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Highlights

- High concentration of MIBK had higher inhibition on methanogenesis than phenols degradation.
- Anaerobic degradation of MIBK fitted well with the pseudo-first-order kinetic behavior.
- Relative methane generation rate constants decreased with the increase of MIBK concentrations.
- Toxic effect of MIBK on phenols degradation varied considerably depending on the type of phenols.

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Potential impact of methyl isobutyl ketone (MIBK) on phenols degradation in an UASB reactor and its degradation properties

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Abstract: Methyl isobutyl ketone (MIBK) as a solvent is extensively used for the phenols extraction from the wastewater, so it is unavoidable to expose in the effluent due to the solubility and leakage problem. The present study evaluated the impact of MIBK on phenols degradation in an UASB reactor and analyzed its degradation properties. The results indicated that the continuous dosing (0.1 g L^{-1}) and impact (10 g L^{-1}) of MIBK had limited effect on phenols removal (1-2% reduction) in the UASB reactor, but the specific methanogenic activity (SMA) values of sludge decreased by 45-75% after MIBK exposure. Anaerobic degradation rate of MIBK fitted well to a pseudo-first-order kinetic equation with respect to the initial concentration of 35 mg L^{-1} (k=0.0115 h^{-1}, R^2=0.9664). Furthermore, the relative methane generation rate constants of MIBK were 0.00816, 0.00613, 0.00273, and 0.00207 d^{-1} at the initial concentrations of 0.1, 0.5, 5, and 10 g L^{-1}, respectively. MIBK showed higher inhibitory effect on the methanogenesis than on phenols degradation. This study pointed out that the industrial installations should consider the influence of solvent on anaerobic treatment of phenolic wastewater.

Keywords: methyl isobutyl ketone; phenolic compounds; UASB; specific methanogenic activity; solvent

1. Introduction

Phenolic wastewater is one of the most prevalent industrial effluents in China, which is generated from the manufacturing processes of coal gas, coke, pharmaceuticals, and petroleum [1]. It contains hundreds to thousands of milligram phenolic compounds per liter becoming an important threat to the ecological environment [2]. Solvent extraction is a preferential technology used in the industrial installations to extract phenols from wastewater streams [3]. Methyl isobutyl ketone (MIBK) is commonly used for phenols recovery due to its advantages in high extraction efficiency of dihydric and trihydric phenols [4, 5]. Continuous phenols extraction minimized the toxic effect of phenols on the microorganisms, but there were few literatures to report the influence of MIBK on the microorganisms.

Recently, anaerobic biotechnology has been widely used in the treatment of phenolic wastewater due to its characteristics of low sludge yield, good tolerance and decomposing ability to phenols [6-8]. The strict environmental requirement is one of the main limiting factors for its industrial application. There are a lot of reasons such as temperature changes, impact of phenols or other toxic substances causing operational failure in the anaerobic reactor [8, 9]. For the industrial installations, the impact of toxic substances is the most frequent problem. After the solvent extraction process, MIBK also become one of the main compounds of phenolic wastewater. The dissolved MIBK always exists in the effluent and it leaks occasionally into the biological treatment system. However, the impact of MIBK on the phenols degradation and methanogenesis is still unknown.

MIBK is a ketone compound with the formula $(CH_3)_2CHCH_2C(O)CH_3$, and its solubility in water is 19.1 g L^{-1} at the temperature of 20 °C. Although the highly branched MIBK is more persistent to biological oxidation [10], some complex enzymes are known to carboxylate the ketone group [11, 12]. Wikandari et al (2012) investigated the effects of furaneol and mesifurane on methane production during anaerobic digestion, and found these compounds were readily biodegradable under anaerobic conditions [12]. Meanwhile, some researchers have recognized the inhibitory effect of ketones on the biochemical processes. Quesnel and Nakhla [13] reported that acetone exerted an inhibitory impact on the aerobic biodegradation of MIBK. Despite plenty information regarding biodegradation of ketones, there is a lack of kinetic information for anaerobic degradation of MIBK.

The aims of this study were to demonstrate (1) the potential impact of MIBK on anaerobic degradation of phenolic compounds (phenol, catechol, resorcinol, hydroquinone), SMA and substrate utilization rate (SUR) of sludge in an UASB reactor and (2) kinetics of anaerobic degradation of MIBK.

2. Materials and methods

2.1 Experimental setup

The UASB reactor consisted of a plexiglass cylinder with a diameter of 7 cm and a working volume of 3.5 L, which was maintained at 35 ± 1 °C by using a jacket of warm water. The liquid upflow velocity was maintained at 1 m h^{-1}. The mixture of biogas, sludge, and wastewater was separated in the three phase separator in the top of the reactor. The biogas volume was measured daily using the water replacement method [14].

2.2 Inoculum and synthetic wastewater

The UASB reactor was inoculated with activated sludge taken from a municipal wastewater treatment plant located in Hefei, China. The sludge concentrations were 7.17 g MLSS L^{-1} and 4.83 g MLVSS L^{-1} in the UASB reactor at the beginning of this study. The synthetic wastewater was composed of sodium acetate, phenol, hydroquinone, catechol, and resorcinol, macronutrients, and micronutrients. Before this experiment, the UASB reactor was operated for a period of 160 days. During this period, the influent concentration of total phenols was gradually increased from 100 to 500 mg L^{-1} with equal proportions of phenol, hydroquinone, catechol, and resorcinol (1:1:1:1). The concentration of sodium acetate was 3.85 g L^{-1}. The dosages of macronutrients and micronutrients were 4 mL and 0.4 mL per liter wastewater, respectively. The feed nutrients were composed of the following macronutrients (in mg L^{-1}): $K_2HPO_4 \cdot 3H_2O$ 136.95, $NaH_2PO_4 \cdot 2H_2O$ 62.40, NH_4Cl 680, $CaCl_2 \cdot 2H_2O$ 32, and $MgSO_4 \cdot 7H_2O$ 36; micronutrients (in mg L^{-1}): $FeCl_3 \cdot 4H_2O$ 0.8, $CoCl_2 \cdot 6H_2O$ 0.8, $MnCl_2 \cdot 4H_2O$ 0.2, $CuCl_2 \cdot 2H_2O$ 0.012, $ZnCl_2$ 0.02, HBO_3 0.02, EDTA 0.4, $(NH_4)_6Mo_7O_2 \cdot 4H_2O$ 0.036, $Na_2SeO_3 \cdot 5H_2O$ 0.04, $NiCl_2 \cdot 6H_2O$ 0.02.

2.3 Operational procedure

The operational procedures of the UASB reactor were divided into four phases. The operational conditions of each phase including hydraulic retention time (HRT), organic loading rate (OLR), phenols loading rate (PLR), and MIBK load are described in Fig. 1. During the period of phase I (161-183 days), the influent concentrations of

COD and total phenols were maintained at around 5200 and 1000 mg L^{-1}, respectively with the organic components of sodium acetate (3.85 g L^{-1}), phenol (625 mg L^{-1}), hydroquinone (125 mg L^{-1}), catechol (125 mg L^{-1}), and resorcinol (125 mg L^{-1}). At phase II (184-227 days), 0.1 g L^{-1} of MIBK was continuously added to the influent with a MIBK load of 0.05 g L^{-1} d^{-1}. At the start of phase III (228-240 days), the UASB reactor was fed with a MIBK concentration of 10 g L^{-1} in the influent for 24 h and subsequently returned to the MIBK concentration of 0.1 g L^{-1}. At the start of phase IV (241-247 days), the MIBK concentration in the reactor was immediately increased to 10 g L^{-1} on day 241 and subsequently decreased to the MIBK concentration of 0.1 g L^{-1}. The PLR of the reactor was always 0.49 g L^{-1} d^{-1} for the whole phases. The OLR values of the reactor were 2.52 g COD L^{-1} d^{-1} at the phase I and 2.65 g COD L^{-1} d^{-1} at the phases II, III and IV, except for 15.72 g COD L^{-1} d^{-1} on day 228 (phase III) and 29.85 g COD L^{-1} d^{-1} on day 241 (phase IV).

2.4 Analytical methods

2.4.1 Conventional indexes

COD, MLSS and MLVSS were measured according to the Standard Methods [15]. pH values were determined daily with a pH meter (pHS-3C, Leici, China). Methane content in the biogas was analyzed using a GC system (SP-6890 GC, Shandong Ruihong Ltd., China). The temperatures of the column, injector port and detector were 90 °C, 100 °C and 100 °C, respectively. For the analysis of MIBK, the effluent was centrifuged for 10 min at 1000 rpm, and filtered through 0.45 um filters. Filtrates were analyzed using gas chromatography with a flame ionized detector, equipped with a packed column (DB-FFAP, 15m×250μm×0.25μm, Agilent Inc., USA) with H_2 as a burning gas and N_2 as a carrier gas. Phenol, hydroquinone, catechol, and resorcinol were measured using the HPLC system (1260 Infinity, Agilent Inc., USA). The measurement conditions were mobile phase of acetonitrile 25% and water 75% at a flow rate of 1.00 ml min^{-1}, signal wavelength at 280 nm.

2.4.2 Specific methanogenic activity (SMA) tests

The SMA of sludge was determined in the batch assays using 2 g L^{-1} sodium acetate as the substrate. The SMA tests were carried out in 300 mL sealed vials. All batch tests were performed in triplicate and were incubated at 35 °C and 120 rpm. Before the experiment, sludge and substrate were loaded in the vials. Besides, sludge mass (g VSS): substrate COD (g) ratio was 1:1. The vials were sealed by rubber plug after sparing nitrogen gas for about 1-2 min. The samples were taken from the vials and analyzed every 2 h. The SMA values were expressed as mg COD-CH_4 g^{-1}VSS d^{-1}.

2.4.3 Substrate utilization rates (SUR) of phenols

The SUR of phenol, hydroquinone, catechol, and resorcinol were used to evaluate the specific degradation activity of the inoculum and biomass in the UASB reactor. The SUR tests were carried out in 300 mL sealed vials. Each concentration of phenol, hydroquinone, catechol, and resorcinol was 20 mg L^{-1}. In the SUR tests, the sludge mass (g VSS) and phenols mass (g) ratio was 40: 1. All assays were conducted in triplicate and run at 35 °C and 120 rpm. At the beginning of the tests, the vials were purged with nitrogen gas for about 1-2 min. During the experiment, the samples were filtered through a 0.45 μm filter after be taken from the vials every 2 h. The SUR of sludge was calculated by the phenols degradation with the time, which was expressed as mg phenols g^{-1}VSS d^{-1}.

2.4.4 Kinetic tests of anaerobic degradation of MIBK

The kinetic test were used to evaluate anaerobic degradation rate and methane potential of MIBK. The assays were conducted in 300 mL sealed vials using MIBK as the sole carbon resource of the medium. The macronutrients and micronutrients in the medium are described as the section 2.2. In all cases, the ratios of sludge mass (g VSS) and substrate COD (g COD) were kept at 2:1. The bottles were sealed with butyl rubber stoppers and incubated in a shaker chamber set at 120 rpm and 35 °C. Methane production was measured daily. The kinetic tests were run at a series of MIBK concentrations including 0.1, 0.5, 5, and 10 g L^{-1}. In order to compare the influence of MIBK concentrations on its methane potential, the results were exhibited as the actual methane production rates of MIBK divided by its theoretical values. The relative methane generation rate constant was calculated by the methane conversion ratios of MIBK with the time. The equations are presented as follows:

$$R = \frac{V_{act}}{V_{\mathrm{theor}}} \tag{1}$$

$$k_{\mathrm{i}} = \frac{\Delta R}{\Delta t} \tag{2}$$

where R is the actual (V_{act}) and theoretical (V_{theor}) methane production ratio of MIBK, and k_i the relative methane generation rate constant (d^{-1}) is the slope of the variation of R values (ΔR) versus the change of time (Δt) at MIBK concentration of i g L^{-1}. In addition, a plot of ln (C/C_0) versus time could obtain a straight-line relationship with the slope being equivalent to the anaerobic degradation rate of MIBK (k). For this set of experiments, the initial concentration of MIBK was set at 35 mg L^{-1}.

2.5. Statistical analysis

For the significance analysis of the experimental data, the SMA and SUR values of sludge between the tests and the control group were evaluated by analysis of variance (ANOVA) at a level of 0.05 using Origin version 9 (OriginLab Corporation, USA). The sum of squares for calculating the F values were obtained from the analysis of Origin software. The obtained F values were compared with the $F_{0.05}$ to determine whether there were significant differences between two groups of data.

3. Results and Discussion

3.1 Impact of MIBK on the removal of COD and phenols in the UASB reactor

The removal efficiency and effluent concentrations of phenols after MIBK addition in the UASB reactor are presented in Fig. 2. After acclimation, the anaerobic sludge exhibited an excellent ability to remove phenols and convert them into methane in the reactor. In the phase I, the effluent concentration of phenol was around 0.22 mg L^{-1} and the concentrations of catechol, resorcinol, and hydroquinone were not detected. The removal efficiency of COD reached above 97.0% in the influent COD of 5200 mg L^{-1} and total phenols of 1000 mg L^{-1} during this period. In the phase II, MIBK was added continuously with a dosage of 0.1 g L^{-1} in the influent and there were no observed changes in the effluent concentration of COD and phenols. On the first day of phase III (day 228), the concentration of MIBK was increased rapidly to 10 g L^{-1} and lasted for 24 h. This exposure of MIBK caused an increase in the effluent concentrations of COD and phenol, except catechol, resorcinol, and hydroquinone.

The concentration of phenol in the effluent only increased to around 1 mg L^{-1} on day 228. In the phase IV, a short-time exposure of MIBK made effluent phenol increase to 10.9 mg L^{-1} on day 242 and COD removal decrease to 72.5% on day 243. Although the impact of MIBK showed an adverse effect on phenols removal of about 1-2%, the effect was still limited. It was noteworthy that the recovery rate of COD removal was slower than phenols removal in the reactor. Many organics, such as phenols, long chain fatty acids and N-substituted aromatics could potentially inhibit the methanogenesis [16]. Specifically, this inhibitory effect would be worse when these organics had a slow hydrolysis rate and hydrophobic nature. Furthermore, there was a different toxic effect on the aceticlastic and hydrogenotrophic methanogens for these compounds [17]. Obviously, the impact of MIBK posed a threat to the performance stability of the anaerobic reactor. Performance stability was an important operational issue for anaerobic digestion of phenolic compounds. Poirier et al (2016) pointed out that the performance stability of anaerobic digestion was impaired by initial phenol concentrations above 1 g L^{-1} and the community shifts within anaerobic digestion microbiota were also observed [9]. Once the long-time exposure of MIBK on the anaerobic sludge caused the decrease of phenols removal, the increasing concentration of phenols inhibited the methanogenesis. Therefore, it was necessary to clarify the impact of MIBK on the methanogenic activity and phenols degradation activity of sludge.

3.2 SMA and SUR values of sludge in the UASB reactor

The SMA of sludge at different phases is shown in Fig. 3. The high SMA values of 2.742±0.167g COD-CH_4 g^{-1}VSS d^{-1} were obtained during the period of phase I. Previously, the SMA of sludge for treating phenolic wastewater was found in a range from 0.15 to 0.66 g COD-CH_4 g^{-1} VSS d^{-1} [18-20]. The SMA values in this study were much higher than the previous results, which might be the synthetic wastewater containing acetate and the formation of granular sludge. However, there was a reduction of 72.7%, 47.6% and 68.4% of the SMA values in the phases II, III and IV, respectively when the sludge exposed to MIBK. For the phase II, the low concentration of MIBK led to a little increase of OLR while a significant reduction of SMA was observed. Furthermore, the high concentration of MIBK during the phases III and IV caused an obvious increase of OLR in the reactor, but the SMA of sludge remained at a low level. Correspondingly, the toxic effect of MIBK on the methanogenesis could not be underestimated. The SUR of phenols at different phases is shown in Table 1. During the phase II, the exposure of MIBK (0.1 g L^{-1}) had an impact on the SUR of phenol from 37.35±4.12 to 18.44±0.48 mg phenol g^{-1}VSS d^{-1} and resorcinol from 46.72±0.11 to 23.68±3.35 mg resorcinol g^{-1}VSS, while the degradation rates of catechol and hydroquinone increased. The SUR results indicated that the effect of MIBK exposure varied considerably depending on the type of phenols. Subsequently, the short-time and immediate exposure of MIBK during the phases III and IV did not show a sustained inhibitory effect on the SUR of sludge. Certainly, the SUR of sludge could be rapidly recovered when the impact of MIBK was ended in the reactor.

3.3 Kinetic analysis of anaerobic degradation of MIBK

The biochemical specificity acquired by anaerobic microbial consortia when exposed to resorcinol, catechol and hydroquinone for acclimation [21]. It was necessary to clarify the kinetics of phenols degradation and methanogenesis under the exposure of MIBK to reveal the potential toxicity. Fig. 4a shows the anaerobic degradation rate of MIBK. The anaerobic degradation rate constant of MIBK was 0.0115 h^{-1} at the initial concentration of 35 mg L^{-1} (as shown in Fig. 4a). As a single substrate, acetone and MIBK were biodegraded at a rate of 1.7 and 2.23 d^{-1}, respectively by an acclimatized activated sludge [13]. Furthermore, the pseudo-first-order degradation rate constant decreased with the increase of volumetric loading rate of MIBK [22]. The results obtained from the activated sludge system were approximately 6-8 times higher than the observed rates in the anaerobic batch experiments. Ketones are energetically difficult for anaerobic microbial degradation. Anaerobic degradation of ketones required carboxylation-like reactions to introduce carboxylic groups into the carbon skeletons as primary activation reactions [11]. Estrada et al (2013) showed that fungal, bacterial and two-stage biofilters could remove only about 15.0 ± 5.3%, 25.4 ± 4.8%, and 30.0 ± 8.5%, respectively [23]. For treatment of acetone-butanol-ethanol fermentation wastewater in an anaerobic baffled reactor, almost all of the butanol and ethanol were degraded in the first compartment; however more compartments were involved in the removal of acetone [24]. Methyl ethyl ketone (MEK) was degraded at a low rate of 4.0 ± 0.74 and 0.51 ± 0.14 mg L^{-1} d^{-1}, respectively in the MEK-contaminated and uncontaminated sediment microcosms [25]. It required a long period of incubation to complete the mineralization of MEK under nitrate- and sulfate-reducing conditions [26]. The degradation rates of MEK under the iron-reducing conditions were lower than previously reported rates under methanogenic conditions and comparable to previously reported rates under nitrate- and sulfate-reducing conditions [25]. The biodegradation rates of these ketones in the aquifer environments were still not well characterized under anaerobic conditions and more specifically, under methanogenic conditions. The relative methane generation rates are shown in Fig. 4b. The relative methane generation rate constants decreased with the increase of MIBK concentrations. The actual and theoretical methane production ratio of MIBK was below 0.3 under a MIBK concentration of 0.1 g L^{-1}. Around 9% and 6% of MIBK were converted into methane under MIBK concentrations of 5 and 10 g L^{-1}, respectively. Wikandari et al (2015) pointed the experimental methane production of furaneol and mesifurane occupying less than 50% of theoretical methane production at a concentration of 5 g L^{-1} [12]. The results indicated that MIBK could be converted to methane while the conversion rate was slow. In addition, the relative methane generation rates exhibited a linear correlation with time (all of R^2 are above 0.9330). The relative methane generation rate constants were 0.00816, 0.00613, 0.00273, and 0.00207 d^{-1} at MIBK concentration of 0.1, 0.5, 5, and 10 g L^{-1}, respectively. It showed that a higher concentration of MIBK had a stronger negative effect on the bioconversion of MIBK to methane. In this study, the recalcitrance and toxicity of MIBK not only caused a slow degradation rate of MIBK, but also reduced the methanogenesis under anaerobic condition.

3.4 Effect of different MIBK concentrations on the SMA and SUR of sludge

The toxicity of different MIBK concentrations on the SMA and SUR of sludge were conducted in the batch tests. The effect of MIBK concentrations on the SMA of sludge is shown in Fig.5 and the statistical analysis result is supplemented in Table S1. As shown in Fig. 5, the SMA values were similar at the MIBK concentrations of 0, 0.1, and 0.5 g L^{-1}, which were 0.750±0.022, 0.814±0.147, 0.782±0.047 g COD-CH_4 g^{-1}VSS d^{-1}, respectively. The calculated F values were 0.18469 and 0.37118, respectively at MIBK concentrations of 0.1 and 0.5 g L^{-1}, which were lower than the corresponding $F_{0.05}$ values. However, the F values obtained at MIBK concentrations of 5 and 10 g L^{-1} were far higher than their $F_{0.05}$ values. Thus, the toxicity of MIBK on the methane production was significant ($p>0.05$) when the MIBK concentrations reached 5 and 10 g L^{-1}. Certainly, the impact (10 g L^{-1}) of MIBK on phenols removal was underestimated in the UASB reactor due to the short-time exposure of MIBK and dilution effect. Although the SMA of sludge was near to zero at MIBK of 10 g L^{-1}, the complete inhibition was temporary and could be gradually alleviated according the kinetic tests of MIBK. The SUR tests were used to describe the influence of MIBK on the phenols degradation rate of anaerobic sludge. The effect of MIBK concentrations on the SUR of sludge are shown in Fig.6 and the statistical analysis result is supplemented in Table S2. In the control groups, the SURs of phenol, catechol, resorcinol, and hydroquinone were 18.44±0.48, 41.49±0.30, 23.68±3.35, and 12.40±0.60 mg g^{-1}VSS d^{-1}, respectively. These phenolic compounds could be degraded efficiently by the acclimated anaerobic microbes, but they had different

SUR values among them. Previously, Latkar et al (2003) reported that the order of degradation was resorcinol>catechol>hydroquinone in an upflow fixed film-fixed bed reactor, and catechol had an un-competitive inhibition on resorcinol degradation [27]. As shown in Fig. 6, the low concentrations of MIBK (0.1 and 0.5 g L^{-1}) caused a slight adverse effect on the degradation rates of phenols. High concentrations of MIBK had a serious inhibitory effect on the phenols degradation activity of sludge. The SUR values of phenol, catechol, resorcinol, and hydroquinone swiftly decreased to 3.14±0.94, 5.86±0.13, 2.66±0.11, and 4.46±0.2 mg g^{-1}VSS d^{-1} at MIBK concentration of 5 g L^{-1} and 1.30±0.42, 9.18±2.52, 0.21±0.01, and 1.93±0.54 mg g^{-1}VSS d^{-1} at MIBK concentration of 10 g L^{-1}, respectively. Interestingly, the impact of MIBK on these phenolic compounds was different. Especially, the maximum and minimum reductions of SUR values were around 99% and 78%, respectively, which were obtained from the degradation of resorcinol and catechol after exposure to 10 g L^{-1} of MIBK (Fig. 6a and c). So, the long-time exposure of high concentration of MIBK on anaerobic sludge might cause temporary failure due to the toxic effect on methanogenesis and phenols degradation. For the microbial growth process, Chan and Peng (2008) found that the degree of inhibitive effect was methyl isopropyl ketone (MIPK) > methyl ethyl ketone (MEK) > acetone [28]. Furthermore, MIBK showed the most inhibitive effect on the degradation of MEK [29]. As a high-priority toxic chemical, MIBK was extensively used for phenols extraction from the coal gasification wastewater in China, but the impact of MIBK on performance stability of the anaerobic reactor was long been ignored. This study provided a direct evidence for the potential impact of MIBK on phenols degradation and methanogenesis. The temporary inhibitory effect of MIBK became a threat to the performance stability of the anaerobic reactor. Therefore, the industrial phenols extraction installations should be required to avoid the leakage of MIBK in the influent of the anaerobic reactor for preventing performance failure.

Conclusion

The impact of MIBK showed a low toxicity effect on the removals of phenols, but the SMA values of the sludge had a significant reduction in the UASB reactor. The anaerobic sludge exposed to MIBK suggested partial inhibition in the bioconversion of MIBK to methane. Anaerobic degradation of MIBK fitted well with the pseudo-first-order kinetic behavior. Furthermore, high concentration of MIBK had a higher inhibition on the methanogenesis than phenols degradation. The toxicity effect of MIBK on phenols degradation varied considerably depending on the type of phenols. These results indicated that the long-time exposure of MIBK could cause negative impacts on the activity of sludge and therefore its concentration control became critical for the extraction unit.

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Table 1

Table 1 The SUR of phenols at different phases.

Periods	Phenol	Catechol	Resorcinol	Hydroquinone
	mg g^{-1}VSS d^{-1}	mg g^{-1}VSS d^{-1}	mg g^{-1}VSS d^{-1}	mg g^{-1}VSS d^{-1}
Phase I	37.35±4.12	36.09±0.03	46.72±0.11	6.94±1.51
Phase II	18.44±0.48	41.49±0.30	23.68±3.35	12.40±0.60
Phase III	38.67±1.04	66.66±10.76	16.00±3.32	32.07±5.50
Phase IV	61.03±3.13	44.47±1.57	64.09±2.23	8.39±0.45

Figure 1
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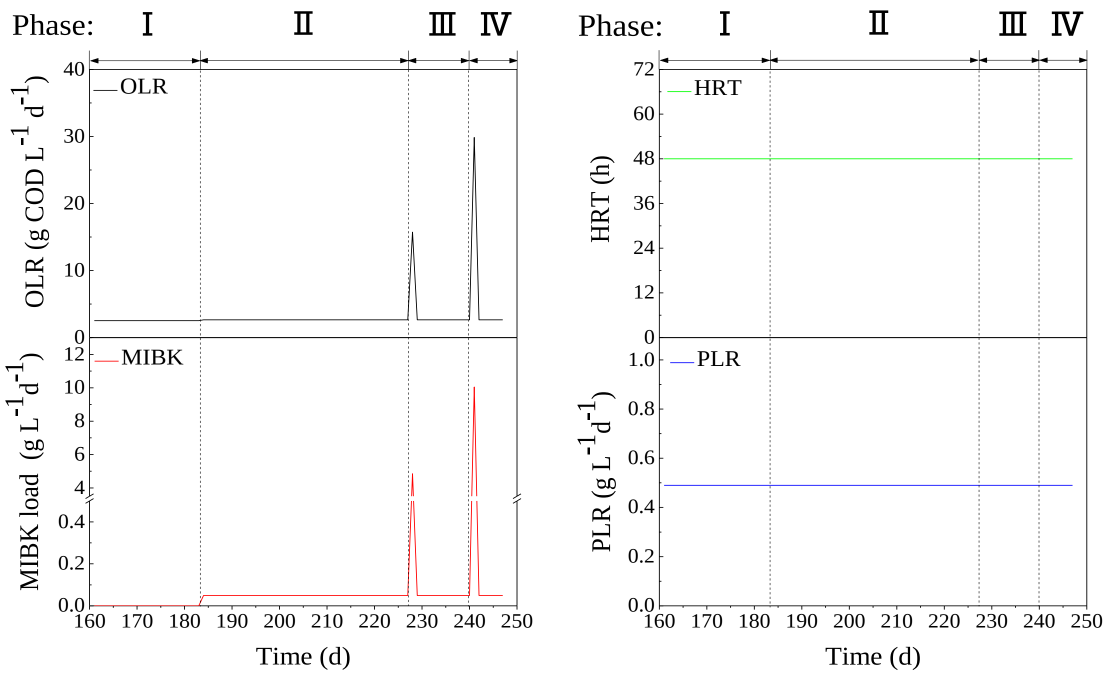

Fig. 1. The operational conditions of different phases in the UASB reactor. (OLR, organic loading rate; HRT, hydraulic retention time; PLR, phenols loading rate; Phase I: control period, 161-183 d; Phase II: continuous dosing of 0.1 g L^{-1} MIBK in the influent, 184-227d; Phase III: short-time exposure of 10 g L^{-1} of MIBK in the influent on day 228, 228-240 d; Phase IV: immediate exposure of 10 g L^{-1} of MIBK in the reactor on day 241, 241-247d)

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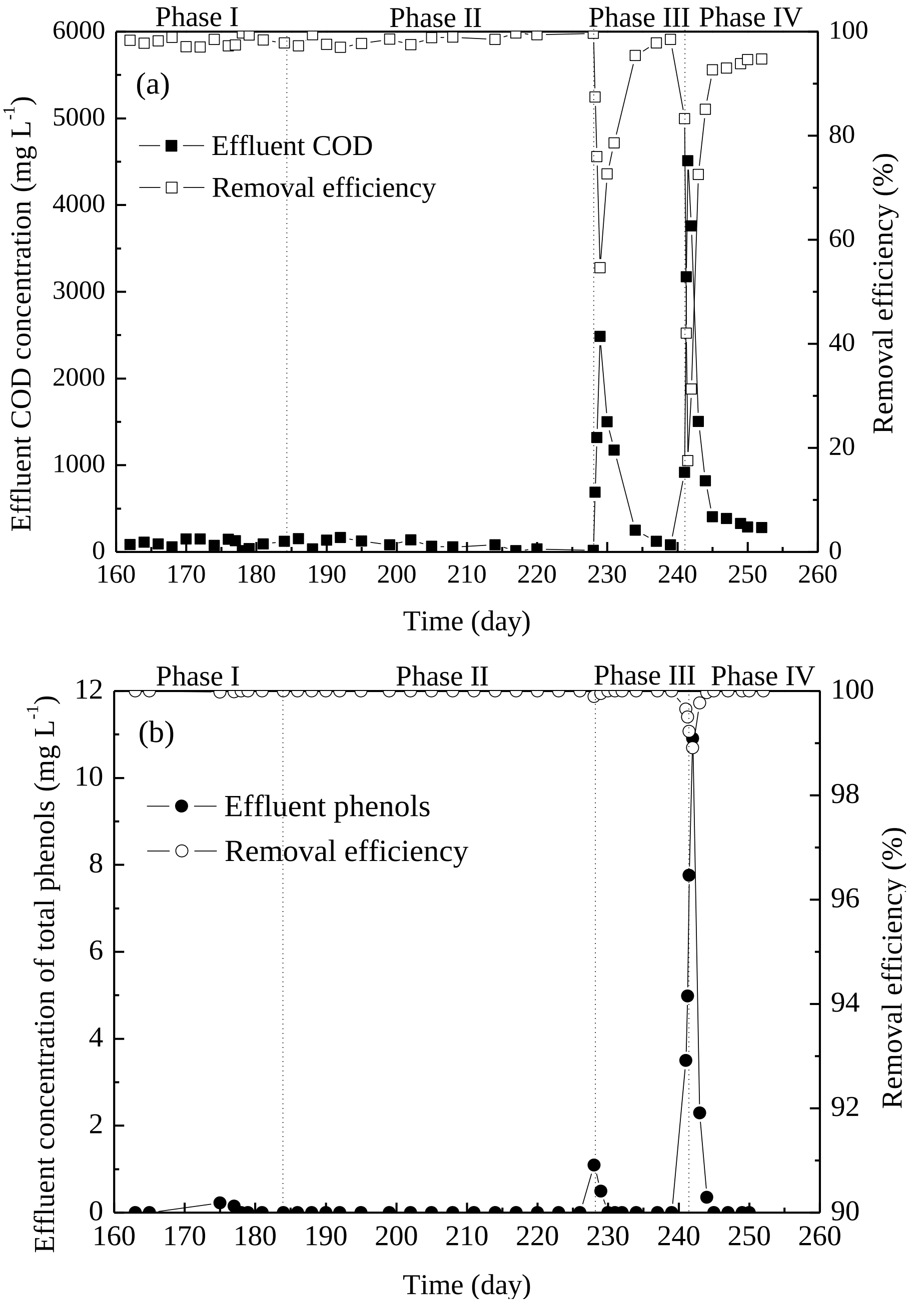

Fig. 2. Impact of MIBK on the performance of the UASB reactor (a) COD, (b) total phenols.

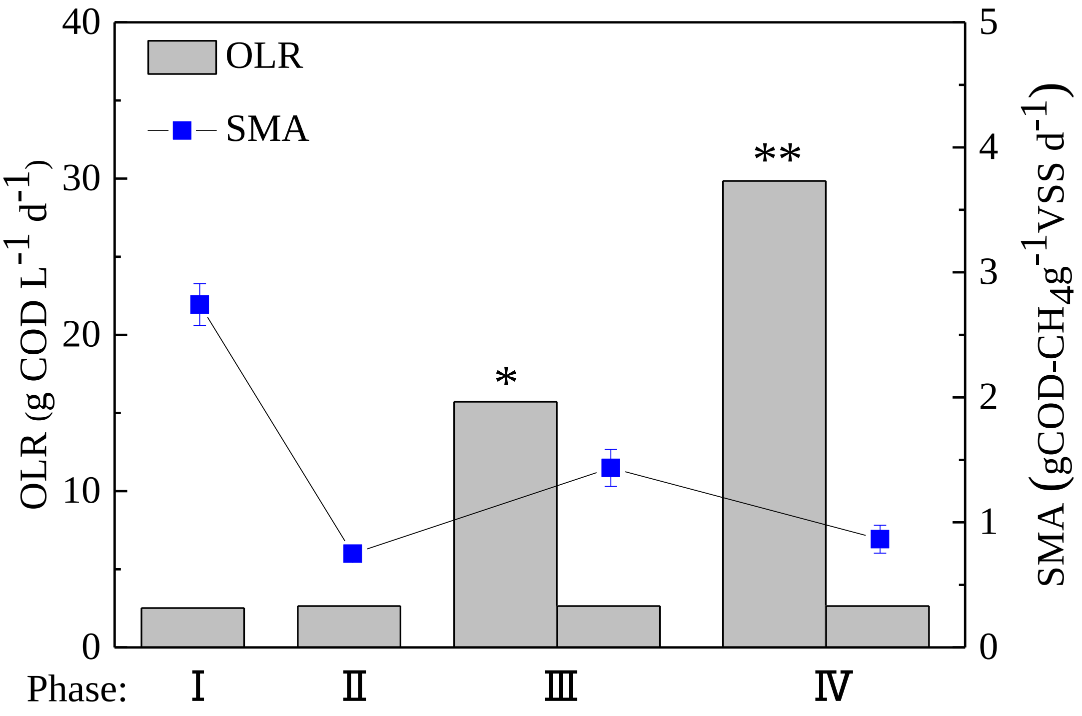

Fig. 3. The SMA of sludge at different phases. (*, short-time exposure of 10 g L^{-1} of MIBK in the influent on day 228; **, immediate exposure of 10 g L^{-1} of MIBK in the reactor on day 241).

Figure 4
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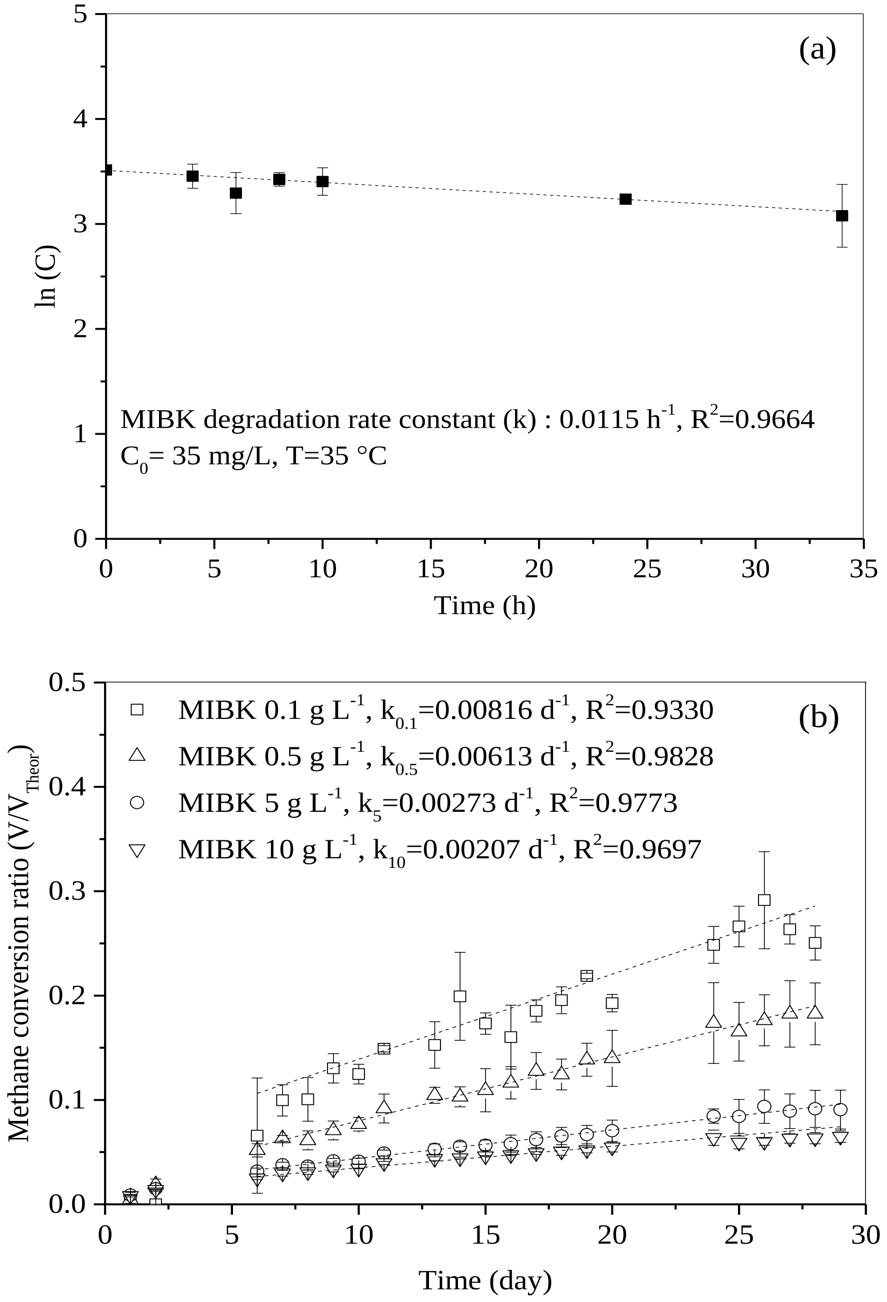

Fig. 4. The anaerobic degradation rate and relative methane generation rates of MIBK (a, anaerobic degradation rate constant; b, relative methane generation rate constant).

Figure 5
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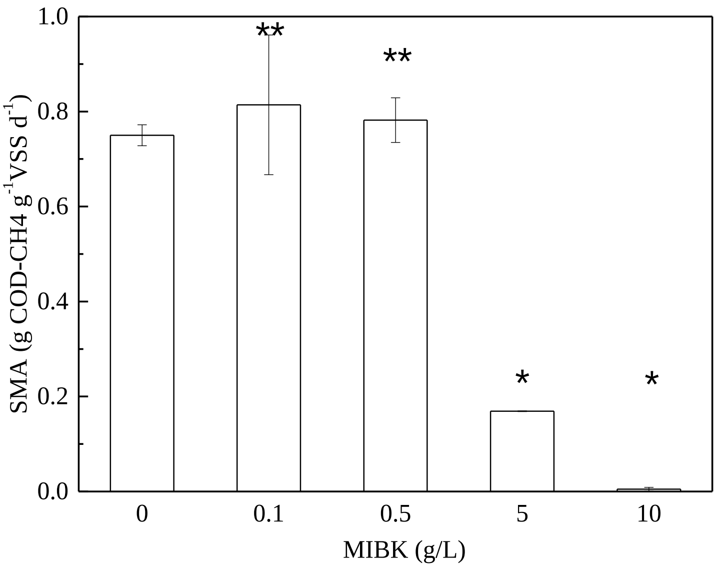

Fig. 5. Effect of different MIBK concentrations on the SMA of sludge

(**, is not significant at the 0.05 level; *, is significant at the 0.05 level).

Figure 6
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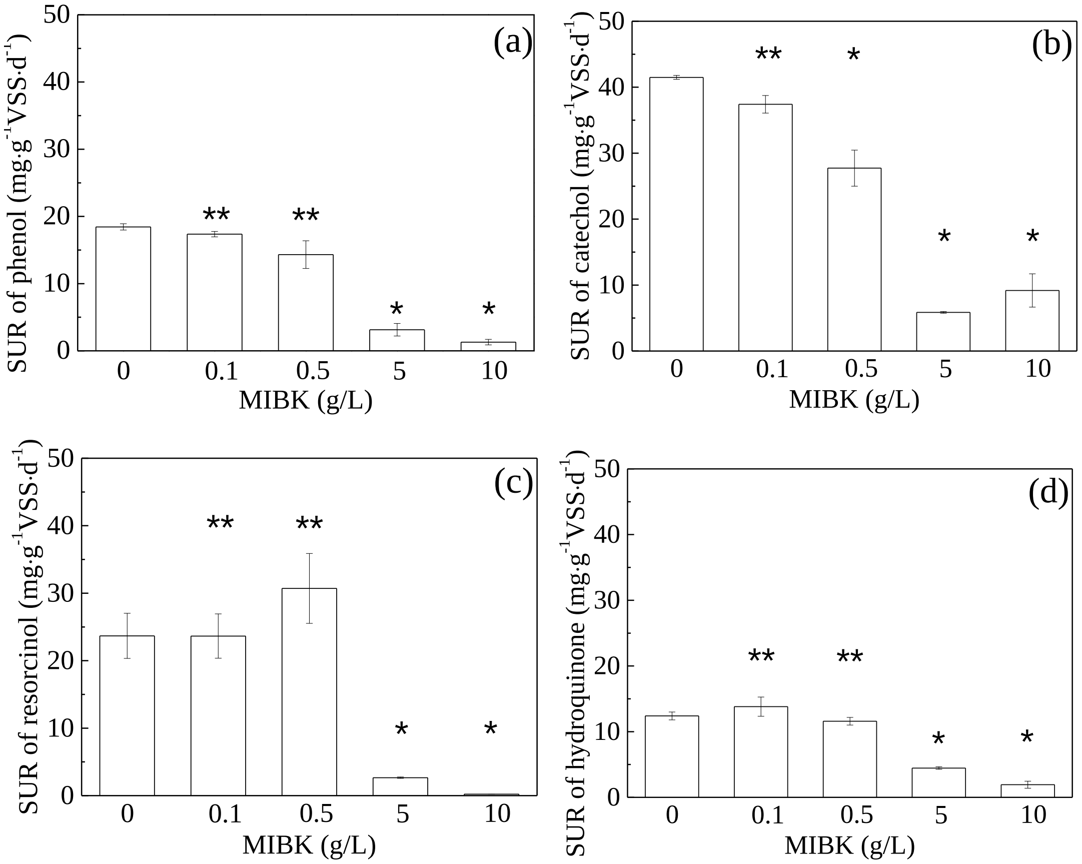

Fig. 6. Effect of different MIBK concentrations on the SUR of sludge (a, the SUR of phenol; b, the SUR of catechol; c, the SUR of resorcinol; d, the SUR of hydroquinone; **, is not significant at the 0.05 level; *, is significant at the 0.05 level).

Table S1 The statistical analysis results for the SMA tests

MIBK concentration (g L^{-1})	Sum of Squares	F Value	Prob>F
0.1	0.00394	0.18469	0.70925
0.5	9.57284E-4	0.37118	0.60435
5	0.32632	722.40151	0.00138
10	0.53726	1150.57494	8.67999E-4

Table S2 The statistical analysis results for the SUR tests

Phenolic compounds	Concentration of MIBK (g L^{-1})	Sum of Squares	F Value	Prob>F
Catechol	0.1	16.77968	2.33622	0.41987
	0.5	189.33760	25.02066	0.03772
	5	1269.14063	12212.08203	8.18761E-5
	10	1043.61302	162.11653	0.00611
Resorcinol	0.1	22.44590	0.51842	0.70068
	0.5	49.42090	1.29867	0.37255
	5	442.05063	39.35102	0.02448
	10	550.79396	49.07928	0.01977
Hydroquinone	0.1	2.69402	0.31381	0.78383
	0.5	0.66422	0.94589	0.43335
	5	63.04360	157.60900	0.00629
	10	109.62090	168.23343	0.00589
Phenol	0.1	1.15563	2.93511	0.22881
	0.5	16.93323	3.78885	0.19098
	5	233.93703	210.90133	0.00471
	10	293.77960	738.41800	0.00135