Diatomite strengthen COD and ammonia removal from an micro-aerobic EGSB reactor treating coking wastewater

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Abstract. The performance of one-stage micro-aerobic MAEGSB (OMAEGSB) reactor and two-stage MAEGSB (TMAEGSB) reactor treating actual coking wastewater with and without supplement of diatomite were investigated. The investigation has demonstrated that the two-stage MAEGSB reactor system treating actual coking wastewater could keep high COD and NH_3-N removal with supplement of diatomite. With only 24h hydraulic retention time (HRT) (12h for MAEGSB Ⅰ and 12h for MAEGSB Ⅱ), when without diatomite supplement, the TMAEGSB reactor system could attain 72.6% COD average removal and 25.8% NH_3-N average removal. However, with $6g \bullet L^{-1} \bullet d^{-1}$ diatomite supplement, the TMAEGSB reactor system could keep 84.3% COD average removal and 78.8%-92.8% NH_3-N average removal. Such high NH_3-N removal efficiency of the TMEGSB was because of the high phenol and thiocyanate (SCN) removal in the MAEGSB I reactor (97.9% and 77.9%) and correspondingly the low influent phenol and SCN concentration for the MAEGSB Ⅱ reactor (33.9 $mg \bullet L^{-1}$ and 10.4 $mg \bullet L^{-1}$). Diatomite supplement could ensure stable and highly efficient phenol and SCN removal in the MAEGSB I reactor. Using TMAEGSB reactor system with diatomite supplement was a simple and high effectively strategy for treatment of actual coking wastewater.

1. Introduction

Coking wastewater had dozens of inorganic and hundreds of organic compounds. The main inorganic compounds in coking wastewater include ammonia, thiocyanate, cyanide, sulfate, etc. And the organic ones in coking wastewater are mainly phenolic compounds, single-ring or polycyclic aromatic compounds, heterocyclic compounds containing N, S, and/or O, aliphatic compounds and so on. Moreover many of them have been shown to be mutagenic and carcinogenic [1-3].

There are many toxic and inhibitory substances in coking wastewater, which are difficult to be removed, and thus a traditional activated sludge technology has problems when treating the coking wastewater. And only very low ammonia removal (-12%) and CN removal (-22%) could be attained. Moreover, it is critical that the activated sludge process is also facing the problem of poor sludge settle ability performance at high COD and phenol loading rates. In the process of biofilm, the problem was overcome. Although the COD and phenol removal efficiencies were relatively increased, the ammonia, SCN and CN removal rates were still very low [4]. The reason for the poor ammonia removal was due to the coexistence of cyanide, thiocyanide and high concentration of free ammonia [2-4]. Moreover, it is well known that nitrifying bacteria that are capable of biological nitrification are sensitive to toxic compounds [5,6].

For this reason, many people began to study how to treat coking wastewater efficiently through biological treatment process [6-9]. In the various biological processes mentioned, the A^2/O system or A/O system were preferred for the treatment of nitrogen, cyanide, thiocyanate, phenols, single-ring or polycyclic aromatic compounds, heterocyclic compounds, and aliphatic compounds in the coking wastewater. However, as the anaerobic conversion of toxic organic substances is often incomplete, there are inherent problems for the sequential anaerobic/aerobic biological treatment system when treating toxic organic pollutants [10-13]. Moreover, the anaerobic metabolites may also inhibit the methanogens themselves, resulting in the reduction of anaerobic treatment efficiency, thereby increasing the load on the subsequent anaerobic treatment system. Because the aerobic bacteria could degrade these anaerobic metabolites in situ, intimate contact with anaerobic bacteria and aerobic bacteria may reduce the accumulation of toxic intermediate metabolites [14-16]. Therefore, coupling of anaerobic and aerobic degradation pathways in a single reactor could be used to improve the overall removal efficiency of the anaerobic/aerobic system [17-19].

A synchronous anaerobic/aerobic treatment strategy with micro-aerobic granular sludge was lately represented (such as the granules in the micro-aerobic EGSB reactor or in the micro-aerobic UASB reactor) [20-23]. In a coupled granules reactor system, the anaerobic granules were surrounded by an aerobic biofilm forming through the way to aerate the effluent recycling liquid of a conventional EGSB reactor, and eventually, the facultative fermentative species and aerobes (responsible for the consumption of oxygen) dominate around the periphery of anaerobic granular sludge, and then, the acetogens and methanogens in the core of the granules were effectively shielded from direct contact with oxygen. Thus, when treating coking wastewater, the recalcitrant xenobiotic and toxic organic compounds could be biodegraded, and NH_3-N could also be removed simultaneously. Therefore, micro-aerobic EGSB reactor would be an optimum alternative for the treatment of coking wastewater to realize the efficient and simultaneous removal of toxic and refractory organic pollutions and NH_3-N from coking wastewater.

Though high COD and NH_3-N removal efficiencies could be attained in the micro-aerobic EGSB reactor, the removal efficiencies are unstable and usually fluctuate between 22% and 80% for COD and between -32% and 64% for NH_3-N [24]. Many researchers had reported that the formation of dense granular sludge was the key to the efficient operation of the granular reactor (example for the UASB or EGSB reactor) [25-27]. Perhaps, at micro-aerobic conditions, the granular sludge in the EGSB reactor had a shift from compact granules to bulking granules, and which caused a port of granular sludge disintegrated and even washed out from the EGSB reactor. However, most of the granules were still retained in the reactor. Perhaps some packing media or carrier could be used to retain more nitrifying bacteria in the coking wastewater treatment system. Thus perhaps combination of the packing media or carrier and the micro-aerobic granular sludge could improve the performance of the actual coking wastewater treatment system.

Diatomite could be used as adsorbents for organic pollutants treatment and/or flocculants for drinking water treatment. Bio-diatomite was also often formed in the biological reactors for the wastewater treatment when using diatomite as carriers for microorganisms. When further treating the secondary sewage effluent, the raw and modified diatomite was found to be effective [28]. And moreover Chu *et al* [29] showed that COD, NH_3-N and TN could be removed simultaneously and efficiently in a bio-diatomite dynamic membrane reactor. Chen *et al* [30] improved the removal efficiency of petroleum in UASB reactors through the addition of diatomite and maifanite. However, at present, there is no report about whether coupling of bio-diatomite and micro-aerobic granular sludge could improve the wastewater treatment performance, especially for the coking wastewater treatment.

In the present study, the actual coking wastewater was treated in the micro-aerobic EGSB reactor system (and simultaneously the diatomite was supplied). The main objective was to evaluate whether adding diatomite could improve the COD and NH_3-N removal. One-stage micro-aerobic EGSB (OMAEGSB) reactor and two-stage micro-aerobic EGSB (TMAEGSB) reactor with and without supplement of diatomite were performed, respectively. The second objective was to analyze the cause for high COD and NH_3-N removal for the micro-aerobic two-stage EGSB. The removal effect and effluent concentration of COD, phenol, NH_3-N and SCN in the MAEGSB Ⅰ and MAEGSB Ⅱ were investigated, respectively.

2. Materials and methods

2.1. Reactor set-up

The research was completed in two lab-scale micro-aerobic EGSB reactors (MAEGSB Ⅰ and MAEGSB Ⅱ). A schematic diagram of the micro-aerobic EGSB reactor (MAEGSB Ⅰ or MAEGSB Ⅱ) used is showed in figure 1. Both of the MAEGSB I and MAEGSB II reactor was acrylic column of 2.3 m height, 12 L working volume, 10cm internal diameter with a conical-shaped bottom. And the MAEGSB I and MAEGSB II reactor were connected to aeration column I and aeration column II with a liquid volume of 2.5 L (50 cm×10.0 cm i.d.), respectively. In order to mix the sludge and transfer oxygen to the granular sludge bed, through a peristaltic pump, the effluent from the top of the reactors (MAEGSB Ⅰ or MAEGSB Ⅱ) was circulated to the aeration columns, and then flowed back to the bottom of the reactors. The recycled fluid had different dissolved oxygen concentrations, which could be obtained by controlling the aeration rate in the aeration column, and finally granular sludge in the EGSB reactor could get different dissolved O_2 and form microaerophilic micro-environments.

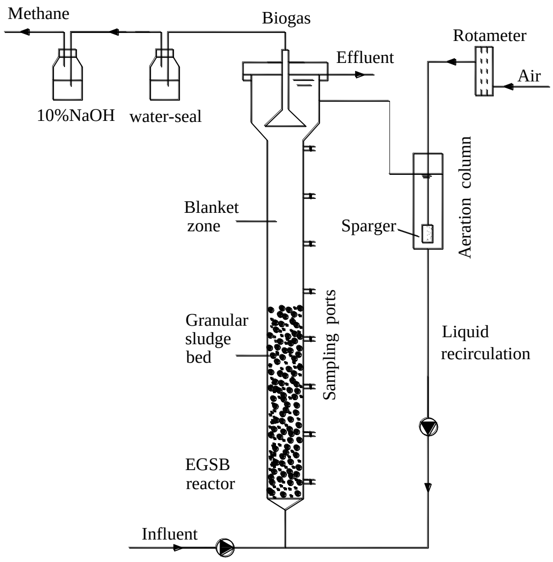

Figure 1. Schematic diagram of the micro-oxygenic EGSB reactor.

Table 1. Ranges of physic-chemical parameters of actual coking wastewater.

Parameter	Value
pH	8.0-9.3
COD (mg·L^{-1})	1000-2940
phenol (mg·L^{-1})	253-624
Ammonia (mg-N·L^{-1})	33-258
NO_2^--N (mg-N·L^{-1})	7-26
NO_3^--N (mg-N·L^{-1})	46-149
Cyanide (mg-CN·L^{-1})	0.08-4.36
Thiocyanate (mg-SCN·L^{-1})	152-404

2.2. Wastewater

The actual coking wastewater (in the buffer tank of the second coking plant of Taiyuan) was used as influent to the MAEGSB reactor (MAEGSB Ⅰ and MAEGSB Ⅱ). The influent parameters were shown in table 1. No KH_2PO_4 or phosphorus acids were added to the influent.

2.3. Seed sludge
The inoculated granular sludge was taken from a pilot-plant anaerobic EGSB reactor for treating actual coking wastewater for about 6 months at 25-30℃. After inoculation, with the same coking wastewater and the same operation temperature of 25-30℃,the granular sludge was acclimated in the micro-aerobic EGSB reactor, and in which the micro-aerobic environments was ensured through continuous supply of dissolved oxygen to the aeration column. And at the bottom of the aerobic column, a porous stone diffuser connected with an air pump was used to supply air (controlling air flow rate through an air flow-meter).

2.4. Operating strategy
The effect of diatomite on the performance process of MAEGSB reactor treating actual coking wastewater based on the removal efficiencies of chemical oxygen demand (COD), phenol, ammonia (NH_3-N), and thiocyanate (SCN) was investigated by following three operation stages:

Stage Ⅰ (from day 1 to days 90): to investigate the performance of OMAEGSB (one-stage micro-aerobic EGSB) reactor system and TMAEGSB (two-stage micro-aerobic EGSB) reactor system treating coking wastewater, the COD removal and NH_3-N removal efficiencies were investigated with 1.0L·h^{-1} influent flow (12h HRT), 2.0-3.2 m·h^{-1} liquid up-flow velocity (V_{up}) and 5000-8000 ml·min^{-1} air flow rate, in which the term "performance of OMAEGSB" was defined as $removal(MAEGSB\,\mathrm{I})(\%) = \frac{\inf luent - effluent(MAEGSB\,\mathrm{I})}{\inf luent} \times 100$ and the term "performance of TMAEGSB" was defined as total $removal(MAEGSB\,\mathrm{I} + MAEGSB\,\mathrm{II})(\%) = \frac{\inf luent - effluent(MAEGSB\,\mathrm{II})}{\inf luent} \times 100$.

Stage Ⅱ (from days 91 to days 150): to investigate the performance with *diatomite supplement*, OMAEGSB reactor system (the MAEGSB Ⅰ and/or MAEGSB Ⅱ reactor) was operated with 1.0 L·h^{-1} influent flow (12h HRT), 2.0-3.2 m·h^{-1} liquid up-flow velocity (V_{up}) and 5000-8000 ml·min^{-1} oxygenation flow rate (air flow rate), and the COD removal and NH_3-N removal efficiencies were still investigated. Meanwhile, at days 92, 60g diatomite was supplied for the MAEGSB Ⅰ and/or MAEGSB Ⅱ, respectively. From days 120, 6g·L^{-1}·d^{-1} diatomite was supplied for the MAEGSB Ⅰ and/or MAEGSB Ⅱ, respectively.

StageⅢ (from days 151 to days 252): to investigate the obtainable NH_3-N removal of the micro-aerobic EGSB reactor with supplement of diatomite, two-stage micro-aerobic EGSB reactor (TMAEGSB reactor)(MAEGSB Ⅰ+MAEGSB Ⅱ) was operated with 1.0 L·h^{-1} influent flow (12h HRT), 2.0-3.2 m·h^{-1} liquid up-flow velocity (V_{up}) and 5000-8000 ml·min^{-1} oxygenation flow rate (air flow rate), and meanwhile with 6 g·L^{-1}·d^{-1} diatomite supplementation, and the COD and NH_3-N removal was investigated. Furthermore, to analysis the influence factors of NH_3-N removal, the phenol and SCN^- removal performances were also investigated. From days 209, no diatomite was supplied, and from days 239, 6g·L^{-1}·d^{-1} diatomite was resumed to supply for the TMAEGSB reactor.

2.5. Analytical method
COD was determined by the method of dichromate [31]. Phenate method was used for ammonia analysis [31], chloroform extraction method was used for phenol [31], and determination of thiocyanate by reaction with ferric nitrate using a spectrophotometer [32]. After distillation, pyridine-pyrazolone method was used to analyse total cyanide concentration [31]. The pH was measured through a pH-3C meter.

3. Results and discussion

3.1. Performance of OMAEGSB reactor system

The concentration and removal efficiency changes of COD and ammonia (NH_3-N) in OMAEGSB reactor treating actual coking wastewater was showed in figure 2.

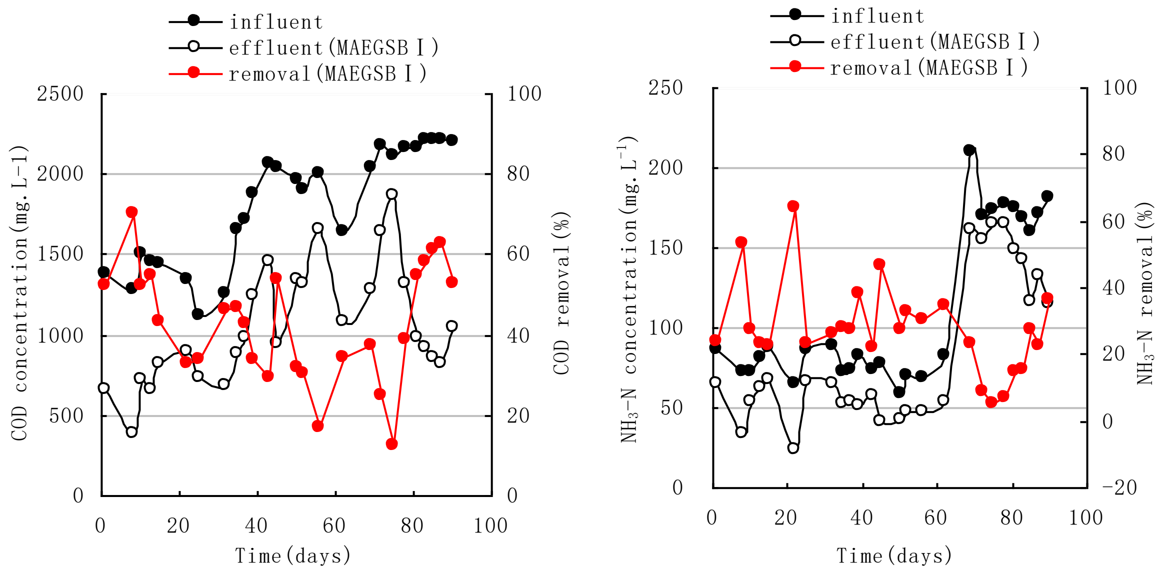

Figure 2. Performance of OMAEGSB reactor.

With 1.2 L·h^{-1} influent flow, 12h HRT, 2.0-3.2 m·h^{-1} liquid up-flow velocity (V_{up}) and 5000-8000 ml·min^{-1} oxygenation flow rate (air flow rate), for the initial 32 days, the concentration of influent COD was kept in the range of 1120-1500 mg·L^{-1}, and the OMAEGSB reactor could have 48.1% COD average removal efficiencies. After the 32th day, the influent COD concentration was gradually increased to about 2100 mg·L^{-1} (fluctuating between 1640 mg·L^{-1} and 2210 mg·L^{-1}), and the COD removal efficiency was decreased down to 12% at days 75. Subsequently, the COD removal resumed to above 50% and then kept higher COD average removal efficiency of 58% from days 81 to days 90.

For the initial 62 days, the concentration of the influent NH_3-N was fluctuated between 59 mg·L^{-1} and 89 mg·L^{-1}, and the NH_3-N average removal efficiency in the OMAEGSB reactor could attain 32.4% (fluctuating between 22% and 64%). After the 62 days, the NH_3-N concentration abruptly increased from 89 mg·L^{-1} to 209 mg·L^{-1}, and then kept a higher NH_3-N average concentration of 176.3 mg·L^{-1}, the NH_3-N removal decreased to 5% at days 75, and then resumed to 37% at days 90 (with 29.0% NH_3-N average removal efficiency).

3.2. Performance of TMAEGSB reactor

The concentration and removal efficiency changes of COD and ammonia (NH_3-N) in TMAEGSB reactor treating actual coking wastewater was showed in figure 3.

The influent flow, HRT, V_{up} and oxygenation flow rate were not changed. For the initial 32 days, the COD average removal efficiency could increase to 73.9%. Subsequently, with gradually increasing COD concentration (from about 1400 mg·L^{-1} to about 2100 mg·L^{-1}), the COD removal decreased down to 41% at days 75. And then the COD average removal efficiency resumed to 72.6% from days 78 to days 90.

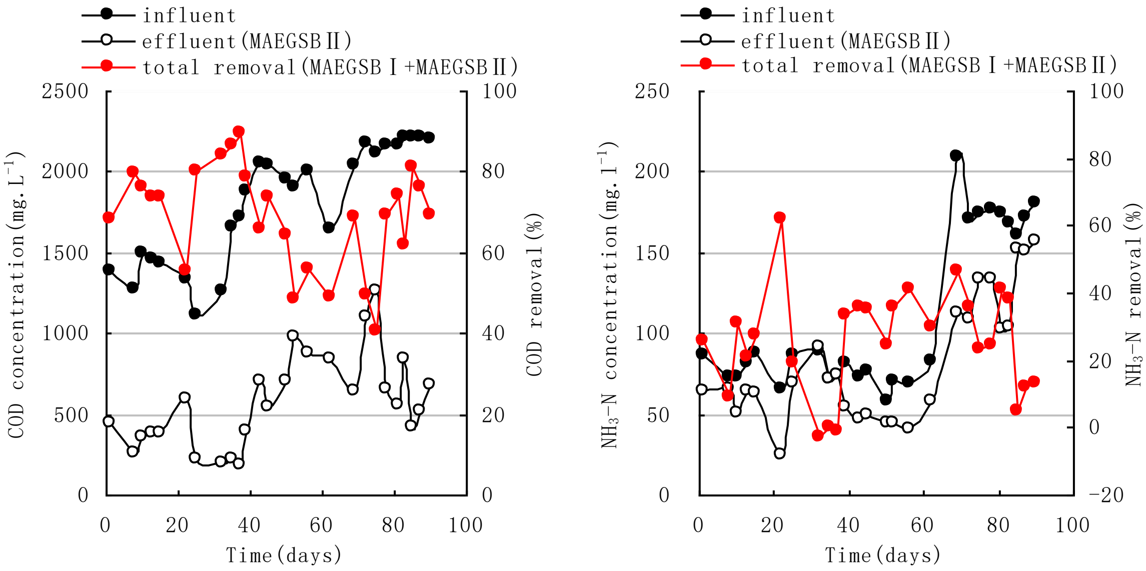

Figure 3. Performance of TMAEGSB reactor.

For the whole operate process (from day 1 to days 90), the TMAEGSB reactor could have an NH_3-N average removal efficiency level of 25.1% (for about 76.5 mg·L^{-1} low NH_3-N average concentration) and 26.5% (for about 176.3 mg·L^{-1} high NH_3-N average concentration), which indicated that two-stage MAEGSB reactor had no strengthened effect on the NH_3-N removal.

3.3. Performance of OMAEGSB reactor with supplement of diatomite

Furthermore, in order to strengthen the removal effect of COD and NH_3-N in the MAEGSB reactor treating coking wastewater, with the same influent flow, HRT, V_{up} and oxygenation flow rate, the OMAEGSB reactor with supplement of diatomite was operated. Figure 4 shows the concentration and removal efficiency changes of COD and ammonia (NH_3-N) in OMAEGSB (MAEGSB Ⅰ) reactor with supplement of diatomite when treating actual coking wastewater.

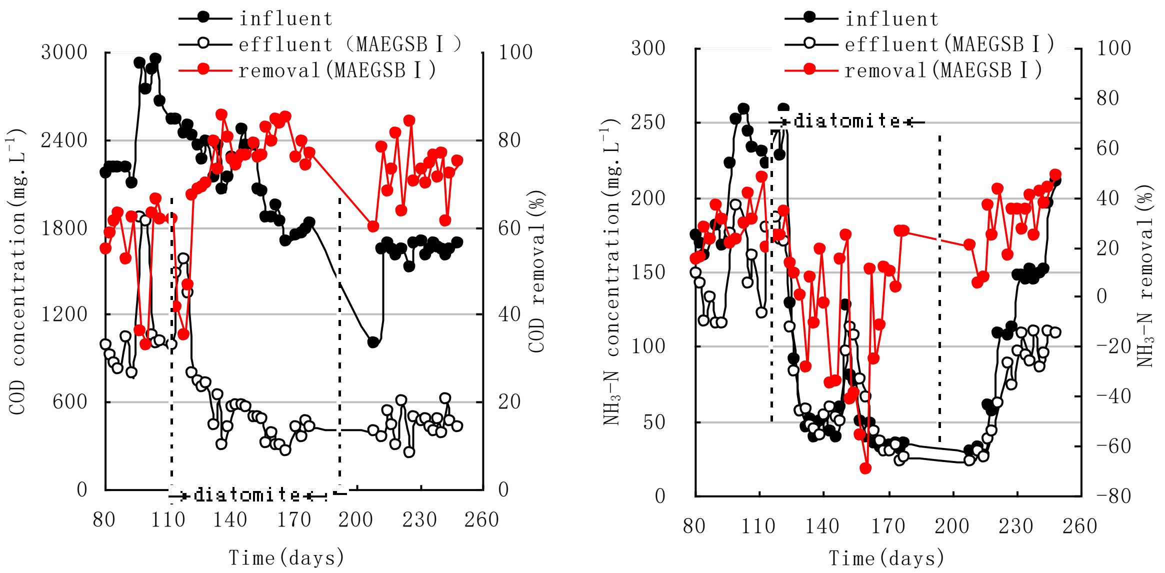

Figure 4. Performance of OMAEGSB reactor with supplement of diatomite.

Also at days 93, adding 60 g diatomite to the MAEGSB Ⅰ, the COD average removal efficiency was increased to 62.8%. However, at days 114, the COD removal decreased to 42% (from 61% at days 112), and low to 35% at days 118. Subsequently, from days 120, with 6 g•L^{-1}•d^{-1} diatomite supplement for the MAEGSB Ⅰ, the average removal efficiency of COD was rapidly increased to 74.9%. And from days 151 to days 178 (stable operation stage for the MAEGSB Ⅰ), the COD average removal efficiency could reach 79.5%.

Diatomite supplement was not advantageous to NH3-N removal of OMAEGSB reactor (e.g. MAEGSB Ⅰ). At days 93, 60g diatomite was supplied, and the NH_3-N average removal efficiency had a slightly increasing between days 93 and days 118 (from 23.4% to 29.8%). However, at days 120, 6 g•L^{-1}•d^{-1} diatomite was supplied, the MAEGSB Ⅰ only had very low NH_3-N average removal efficiency of 4.6% from days 120 to days 178 (fluctuating between -69% and 34%).

3.4. Performance of TMAEGSB reactor with supplement of diatomite

Because of the very low NH_3-N removal for the OMAEGSB reactor with diatomite supplement, TMAEGSB reactor with supplement of diatomite was applied. Figure 5 shows the concentration and removal efficiency changes of COD and ammonia (NH_3-N) in TMAEGSB reactor with supplement of diatomite when treating actual coking wastewater.

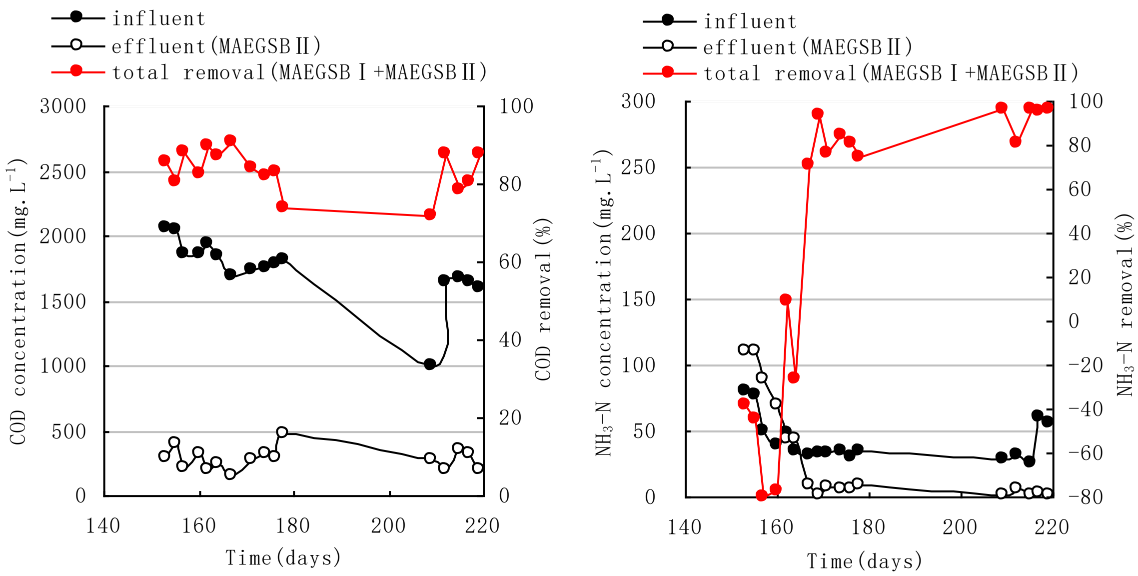

Figure 5. Performance of TMAEGSB reactor with supplement of diatomite.

With supplement of 6g·L^{-1}·d^{-1} diatomite, the TMAEGSB reactor system could gain very high COD and NH_3-N average removal of 84.3% and 79.8%. Furthermore, when the TMAEGSB reactor system was not operated for about one month (from days 179 to days 219) and then operated again (it should be noted that no diatomite was supplied), the TMAEGSB reactor system had a slightly decreased COD average removal efficiency (from 84.3% to 81.2%), but had a distinctly increased NH_3-N average removal efficiency (from 79.8% to 92.8%).

Compared with the OMAEGSB reactor, why could the TMAEGSB reactor system have so high COD and NH_3-N removal efficiencies? Particularly, why could the NH_3-N average removal efficiency quickly increase from 4.6% to 79.8%, and then to 92.8%?

Perhaps for the TMAEGSB reactor system treating actual coking wastewater, stably and highly efficiently removal of toxicant pollutions such as phenol and SCN in the MAEGSB Ⅰ could ensure low concentration of the toxicant pollutions (phenol and SCN) in the MAEGSB Ⅱ, and then ensure high removal of the NH_3-N in the MAEGSB Ⅱ.

Perhaps low influent NH_3-N concentration was the other important reason for the high NH_3-N removal in the TMAEGSB. When not supplying diatomite, the influent NH_3-N concentrations for MAEGSB Ⅰ and MAEGSB Ⅱ were 111.0 mg·L^{-1} and 84.0 mg·L^{-1}, respectively. And when supplying diatomite, only 46.2 mg·L^{-1} and 32.3 mg·L^{-1} were keep in MAEGSB Ⅰ and MAEGSB Ⅱ.

3.5. phenol and SCN removal change with and without supplement of diatomite

The phenol, SCN, and NH_3-N concentration and removal change with and without supplement of diatomite for the TMAEGSB reactor system was presented in table 2.

Table 2. Phenol, SCN and NH_3-N concentration and removal change with and without supplement of diatomite.

			No diatomite			Diatomite		
			MAEGSB Ⅰ	MAEGSB Ⅱ	Total	MAEGSB Ⅰ	MAEGSB Ⅱ	Total
phenol	Phenol removal (%)		62.6	85.0	90.4	97.4	97.6	99.9
	Phenol concentration (mg.L^{-1})	influent	396.2	150.7		463.3	12.0	
		effluent	150.7	39.8		12.0	0.26	
SCN	SCN removal (%)		6.8	35.2	38.0	87.7	33.6	92.0
	SCN concentration (mg.L^{-1})	influent	226.0	210.9		176.5	21.9	
		effluent	210.9	136.9		21.9	14.1	
NH_3-N	NH_3-N removal (%)		27.4	5.5	25.6	30.1	80.9	86.4
	NH_3-N concentration (mg.L^{-1})	influent	111.0	84.0		46.2	32.3	
		effluent	84.0	82.2		32.3	6.3	
pH		influent	8.67	8.79		8.88	8.94	
		effluent	8.79	8.85		9.01	9.08	

When no diatomite was supplied, influent phenol and SCN concentrations were 396.2 mg·L^{-1} and 226.0 mg·L^{-1}, respectively. And MAEGSB Ⅰ only could have 62.6% phenol removal and 6.8% SCN removal, which caused very high influent phenol and SCN concentrations (150.7 mg·L^{-1} and 210.9 mg·L^{-1}) for MAEGSB Ⅱ. Ultimately, TMAEGSB reactor system only could have relatively low phenol and SCN removal efficiencies of 90.4% and 38.0% (correspondingly with relatively high effluent phenol and effluent SCN concentrations of 39.8mg·L^{-1} and 136.9 mg·L^{-1}).

When 6 g·L^{-1}·d^{-1} diatomite was supplied, influent phenol and SCN concentrations were still high to 463.3 mg·L^{-1} and 176.5 mg·L^{-1}, respectively. However, because MAEGSB Ⅰ had very high phenol removal and SCN removal (97.4% and 87.7%), and thus influent phenol and SCN concentration of MAEGSB Ⅱ were low to 12.0 mg·L^{-1} and 21.9 mg·L^{-1}. Ultimately, TMAEGSB reactor system could have very high phenol and SCN removal efficiencies of 99.9% and 92.0%, and effluent phenol and effluent SCN concentrations were low to 0.26 mg·L^{-1} and 14.1 mg·L^{-1}.

TMAEGSB reactor system with diatomite supplement could have very high NH_3-N removal efficiency of 86.4% (79.8%-92.8%). Why could TMAEGSB reactor system have so high NH_3-N removal and so low effluent NH_3-N concentration? Perhaps low phenol and SCN concentrations in MAEGSB Ⅱ reactor were the key. When 6 g·L^{-1}·d^{-1} diatomite was supplied, MAEGSB Ⅰ reactor had very high phenol and SCN removal, and thus MAEGSB Ⅱ reactor could have very low influent phenol and SCN concentration, which caused very high NH_3-N average removal efficiency of 80.9% in MAEGSBⅡ reactor, and thus effluent NH_3-N average concentration was low to 6.3 mg·L^{-1}.

Oppositely, when no diatomite was supplied, MAEGSBⅠ had relatively low phenol and SCN removal, and very high influent phenol and SCN^- concentration of 150.7 mg·L^{-1} and 210.9 mg·L^{-1} were kept for influent of MAEGSBⅡ reactor. Therefore, for MAEGSBⅡ reactor, NH_3-N removal efficiency was very low (only 5.5%), and thus effluent NH_3-N concentration was high to 82.2 mg·L^{-1}.

In summary, with supplement of diatomite, the TMAEGSB reactor system could have high COD, phenol and SCN removal of 84.3%, 99.9% and 92.0%, and thus ensure very high NH_3-N removal (92.8%) and very low effluent NH_3-N concentration (6.3 mg·L^{-1}), which accord with the high distinction A of “discharge standard of pollutants for municipal wastewater treatment plant” (GB 18918-2002 of China).

3.6. NH_3-N removal change for varied influent NH_3-N concentration

There maybe have another cause for high NH_3-N removal of TMAEGSB reactor system with supplement of diatomite. Comparing the operation conditions of the TMAEGSB reactor system before and after supplement of diatomite, except for the difference in the influent phenol and SCN concentration of MAEGSBⅡ reactor, another distinct difference was influent NH_3-N concentration of MAEGSBⅠ reactor. 111.0 mg·L^{-1} was for no diatomite supplement and only 46.2 mg·L^{-1} for diatomite supplement. Perhaps, such low influent NH_3-N concentration of 46.2 mg·L^{-1} was the key to have such high NH_3-N removal efficiency for the TMAEGSB reactor system with supplement of diatomite. It is generally accepted that the inhibition effect of ammonia nitrogen on nitrification is not due to nitrogen ammonia itself, but because of high concentration of free ammonia (FA). Through the following formula presented by Ford *et al* [33]:

$$FA(mg\cdot L^{-1})=\frac{[TotalNH_3]\times 10^{pH}}{\exp[(6334/(273+T))]+10^{pH}} \tag{1}$$

46.2 mg·L^{-1} of total ammonia could contain 17.9 mg·L^{-1} FA at pH 9.0 and 26℃.

Some researcher reported that the FA concentration threshold of inhibition of *Nitrosomonas* and *Nitrobacter* were 10-150 mg·L^{-1} and 0.1-4.0 mg·L^{-1}, respectively [34-35]. Therefore, when the total ammonia concentration was 46.2 mg.L^{-1}, the FA concentration was lower than the FA concentration threshold for *Nitrosomonas*, but higher than the FA concentration threshold for *Nitrobacter.* Moreover, although coking wastewater had 46.4 mg·L^{-1} ammonia, due to the higher effluent circulation ratio of 18-24 for the TMAEGSB reactor system, only about 34.7 mg·L^{-1} and 7.5 mg·L^{-1} of ammonia (13.4 mg·L^{-1} and 2.9 mg·L^{-1} of FA) were existed in the MAEGSBⅠand MAEGSBⅡ, respectively. Therefore, it is impossible to produce incomplete nitrification due to inhibitory effect of ammonia nitrogen itself.

Subsequently, we gradually increased influent NH_3-N concentration, and the COD and NH_3-N removal efficiencies were investigated, which was presented in figure 6. From days 209 to days 237, still not resuming supplement of diatomite, influent NH_3-N concentration change was 30→60→110→150 mg·L^{-1}. From days 239 to days 252, resuming supplement of diatomite, influent NH_3-N concentration change was 150→200 mg·L^{-1}.

The results (figure 6) showed that, for 30-60 mg·L^{-1} low influent NH_3-N concentration, though diatomite supplement was still not resumed (diatomite supplement was ceased for about one month), the NH_3-N average removal efficiency was high to 92.8%. When influent NH_3-N concentration increased to 110 mg·L^{-1}, the NH_3-N removal rapidly decreased to 50% and then rose to 61%. Subsequently, influent NH_3-N concentration was continuously increased to150 mg·L^{-1}, the NH_3-N removal efficiency was slightly increased instead of decreased, and with 66.0% average removal efficiency (which was still much higher than the removal of the paralleled MAEGSB reactor without diatomite supplement). At days 239, 6 g.L^{-1}.d^{-1} diatomite supplement was resumed, the NH_3-N removal rapidly increased to 80%, and though at days 245, the influent NH_3-N concentration was increased to 200mg·L^{-1} (Accordingly, the FA concentration was high to 81.0 mg·L^{-1} on the base of equation (1)), the NH_3-N average removal could still attain to 78.8%, which adequately indicated that supplement of diatomite could strengthen

NH_3-N removal regardless of influent NH_3-N concentration(from 30 mg·L^{-1} to 200 mg·L^{-1}), and which also meant that the high NH_3-N removal efficiency with supplement of diatomite was not because of the low influent NH_3-N concentration but of the high phenol and SCN^- removal in the MAEGSB Ⅰ reactor (97.9% and 77.9%) and correspondingly the low influent phenol and SCN^- concentration for the MAEGSB Ⅱ reactor (33.9 mg·L^{-1} and 10.4 mg·L^{-1}).

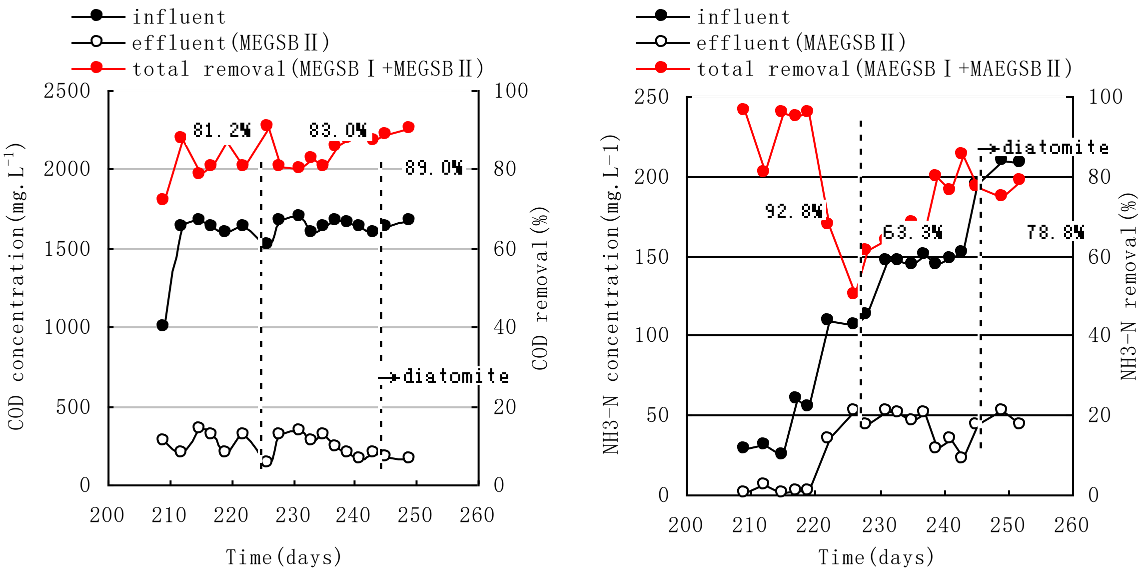

Figure 6. COD and NH_3-N removal change of TMAEGSB for varied influent NH_3-N concentration.

4. Summary and conclusions

The effect of diatomite on the operation process of MAEGSB reactor treating actual coking wastewater was investigated. And One-stage MAEGSB (OMAEGSB) reactor and two-stage MAEGSB (TMAEGSB) reactor with and without supplement of diatomite were performed, respectively. It can be said from the results of this study that OMAEGSB could keep 58.0% COD average removal and 32.4% NH_3-N average removal and TMAEGSB could attain 72.6% COD average removal and 25.8% NH_3-N average removal when without diatomite supplement and with 1.2 L·h^{-1} influent flow (12h HRT), 1120-2210mg·L^{-1} influent COD and 59-89 mg·L^{-1} influent NH_3-N. TMAEGSB had no strengthened effect on the NH_3-N removal.

Through adding 6 g·L^{-1}·d^{-1} diatomite, and with influent flow of 1.2 L·h^{-1} (HRT of 12h), influent COD of 1520-2940 mg·L^{-1} and influent NH_3-N of 23-42 mg·L^{-1}, OMAEGSB could have higher COD average removal of 79.5%, but only very low NH_3-N average removal of 4.6%. Furthermore, TMAEGSB could gain very high COD average removal of 84.3% and NH_3-N average removal of 92.8%. Especially, the MAEGSB Ⅱ could have very high NH_3-N average removal of 91.9% (80%-96.3%) and the effluent NH_3-N average concentration could low to 6.3mg.L^{-1} (1-9 mg.L^{-1}).

Through adding 6 g·L^{-1}·d^{-1} diatomite, for gradually increased influent NH_3-N concentration of 30 mg·L^{-1} to 200 mg·L^{-1}, TMAEGSB could gain high NH_3-N average removal of 92.8-78.8%. Such high NH_3-N removal efficiency of the TMEGSB was because of the high phenol and SCN removal in the MAEGSB Ⅰ reactor (97.9% and 77.9%) and correspondingly the low influent phenol and SCN concentration for the MAEGSB Ⅱ reactor (33.9 mg·L^{-1} and 10.4 mg·L^{-1}). Diatomite supplement could ensure stable and highly efficient phenol and SCN^- removal in the MAEGSB Ⅰ reactor.

In summary, TMAEGSB treating actual coking wastewater with diatomite supplement could simultaneously gain high COD, phenol, SCN removal and high NH_3-N removal for very low HRT of 24h (12h for MAEGSB Ⅰ and 12h for MAEGSB Ⅱ).

Acknowledgments
This research was supported by grants from the Shan-Xi Province Key Technologies R & D Program of Shan Xi (NO. 20150313002-1).

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