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\textsubscript{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\textsubscript{3}-N average removal. However, with 6g•L\textsuperscript{-1}•d\textsuperscript{-1} diatomite supplement, the TMAEGSB reactor system could keep 84.3% COD average removal and 78.8%-92.8% NH\textsubscript{3}-N average removal. Such high NH\textsubscript{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•L\textsuperscript{-1} and 10.4 mg•L\textsuperscript{-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 A2/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 NH3-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 NH3-N from coking wastewater.

Though high COD and NH3-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 NH3-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, NH3-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 NH3-N removal. One-stage micro-aerobic EGSB (OMAEGSB) reactor and two-stage micro-aerobic EGSB (TMAEGSB) reactor with and without supplementation 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.](image)

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 KH₂PO₄ 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°C. After inoculation, with the same coking wastewater and the same operation temperature of 25-30°C, 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 flowmeter).

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 (NH₃-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 NH₃-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₊) and 5000-8000 ml·min⁻¹ air flow rate, in which the term “performance of OMAEGSB” was defined as

$$removal_{\text{(MAEGSB I)}}(\%) = \frac{\text{influent} - \text{effluent}_{\text{(MAEGSB I)}}}{\text{influent}} \times 100$$

and the term “performance of TMAEGSB” was defined as total

$$removal_{\text{(MAEGSB I + MAEGSB II)}}(\%) = \frac{\text{influent} - \text{effluent}_{\text{(MAEGSB II)}}}{\text{influent}} \times 100$$

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₊) and 5000-8000 ml·min⁻¹ oxygenation flow rate (air flow rate), and the COD removal and NH₃-N removal efficiencies were still investigated. Meanwhile, at days 92, 60 g 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.

Stage III (from days 151 to days 252): to investigate the obtainable NH₃-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₊) 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 NH₃-N removal was investigated. Furthermore, to analysis the influence factors of NH₃-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.](image)

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.

![Figure 3. Performance of TMAEGSB reactor.](image)

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.
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 3. Performance of TMAEGSB reactor.](image)

![Figure 4. Performance of OMAEGSB reactor with supplement of diatomite.](image)
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 NH\(_3\)-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.](image)

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 (%) |             |           |         |          |           |         |
| influent | 396.2        | 150.7     | 463.3   | 12.0     |           | 0.26    |
| effluent | 150.7        | 39.8      | 12.0    | 0.26     |           |         |
| SCN      |              |           |         |          |           |         |
| SCN removal (%) |             |           |         |          |           |         |
| 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 (%) |             |           |         |          |           |         |
| 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 concentrations 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 MAEGSB II reactor, and thus effluent NH$_3$-N average concentration was low to 6.3 mg·L$^{-1}$.

Oppositely, when no diatomite was supplied, MAEGSB I 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 MAEGSB II reactor. Therefore, for MAEGSB II 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 MAEGSB II reactor, another distinct difference was influent NH$_3$-N concentration of MAEGSB I 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]:

\[
FA(\text{mg} \cdot \text{L}^{-1}) = \frac{[\text{TotalNH}_3]}{\exp\left(6334/(273 + T)\right) + 10^{\text{pH}}} \tag{1}
\]

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

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 (15.4 mg·L$^{-1}$ and 2.9 mg·L$^{-1}$ of FA) were existed in the MAEGSB I and MAEGSB II, 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 to 150 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 200 mg·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.](image)

### 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).
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