency of COD, SS and TP, was monitored. Before the iron shavings were added, the effluent COD, SS and TP were approximately 104, 21 and 3.62 mg L^{-1}, respectively. After the iron shavings were added, the corresponding values in the effluent were approximately 46, 8.6 and 1.36 mg L^{-1}. These changes correspond to increases in the removal efficiencies of COD, SS and TP of 59–81.5%, 75.8–89% and 0–62.4%, respectively. In the EGSB reactor, the average pH value was 7.4, which is more stable and suitable for methanogens. NH_3–N was not removed by the EGSB reactor, and the average concentration in the effluent was 26.3 mg L^{-1}.
(2) An EC reactor with IrO_2/Ti anodes was employed as a post-treatment process following the EGSB to remove NH_3–N and TN. With a current density of 55.3 A m^{-2}, the NH_3–N and TN concentrations decreased from 25 to 12 mg L^{-1} and from 29 to 15 mg L^{-1}, respectively, with a HRT ranging from 5 to 30 min. Moreover, NH_3–N was directly oxidized to N_2 and did not transform into any other compounds in water. To reach the second level of discharge criteria (<25 mg L^{-1}), the average consumption was approximately 3.54 kWh g^{-1} NH_3–N.

These results verified the possibility of removing carbon and nutrients with high efficiency in a SITS. Furthermore, the system operated efficiently and flexibly, making it suitable for low-strength wastewater. The final effluent could be discharged directly into a drainage ditch. The results obtained in this pilot-scale plant demonstrated the successful performance of the proposed technology.

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