

Performance of an anaerobic baffled reactor (ABR) for the pretreatment of dyeing industry wastewater

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ABSTRACT

An anaerobic baffled reactor (ABR) for the pretreatment of dyeing industry wastewater was investigated. The influence of different hydraulic retention times (HRTs) on the profiles of chemical oxygen demand (COD), biochemical oxygen demanded (BOD), color, oxidation reduction potential (ORP) and volatile fatty acid (VFA) was examined. Results showed that the ABR can effectively remove COD and color from the raw wastewater, and the BOD/COD ratio can increase to more than 0.3. The reactor's efficiency in removing VFA decreased as the HRT decreased and ORP remained less than -165 mV. This indicates that the ABR process is suitable for pretreating the dyeing industry wastewater, forming good conditions for subsequent aerobic biodegradation.

Keywords: Anaerobic baffled reactor; Biodegradation; Dyeing industry wastewater

1. Introduction

Dyeing industry wastewater is characterized by high chromaticity, complex composition and poor biodegradability [1–3]. The effective treatment of the wastewater presents a great challenge to professionals in the field of environmental protection throughout the world. Approximately 60% of the components in dyeing industry wastewater are azo dyes and aromatic amines, and most azo dyes can be effectively decolorized and degraded only through anaerobic treatment. However, aromatic amines have higher toxicity [4–6] than azo dyes. Existing treatment processes such as coagulation, oxidation and electrolysis cannot effectively remove these aromatic amines.

In the anaerobic process, microbial hydrolytic acidification is used to facilitate the disintegration, substitution, or decomposition of recalcitrant organics and their chromophoric groups [7,8]. The anaerobic baffled reactor (ABR)

is one of the most effective methods for treating many wastewaters and has been widely applied. The ABR is a new high efficiency anaerobic reactor in which vertical baffle plates are used to separate the inner space of the reactor into several compartments. Each compartment is further divided into up-flow and down-flow chambers. Because each compartment works almost independently, gradient microbial phases can be cultured successively within these compartments, leading to the temporal and spatial separation of different stages of the anaerobic reaction [9–11].

Thus, the ABR has many favorable features, such as high efficiency, separation of the microbial phases, and operational stability. Currently, the ABR has been widely used for the treatment of industrial wastewater, and can effectively increase the biodegradability performance [12–14]. Ozdemir et al. [15] reported a method for the treatment of dyeing industry wastewater using an ABR. The experimental results showed that the removal rates of chemical oxygen demand (COD) and azo dyes were both 98%.

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However, research has shown that anaerobically treated dyeing industry wastewater contains a high concentration of ammonia nitrogen. Therefore, we developed an ABR reactor for the pretreatment of the dyeing industry wastewater. The objective of this research was to investigate the overall performance of the reactor and the factors that influenced the performance.

2. Experimental apparatus and methods

2.1. Experimental apparatus

The ABR used in this experiment (Fig. 1) was made of Plexiglas, with an effective height of 300 mm and an effective volume of 45 L. The inner space of the ABR was divided into five compartments, and the width ratio between the up- and down-flow chambers in each compartment was 4:1. A guide plate inclined at 45° was placed at the lower end of each baffle plate. There was a sampling port at the top of each compartment and a sludge-discharging port at the bottom of each compartment. A secondary sedimentation tank was serially connected to the ABR.

2.2. Seed sludge

The seed sludge used in the ABR experiment was a mixture of two different sludges. One was a flocculent sludge taken from an anaerobic hydrolysis tank of a wastewater treatment plant in an industrial park (Changshu, China), and the other was a granular sludge taken from an internal circulation reactor for the treatment of paper-making wastewater (Wuxi, China). The sludges were mixed in a ratio of 4:5 (flocculent sludge to granular sludge), producing a mixed sludge that was dark brown in color. The concentration of suspended solids (SS) in the mixed sludge was 36.5 g/L, and the ratio between the volatile suspended solids (VSS) and SS was 0.51:1. The seed sludge was added into the five compartments of the ABR at a ratio of 2:1:1:1:1.

2.3. Raw wastewater

Raw wastewater was a mixture of actual wastewater and glucose; initially, the quantity of glucose added to 1 L of wastewater was 0.3 mg. Approximately 80% of the actual wastewater was comprised of dyeing industry wastewater and small amounts of other industrial wastewater and domestic sewage. Therefore, the raw wastewater used in

the experiment was considered to be typical of wastewater produced by the dyeing industry. The quality of the raw wastewater is summarized in Table 1.

2.4. Operational procedure

The operational procedure of the experiment consisted of three phases: a start-up phase, a load-raising phase and an operational phase. (1) In the start-up phase, the ABR was operated with a continuous flow in a low loading mode. The hydraulic retention time (HRT) in the early start-up phase was 32 h, which was gradually decreased to 24 h. The proportion of dyeing industry wastewater in the influent mixture of wastewater and glucose was gradually increased over time. The COD was approximately 1000 mg/L and the average start-up loading rate was 0.97 kg COD/(m³·d). (2) In the load-raising phase, the ABR was operated stepwise under HRTs of 32, 24, 18, 14 and 10 h, and the temperature was maintained at 20°C. Furthermore, no glucose was added to the influent wastewater. (3) In the operational phase, the ABR was operated with at a HRT of 24 h, dissolved oxygen (DO) was maintained at 0.1–0.5 mg/L and the reaction temperature was maintained at 20°C.

2.5. Analytical methods

The analytical methods stipulated in the Chinese National Standards were adopted for the determination of COD, 5-day biochemical oxygen demand (BOD₅), volatile fatty acids (VFA), pH, mixed liquor suspended solids, mixed liquor volatile suspended solids, temperature, ammonia nitrogen, chromaticity, oxidation reduction potential (ORP) and DO [16]. A gas chromatography–mass spectrometry (GC–MS) method (TQ8030, Japan) was used for the analysis of organic substances in the wastewater. A B-5 type low-polarity capillary column was used with a helium carrier gas flow rate of 0.8 mL/min and consecutive column temperatures of 60°C (2 min), 10°C (2 min) and 300°C (30 min). Electron ionization was used as the detector in the mass spectrometry, with the electron energy set to 70 eV, source temperature to 200°C, amplifier voltage to 1050 V, and full scan mode used at a speed of 500 u/s and range of 35–400 u. The extraction of organic substances in the wastewater was conducted in accordance with the methods for sampling and analyzing industrial wastewater used by the United States Environmental Protection Agency [17].

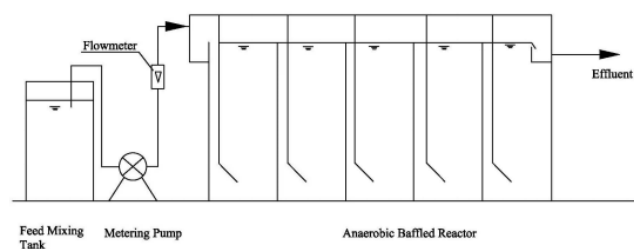


Fig.1. Schematic diagram of ABR experimental apparatus.

Table 1
The raw wastewater quality

Water quality index	Range	Mean value
COD/mg·L ⁻¹	418–766	517
BOD ₅ /mg·L ⁻¹	574–124	95
BOD ₅ /COD	0.15–0.23	0.2
Chromaticity/times	250–512	380
pH	7.86–8.96	8.37
NH ₃ -N/mg·L ⁻¹	9.4–75.9	38.7

3. Results and discussion

3.1. Start-up of the ABR

In the early start-up phase, the HRT was 32 h, and the influent COD was controlled to be approximately 1000 mg/L, with 20% of the COD attributed to the actual dyeing industry wastewater (and 80% attributed to the added glucose). In the middle start-up phase, the HRT was kept at 24 h, and the COD attributed to the dyeing industry wastewater constituted an increasingly higher proportion of the total COD of the influent. This proportion was 20, 40, 60, 75 and 100%, respectively, on the first successive five days after each incremental increase in loading rate, before another round of load-raising began.

In the early start-up phase (days 0–5), the COD removal rate was as high as 60%, because most of the COD was attributed to the easily degradable glucose, and some of the pollutants, such as particulate COD and suspended solids, were only adsorbed by sludge [18]. During the first 20 days of the middle start-up phase, the COD removal rate in the reactor initially increased but then decreased. The initial upward tendency was attributed to the gradual adaption of microbes to the new environment and their gradually increasing ability to degrade glucose. However, with the increasing proportion of dyeing industry wastewater in the influent, particularly from day 18 onward when it constituted the total volume of the influent, the COD in the influent tended to be recalcitrant, which resulted in a decreased efficiency of the microbes to utilize the substrate and consequently decreased the COD removal rate. On day 25 of the experiment, the influent COD was rapidly increased to 1200–1500 mg/L by adding glucose into the influent. However, the effluent COD remained unchanged at approximately 400 mg/L. The operating conditions of the reactor were maintained as before, which indicates that the whole system had a “buffering” capacity to resist the impact of increased loading. On day 32 of the experiment, the COD removal rate of the system remained at 40% when no glucose was added in the influent, and the reactor reached a steady state. During this phase of the experiment, the sludge yield rate was 0.22–0.28 kg VSS/kg BOD.

During the experiment, the influent chromaticity fluctuated substantially, with a mean value approximately 300 times, ranging from 200 times to 500 times. The effluent chromaticity was about 105 times, ranging from 40 times to 150 times. The mean removal rate of chromaticity was approximately 62.2%. As shown in Fig. 2b, the performance of the ABR was satisfactory in terms of reducing chromaticity. Even though the influent chromaticity fluctuated, decolorization remained stable. This indicates that the reactor had a buffering capacity against influent chromaticity. For example, the azo dyes were converted into aromatic amines under anaerobic conditions by a series of open-ring reactions, and the aromatic amines were degraded into some small molecular substances by some metabolite from the anaerobic digestion process. The small-molecule substances can be utilized by microorganisms. Thus, the aromatic amines concentration of the effluent was zero, which satisfies “the discharge standard of water pollutant for dyeing and finishing of textile industry in China”(GB4287-2012).

During the early and middle start-up phase, the biodegradability remained high due to the glucose added to the

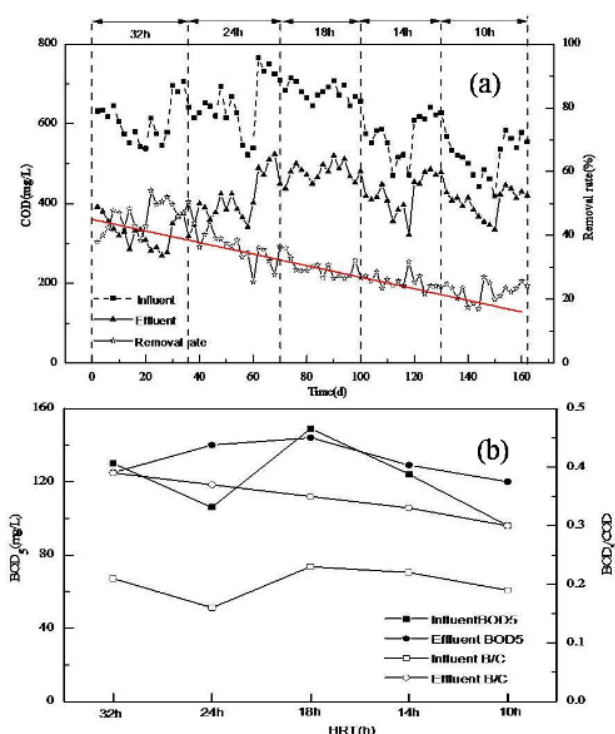


Fig. 2. Profiles of COD, BOD₅ and BOD/COD ratio at different HRTs.

influent, and BOD₅ was not detected during this period. As the experiment progressed, the microbes within the reactor gradually adapted to the environment of the influent and began to play an increasingly important role in the system. The hydrolytic and acidogenic bacteria contained therein degraded large-molecule substances such as residual dyes, their assistants, and sizing agents into small-molecule organics, which consequently greatly improved the biodegradability of the effluent [19,20]. The influent BOD₅ concentration was 130–156 mg/L in the steady-state phase while the effluent BOD₅ concentration was 110–180 mg/L. The mean influent BOD/COD ratio was 0.21 and the mean effluent BOD/COD ratio was 0.36, which indicates a significant improvement in biodegradability. On the basis of these results, reactor start-up was considered to be successful.

3.2. The influence of HRT on the operation of the ABR

During this experiment, the HRT was consecutively adjusted to 32, 24, 18, 14 and 10 h, so that its influence on the operational performance of the ABR could be investigated.

3.2.1. The influence of HRT on COD and BOD₅ removal

As shown in Fig. 2a, the influent COD was 418–766 mg/L. At HRTs maintained at 32, 24, 18, 14, and 10 h, the effluent COD was 270–524 mg/L and the average COD removal rates were 46.1%, 36.3%, 29.4%, 25.5%, and 22.5%, respectively. The COD removal rate peaked when the HRT was 32 h. The long HRT ensured a prolonged con-

tact time between organics and sludge, which provided a favorable environment for anaerobic or facultative bacteria, and consequently enhanced the efficiency of organic degradation in the wastewater. In addition, the prolonged HRT contributed to the adsorptive retention of the sludge and the precipitation of large organic particles; both processes can effectively remove part of the insoluble COD, such as suspended or colloidal COD. In contrast, shorter HRTs changed the hydraulic state of the system resulting in rapid water flow between the baffles. Consequently, the flocculent sludge, which has comparatively poor settleability, could be flushed up to the upper layer of water within the reactor. If the hydraulic load was disproportionately large, the dead volume in the reactor would increase, which could lead to both channel flow and short-circuiting flow, with some of the granular sludge becoming deactivated and then flushed out of the reactor. With a shortened contact time between the organics in the influent and the microbes in the reactor, the organics were not sufficiently degraded, which consequently led to a reduced rate of COD removal.

The BOD₅ and BOD/COD (B/C) ratio profiles for both the influent and the effluent at different HRTs are shown in Fig. 2b. During the experiment, when the influent BOD₅ concentration was 96–149 mg/L, the concentration of effluent BOD₅ was 120–144 mg/L. The anaerobic microorganisms could not effectively degrade the BOD, and the degradation quantity of BOD was limited. In addition, some of the refractory COD was converted into BOD when the HRT was decreased, adding to the effluent BOD. Consequently, the BOD removal was not significantly affected by decreasing the HRT. With a shortening of the HRT, the effluent B/C ratio decreased, and reached its lowest value (0.3) when the HRT was 10 h (the shortest HRT examined). In contrast, the effluent B/C ratio was at its maximum (0.39), when the HRT was 32 h (the longest HRT examined). This is because the B/C ratio of the effluent is directly influenced by that of the influent, and a shortened HRT will lead to incomplete degradation of large-molecule substances (such as aromatic hydrocarbons) by hydrolytic and acidogenic bacteria, which consequently results in poor biodegradability of the effluent.

During this part of the experiment, the sludge yield rate was 0.16–0.24 kg VSS/kg BOD, which was lower than during the start-up period.

3.2.2. The influence of HRT on color removal

As is shown in Fig. 3, when the HRT was maintained at 32, 24, 18, 14 and 10 h, the color removal rate was 60.6, 63.5, 62.6, 55.9 and 51%, respectively, which indicated that the ABR had the desired effect by decolorizing the wastewater. Dye molecules are heterocyclic compounds (including polycyclic aromatic hydrocarbons), whereas anaerobic microbes, particularly hydrolytic and acidogenic bacteria, contain a range of ring-opening enzymes that are very diverse and easily activated. The existence of hydrolytic and acidogenic bacteria in the reactor facilitated the anaerobic fermentation and effective degradation of polycyclic aromatic hydrocarbons and heterocyclic compounds by ring-opening reactions. The ring-opening reaction destroys the molecular structure of dye compounds and

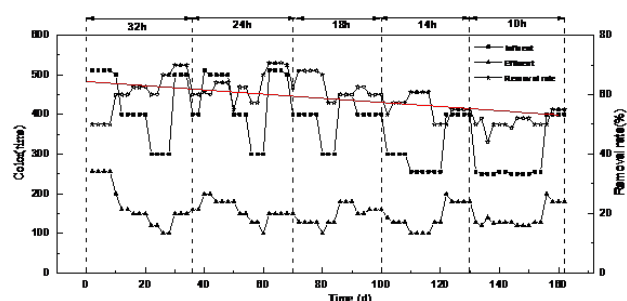


Fig. 3. Color removal at different HRTs.

the chromophoric groups contained therein, which consequently results in decolorization of the wastewater [3,7]. As HRT was shortened, the color removal rate in the reactor decreased. Color removal reached a minimum when the HRT was 10 h (the shortest HRT examined), because some of the dye molecules that were adsorbed on the sludge surface were flushed out of the reactor before they were sufficiently degraded by hydrolytic and acidogenic bacteria; the natural decomposition of the dye molecules was also greatly restricted by the shortened retention time [21]. Furthermore, when the influent color turned dark, the effluent from the reactor was generally light red or pink, which indicated that the ABR had the effect of decolorizing the wastewater.

3.2.3. The influence of HRT on oxidation reduction potential (ORP)

The ORP profiles when the HRT was 32, 24, 18, 14 and 10 h are shown in Fig. 4.

As is shown in Fig. 4a, the effluent ORPs at all HRTs were lower than the influent ORPs, and the average ORP of the effluent was about -150 mV, which indicates that the environment within the reactor was anaerobic. As shown in Fig. 4b, the ORP in all compartments increased as the HRT decreased. The average ORPs in each of the different compartments were -165 , -190 , -205 , -215 , and -222 mV, respectively. At a given HRT, the ORPs in the different compartments decreased along the flow direction. Other researchers have shown that acidogenic bacteria can tolerate very high ORPs, and can even proliferate under facultative conditions with an ORP ranging from $+100$ mV to -100 mV [22–24]. In contrast, a low ORP is required for the growth of methanogenic bacteria. Acidogenic bacteria were found to be highly adaptable to the environment and had a high metabolic rate. They grew mainly in the front compartments of the ABR, whereas the hydrogen-producing acetogenic and methanogenic bacteria that were responsible for the metabolism of ethanol and VFAs grew mainly in the rear compartments. These differences therefore led to a gradual decrease in the ORP in the different compartments along the flow direction.

The results demonstrate that different bio-phases produced separate distributions within the ABR. When the HRT was long, the substrate in the influent had sufficient contact with microbes, which therefore guaranteed the

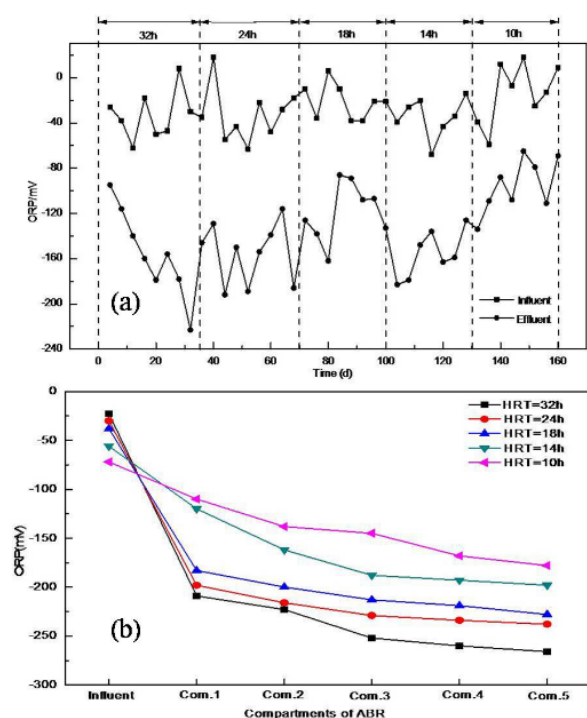


Fig. 4. ORP profiles at different HRTs.

complete degradation of organic substances. However, when the HRT was short, the degradation of organic substances by the microbes depended only on hydrolytic acidification [24]. Thus, for a full scale degradation process, a long HRT and low ORP should be maintained within the ABR to sustain the growth of hydrogen-producing acetogenic and methanogenic bacteria.

3.2.4. The influence of HRT on VFA

As shown in Fig. 5, the VFA profiles at all HRTs exhibited a stepwise decrease.

The dominant microbial communities in the first two ABR compartments were found to be acidogenic bacteria, while VFA-degrading bacteria were dominant from the third compartment onward. When the HRT was extended from 10 to 32 h, the total VFA in the first and second ABR compartments increased, and the activity of acidogenic bacteria also increased. The total VFA in the last three compartments decreased accordingly, which indicates that the activity of VFA-degrading bacteria was also enhanced by the extension of the HRT. In a study of the performance of an ABR for wastewater treatment Krishana et al. [25] also reported a stepwise decrease in the VFA concentration that started from the second ABR compartment. The results of the present experiment demonstrated that the ABR could effectively realize a distribution of bio-phases (i.e., acidogenic, hydrogen-producing acetogenic, and methanogenic bacteria) in the reactor and a stepwise dominance of different microbes in different compartments. Furthermore, the extension of HRT enhanced the metabolic activity of the microbes in the ABR.

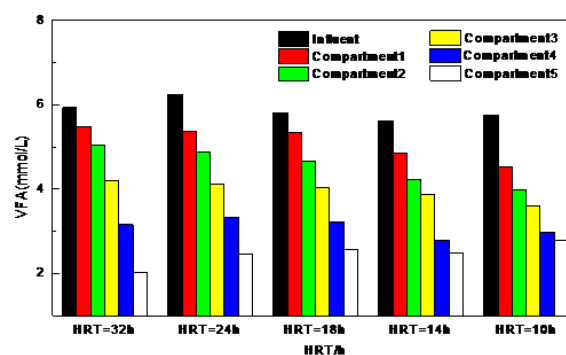


Fig. 5. VFA profiles at different HRTs.

Table 2
Organic substances detected by GC-MS analysis

Major organic substances	ABR influent	ABR effluent	A/O effluent
Straight-chain alkanes	10	15	15
Methyl alkanes	5	4	3
Cyclanes	1	1	1
Benzenes	1	1	1
Phenols	1	1	1
Aminobenzenes	1	1	–
Organic acids	1	–	–
Esters	4	2	–
Miscellanies	4	2	1
Unidentified components	8	5	1
Total (types)	36	32	23

3.3. GC-MS analysis of organic substances

The GC-MS analysis confirmed that the microbes in the ABR degraded complex organics or large-molecule organics into intermediate products; for example 2,5-dichloro-*p*-phenylenediamin was detected in the ABR effluent. Methylbenzene and 2,6-di-*tert*-butyl-*p*-cresol were detected in both water samples; however, from the total inorganic carbon (TIC) levels of the influent and effluent. Phthalates, a group of recalcitrant substances widely used as a plasticizer in the dyeing industry, were detected in both the raw water and the ABR effluent.

There is one reason for such an overall improvement: the internal circulation of the ABR process extended the retention time of recalcitrant organics in the reactor, which consequently enhanced their microbial degradation.

The ion current chromatograms was shown in Table 2, a large quantity of C₂₀–C₃₃ straight-chain alkanes were detected in the ABR effluent. This was a result of the effective microbial degradation of large-molecule organics in the wastewater, such as through the ring-opening decomposition of cyclic compounds. The existence of these straight-chain alkanes confirms the desirable effect of microbial degradation of recalcitrant organics in the ABR compartments.

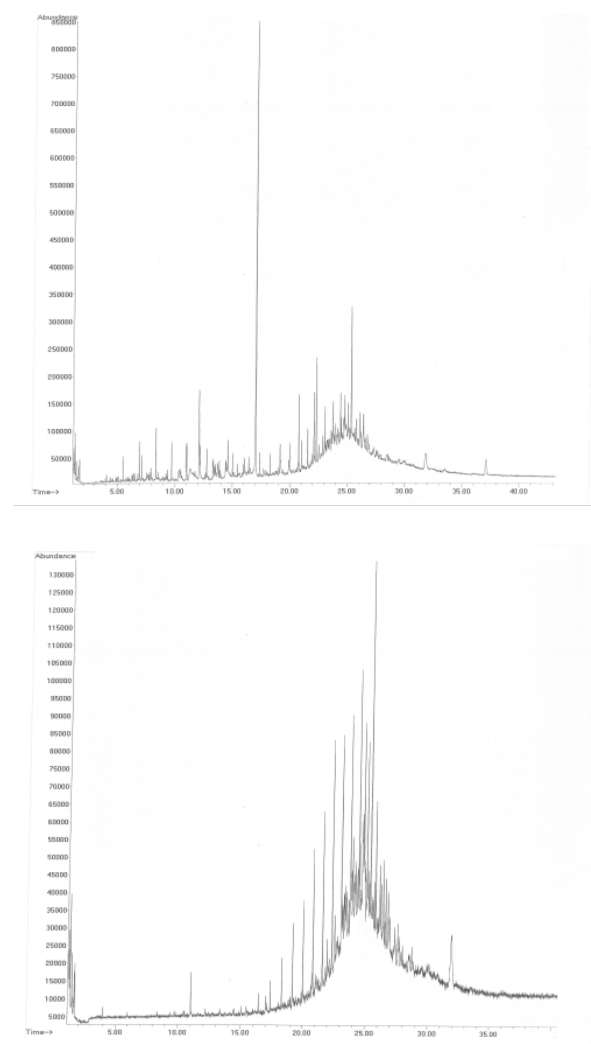


Fig. 6. GC-MS chromatograms of (a) raw water and (b) ABR effluent.

4. Conclusions

The ABR is suitable for pretreatment of dyeing industry wastewater, achieving COD removal in excess of 40% and 62.2% decolorization. The biodegradability of the ABR effluent was enhanced significantly compared to the influent, and the ABR effluent can be post-treated using an aerobic process. Both the concentration and number of different complex organics in the effluent treated by the ABR process decreased substantially compared to the levels in the raw water; these improvements were helpful in forming a good environment for a post-treatment process. Nevertheless, the treatment performance of the ABR was influenced significantly by HRT, with poorer removal of measured parameters as HRT was shortened.

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