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# Biological pretreatment of Yellow River water

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Abstract: Bio-ceramic filter(BF) and moving-bed biofilm reactor(MBBR) were used for biological pretreatment of Yellow River water in this study. The BF only had slight advantage over MBBR for TOC and ammonia removal. However, like UV<sub>254</sub>, the average removal rate of THMFP in the BF was much higher than that in the MBBR. UV<sub>254</sub> removal did not show obvious correlation with trihalomethane formation potential(THMFP) removal. Hexachlorocyclohexane could be effectively removed in both BF and MBBR. As for diatom and cyanobateria removal the MBBR had better performance than the BF, which was contrary to the average chlorophyll-a(Chl-a) removal rate. The proposal was made in this study that biological flocculation and sedimentation of sloughed biofilm should play a more important role on algae removal in the MBBR than in the BF. The BF and MBBR could effectively remove microcystins. Moreover, MBBR could be a promising technology for biological pretreatment.

Keywords: bio-ceramic filter(BF); moving-bed biofilm reactor(MBBR); Yellow River; biological pretreatment

#### Introduction

Yellow River is one of the largest drinking water sources in China which is now faced with serious problems caused by pollution and eutrophication. The tap water quality of most of water supply systems, which abstract water from Yellow River, cannot meet increasingly stringent drinking water quality criteria due to limitation of conventional drinking water treatment. The main processes of the conventional drinking water treatment consist of sedimentation. coagulation/flocculation, phase separation, rapid filtration, and disinfection, for removing turbidity, color and pathogens. However, it cannot remove the ammonia, THM precursors, and various synthetic organic chemicals (SOCs) effectively, so that advanced water treatment has to be considered for the production of safer and cleaner drinking water.

Biological pretreatment process (prior to conventional treatment chain) is considered as an economic and effective treatment process to remove pollutants from raw water. The kind of advanced process has been widely studied in European and Asian countries. Among various bioreactors for pretreatment, the biological contact oxidation reactor (BCOR) and BF have been most widely studied in China, especially in the southern regions (Wang, 1999). They have many advantages such as improvement of sequential treatment chain, reduction of chlorine demand, less production of THMs, and increase of biological stability of finished water (Bruce, 1989). Unfortunately, the data concerning biological pretreatment of Yellow River water has not been available up to date.

MBBR is an innovative fixed biofilm reactor, which has gained increasing attention from wastewater treatment industry. It has been successfully applied for full-scale treatment of municipal and industrial wastewaters. MBBR is a continuously operating non-cloggable biofilm reactor with no need for backwashing low head-loss and high specific biofilm surface area. This can be achieved by having the biofilm grow on small carrier elements that move along with the water in the reactor. The movement is normally caused by aeration in the aerobic version of the reactors (Pastorelli, 1997; Rusten

1996; Aspegren, 1998). However, this innovative biofilm reactor has not been introduced for the pretreatment of drinking water.

The objective of this study was to investigate the feasibility of biological pretreatment of Yellow River water. The removal rates of various pollutants were evaluated in this study, which could be very useful and fundamental data for the design of future water supply project taking Yellow River water as raw water source.

## 1 Materials and methods

### 1.1 Experimental setup

Two kinds of bioreactors: BF and MBBR (Fig. 1 and Fig. 2) were used to investigate the feasibility of biological pretreatment of Yellow River water. The BF was cylinder made of plexiglas and with dimensions of 3 m high and 0.5 m of inside diameter (Fig. 1). The filter was filled with ceramic particles up to 2 m depth. Ceramic particles had an average diameter of 3—5 mm, a porosity of 0.09, a density of 1.56 g/cm³, and a specific surface area of 2.5 m²/cm³. Inlets for air influent were located at the bottom of the reactors. Liquid and gas phases flowed up through the filter in counter-current mode.

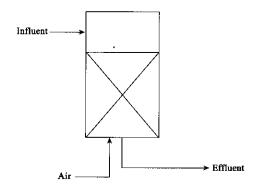


Fig.1 Experimental setup of BF process

The MBBR was cuboid made of steel with a total liquid volume of 6  $\text{m}^3$ . The reactor was filled 50% LT hollow ball media (density 0.98 g/cm<sup>3</sup>, diameter 100 mm, specific surface area 360  $\text{m}^2/\text{cm}^3$ ), occupying 11.5% of the

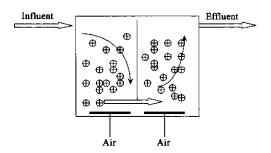


Fig.2 Experimental setup of MBBR process

reactors. Mixing and aeration were provided by pressurized air through aerators in the bottom of the reactor.

The study was performed in Shiyuan Water Works in Zhengzhou City in the year of 2004. The two reactors were fed with the same raw water, which was Yellow River water after sedimentation for sand removal. The influent flow for BF and MBBR was 1 and 4 m³/h respectively. The pH values of raw water ranged between  $8.0\!-\!8.5$ . Oxygen concentration in the both reactors was keep at  $4\!-\!5$  mgO $_2/L$ . During this study the water temperatures ranged between  $10\!-\!32\,^\circ\!\mathrm{C}$ . Before this study the two reactors had been operated for about seven months allowing for the maturation of biomass.

## 1.2 Analysis

Dissolved oxygen (DO), pH and water temperatures were determined using selective electrode. Total organic carbon (TOC) was determined by TOC analyzer. UV<sub>254</sub> absorbance and THMFP were determined according to the literature (Liu, 2003). Algae and Chl-a were determined according to Methods for the Examination of Water and Wastewater (WWMA, 1988). SOCs were determined using gas chromatography (GC) and liquid chromatography (LC) according to Sanitary Standard for Drinking Water Quality—2001. Microcystin was determined using enzyme-linked immunosorbent assays (Li, 2003).

## 2 Results and discussion

#### 2.1 TOC removal

There are a variety of organic compounds including natural and synthetic organics in polluted raw water for drinking water supply and it is extremely difficult to discriminate all these organic compounds if possible. Therefore, TOC analysis is often used as a surrogate parameter to measure the total amount of organic substances (Wang, 1999). As regards the prevention of THM generation, the TOC level is more important than the levels of easily biodegradable organic matter in water (Takasaki, 1990). As for TOC removal it is commonly believed that the BF always performed much better than the other traditional biological pretreatment processes like BCOR. It has ever been reported that TOC removal rate by the BF was almost twice that by BCOR(Wu, 1999).

The TOC removal by the BF and MBBR is shown in Fig. 3. During this study the TOC concentrations varied between 3.7 and 5.9 mg/L with an average of 4.4 mg/L, and the average removal rate in the BF(20.1%) was only slightly higher than that in MBBR(17.0%). The TOC removal rates in the two reactors did not show obvious relationship with the TOC in influent. However, the TOC removal rates in the BF

and MBBR were relatively higher (above 25 % and 30% respectively) when the TOC in influent reached the high level (above 5.3 mg/L), which indicated, to some degree, the two bioreactors had the buffer capacity for abrupt increase of organic loading.

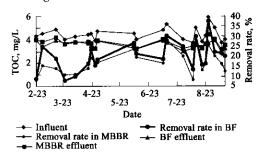


Fig. 3 TOC removal by BF and MBBR

## 2.2 UV<sub>254</sub> and THM precursor removal

Humic substances in natural waters have been shown to be especially reactive with a variety of oxidants and disinfectants that are used for the purification of drinking water, particularly chlorine. These substances react with chlorine to produce THMs and other halogenated disinfection by-products(DBPs), a number of which have been shown to cause cancers in laboratory animals.

UV<sub>254</sub> is a surrogate of humic substances in raw water for drinking water supplies. UV<sub>254</sub> usually shows good correlation with THM precursor and thus it is also regarded as a surrogate parameter of THM precursor(Wang, 1999; Wu, 1999). The  $UV_{254}$  removal by the BF and MBBR was shown in Fig. 4. During this study the UV<sub>254</sub> values varied between 0.069 and 0.2295 with an average of 0.150, and the average removal rate in the BF(20.3%) was much higher than that in the MBBR (6.5%). Humic substances have complicated and large molecular structure, and poor biodegradability. Therefore, in biofilm reactors humic substances are removed mainly by adsorption (Fang, 1995). In the BF, biological flocculation of biofilm and interception of filter layer could effectively absorb suspended matters and colloids that contain large amounts of humic substances, which played an important role in the removal of humic substances or UV254 . However, in the MBBR the media was under state of freefloating motion and thus biological flocculation of biofilm and interception of filter layer were very poor. Therefore, humic substances or UV<sub>254</sub> could not be effectively removed. THMFP indirectly presents the amount of THM precursor in waters (Wu, 1999). The THMFP removal by the BF and MBBR is shown in Fig.5. During this study the average removal rate of THMFP in the BF(36.2%) was also much higher than that in MBBR(22.1%). It was interesting to be noted that the ratio of the average removal rate of THMFP to that of UV254 in the BF(1.8) was much lower than that in MBBR(3.4), which indicated  $UV_{254}$  removal did not show obvious correlation with THMFP removal. This conclusion could be sustaniated by the operating data on a specific day, for example, July 26, the ratio of the average removal rate of THMFP to that of UV<sub>254</sub> in the BF was 1.1, much lower than that in MBBR(3.1). It brought about the question whether UV<sub>254</sub> removal rate could be used as a parameter of THM

precursor or THMFP removal rate in biological pre-treatment

even if  $UV_{254}$  had good correlation with THM precursor in raw water(influent). Therefore, it should be cautious when use  $UV_{254}$  removal to predict THM precursor or THMFP removal in biological pre-treatment processes or other treatment processes.

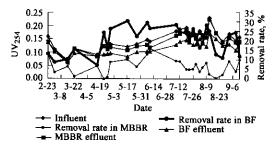


Fig. 4 UV254 removal by BF and MBBR

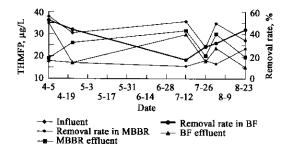


Fig. 5 THMFP removal by BF and MBBR

# 2.3 Algae, Chl-a and microcystin removal

Algae present an increasing problem worldwide due to production of excessive growths (blooms) as a consequence of increasing eutrophication in water bodies used for drinking supplies. Beside filter blockage in water treatment and offflavor and odor production, all of the cyanobateria (blue-green algae) which commonly form blooms including toxinproducing species and strains (Li, 2003). Cyanobaterial toxins present acute and chronic hazards to human health and include potent hepatotoxins (microcystins and nodularins) and neurotoxins. Microcystins are a family of related cyclic heptapeptides of which around 50 so far have been characterized. Microcystins are potent liver toxins whose toxicity can be attributed to their specific and irreversible inhibition of protein phosphatases 1 and 2A. As result of their biochemical activities, microcystins are tumor promoters, which is a cause for concern since the consumption of sub-acute levels may be harmful to human health. Therefore, it is important human exposure to microcystins (Dawson, 1998). The maximum admissible concentration (1 µg/L) of microcystins has been regulated for drinking water in many countries, including China (Bell, 1994). However, it is widely suspected many conventional water treatment methods are ineffectual in removing them (Zhu, 2003). In some Chinese cities, including Zhenzhou City, their existence in tap water has been reported (Meng, 2000).

During this study diatom and cyanobateria were the predominant algal species in raw water. The diatom and cyanobateria removal by the BF and MBBR are shown in Fig. 6 and Fig.7. The average diatom removal rate in the MBBR (48.6%) was similar to that in BF(47.4%). However, the difference of the diatom removal between the two biological

pretreatment processes fluctuated greatly during the study, which suggested different diatom removal mechanisms of the two reactors. The average cyanobateria removal rate in the MBBR (53.2%) was obviously higher than that in the BF (41.9%). Moreover, the difference of the cyanobateria removal between the two biological pretreatment processes also fluctuated greatly during the study.

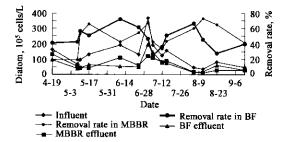


Fig. 6 Diatom removal by BF and MBBR

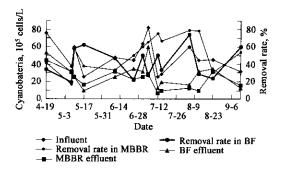


Fig. 7 Cyanobateria removal by the BF and MBBR

It is commonly believed the biological removal of algae may depend on several processes such as biofilm adsorption, biological oxidation, particulate flocculation and mechanical entrapment, protozoon's predacity, biological flocculation and sedimentation of sloughed biofilm (Wang, 1999). Unfortunately, there has been no definitive conclusion on algae removal mechanism of biological treatment up to date. Based on comprehensive experiments, Wu suggested biofilm adsorption, and biological flocculation and sedimentation of sloughed biofilm should play a major role on algae removal while the role of biological oxidation and protozoon's predacity should be minor (Wu, 1999). Since the media in the MBBR are under free-moving state the algae removal by biofilm adsorption, and particulate flocculation mechanical entrapment in the MBBR should be poorer than that in the BF. However, biofilm attached on media tended to be sloughed more easily when media was constantly moving. Therefore, the feasible reason why average diatom and cyanobateria removal rates were higher in the MBBR was that biological flocculation and sedimentation of sloughed biofilm played a more important role on algae removal in MBBR than in the BF.

Chl-a is regarded as a surrogate for total algae to evaluate algae removal efficiency by different treatment processes such as chemical oxidation and biological treatment (Wang, 1999; Liu, 2000). The total algae (the sum of diatom and cyanobateria) and Chl-a removal by the BF and MBBR are shown in Fig. 8 and Fig. 9 respectively. The average total algae removal rate in the MBBR (47.3%) was

560 XIE Shu-guang *et al* . Vol. 17

also higher than that in the BF (46.3%). However, the average Chl-a removal rate in the MBBR (35.0%) was far less than that in the BF (47.4%). Zhou had ever reported a similar phenomenon for the evaluation of algae removal by BF and BCOR used for the pretreatment of Taihu water (Zhou, 1996). Therefore, further investigation is needed on the feasibility of Chl-a as a surrogate for total algae when compare algae removal efficiency by different biological pretreatment processes. Liu et al. had ever proposed that Chl-a was more suitable to evaluate algae removal efficiency in chemical oxidation processes (Liu, 2000).

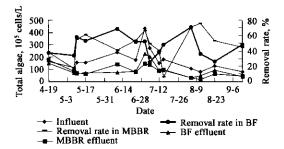


Fig. 8 Total alage removal by BF and MBBR

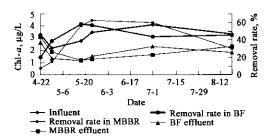


Fig. 9 Chl-a removal by the BF and MBBR

Pre-chlorination is often adopted to remove algae against blockage. However, microcystins, which cannot effectively removed by conventional treatment process, may be released from algae cell during chlorination. Since algae are equally potent as THM precursor as humic substances, pre-chlorination can produce THM, which also cannot be effectively removed by conventional treatment process. Therefore, pre-chlorination is not an ideal choice for algae removal. Ozonation and ClO2 oxidation can effectively remove algae and microcystins, but their application in China is limited due to high investment and operation cost. Biological pre-treatment process may be effective and economic in removing algae although the data concerning microcystin removal by this process is very sparse. Moreover, the data concerning mechanism of microcystin removal by biological treatment process has not been available up to date. However, a high removal rate of microcystins by three-step BCORs treating Taihu water has been reported (Yu, 2002).

For the raw water with relatively high level of cyanobateria on May 10, the microcystin removal by the BF and MBBR is shown in Fig.10. It was demonstrated that the BF and MBBR could effectively remove microcystins although the level of microcystins was low  $(0.16~\mu g/L)$  during this study. The removal rates of microcystin in the BF and MBBR were different, 56.3% and 62.5% respectively, although the removal rates of cyanobateria were the same (57.8%) on the given day.

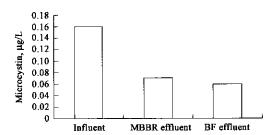


Fig. 10 Microcystin removal by the BF and MBBR

#### 2.4 SOCs removal

In raw water, the total organic carbon is mainly constituted of humic substances. However, SOCs may also be present, especially in surface waters. These pollutants come about mainly from discharges of industrial and municipal wastewaters, urban and agricultural runoff. A variety of SOCs can contribute to health risks and problems of tastes and odors. Examples include gasoline components, such as benzenes, toluene, xylenes, and alkylbenzenes; phenolics; naphthalene; chlorinated phenols and benzenes; PCBs; and pesticides and herbicides and so on. Various kinds of hazardous organic pollutants such as chlorinated compounds can be removed by microbial secondary utilization (Bruce, 1989). High removal rates of pesticides and chlorinated compounds have ever been reported as for one pilot-scale BF used for biological pre-treatment of raw water from Shenzhen reservoir(Wu, 1999).

Hexachlorocyclohexane was frequently detectable in drinking water distribution system although its concentration was always very low(data not shown). In this study, among SOCs regulated by Sanitary Standard for Drinking Water Quality-2001 only Hexachlorocyclohexane was detected in raw water(0.02  $\mu g/L)$  but it was non-detectable in both effluents of biofilm reactors. Therefore, Hexachlorocyclohexane could be effectively removed by the two biological treatment processes.

#### 2.5 Ammnonia and nitrite removal

Ammonia is one of the most important water quality parameters used to assess a water supply source. Ammonia affects the pre-chlorination process and /or the disinfection so the amount of chlorine has to be increased to ten times the concentration of ammonia in the raw water. This large amount of chlorine used in water treatment then generates THMs. Therefore, ammonia elimination is necessary before chlorination process. Moreover, Nitrite is a cause of methemoglobinemia so its concentration must be kept low.

As for ammonia removal, it is commonly believed that the BF has better performance than BCOR (Wu, 1999; Zhou, 1996). The ammonia removal by the BF and MBBR is shown in Fig.11. Although the ammonia concentrations were not very high (0.15—0.65 mg/L) the two reactors could effectively remove ammonia. The average ammonia removal rate in the MBBR (63.1%) was slightly lower than that in the BF (67.4%). However, in some days the MBBR even had better performance than the BF.

The nitrite removal by the BF and MBBR is shown in Fig. 12. The nitrite concentrations in both effluents were lower than those in influent, which indicated the biological nitrification could successfully advance without nitrite accumulation. Moreover, it was demonstrated that nitrite

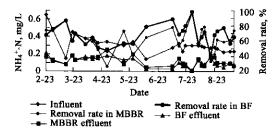


Fig. 11 Ammonia removal by the BF and MBBR

concentrations in BF effluent were always lower than that in MBBR effluent.

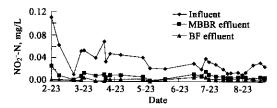


Fig. 12 Nitrite removal by the BF and MBBR

#### 3 Conclusions

The BF and MBBR were used for biological pretreatment of Yellow River water in this study. The average removal rate of TOC in the BF was only slightly higher than that in MBBR and both biofilm reactors had the buffer capacity for abrupt increase of organic loading. Like UV<sub>254</sub>, the average removal rate of THMFP in the BF was much higher than that in the MBBR. However, for biological pretreatment process, UV<sub>254</sub> removal did not show obvious correlation with THMFP removal. Hexachlorocyclohexane could be effectively removed by biological treatment process although the level in influent was very low. Moreover, both BF and MBBR could effectively remove ammonia and nitrite.

As for diatom and cyanobateria removal the MBBR had better performance than BF. However, the average  $\mathrm{Chl}\text{-}a$  removal rate in MBBR was far less than that in BF. Further research was necessary to investigate the feasibility of  $\mathrm{Chl}\text{-}a$  as a surrogate for total algae when to compare algae removal efficiency by different biological pretreatment processes. It was also proposed that biological flocculation and sedimentation of sloughed biofilm should play a more important role on algae removal in MBBR than in BF. BF and MBBR could effectively remove microcystins although the level of microcystins was low during this study.

As biological pretreatment reactors, the BF and MBBR could effectively remove various kinds of pollutants, organic and inorganic, in Yellow River water. Although the BF outweigh the MBBR in the removal of some kinds of pollutants, the latter still could be a promising technology for biological pretreatment due to its two obvious advantages: no need for backwashing and easy management.

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