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Removal of disinfection by-products formation potential by biologically intensified process

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Abstract: The removal of disinfection by-products formation potential (DBPFP) in artificially intensified biological activated carbon (IBAC) process which is developed on the basis of traditional ozone granular activated carbon was evaluated. By IBAC removals of 31% and 68% for THMFP and HAAFP were obtained respectively. Under identical conditions, the removals of the same substances were 4% and 32% respectively only by the granular activated carbon (GAC) process. Compared with GAC, the high removal rates of the two formed potential substances were due to the increasing of bioactivity of the media and the synergistic capabilities of biological degradation cooperating with activated carbon adsorption of organic compounds. A clear linear correlation ($R^2 = 0.9562$ and $R^2 = 0.9007$) between DOC HAAFP removal rate and Empty Bed Contact Time (EBCT) of IBAC process was observed, while that between THMFP removal rate and EBCT of GAC was $R^2 = 0.9782$. In addition certain linear correlations between THMFP, HAAFP and UV_{254} ($R^2 = 0.855$ and $R^2 = 0.7702$) were found for the treated water. For IBAC process there are also more advantages such as long backwashing cycle time, low backwashing intensity and prolonging activated carbon lifetime and so on.

Keywords: intensified biological activated carbon (IBAC); disinfection by-products formation potential (DBPFP); empty bed contact time; water treatment

Introduction

Natural organic matters (NOM) are mostly the disinfection by-product formation potentials in water. Traditional chlorination of water can lead to the formation of organic halides by the reaction of free chlorine with organic matter in the water. In all of the DBPs, THMs and HAAs are reported most extensively. The THM group of compounds includes: chloroform, bromodichloromethane, chlorodibromomethane and bromoform. Chloroform is generally the predominant and bromoform has its proportion also. World Health Organization (WHO) rules the maximum contamination levels (MCL) for THMs is less than 80 μg/L (Joanne, 1995). Brominated THMs are formed when chlorine in the form of hypochlorous acid/hypochlorite ion ($HOCl/OCl^-$) oxidizes bromide in the water to hypobromous acid/hypobromite ion ($HOBr/OBr^-$). When they exist in water the four DBPs types come into being. Generally speaking, chlorine acts preferentially as an oxidant, whereas bromine is a more effective halogen substituting agent so their reaction theory is not the same (Owen, 1995). HAAs include nine substances but the most common are monochloroacetic (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA). In Stage Ⅰ of the USEPA D/DBP rule, the maximum contamination levels for HAAs are 60 μg/L (Joanne, 1995). Since the discovery of THMs in drinking water, studies have been directed towards methods of controlling or minimizing their formation, including the removal of organic precursors prior to chlorination or the use of alternate disinfectants. The former approach is advantageous because as an added benefit of removing THM precursor material it also removes organics that may present other problems, such as taste and odour (Woo, 1997). Several studies have shown that THM formation depends on several factors: organic precursor concentration, quality of organics, temperature, pH, chlorine dose, and the bromide ion concentration of the water. The most common indicators for NOM are total organic carbon (TOC) and ultraviolet absorbance at wavelength of 254 nm (UV_{254}). It tends to form more THMs and HAAs while those parameters values are higher (Stuart, 2001).

Biological activated carbon technique has been recognized as a kind of most effective means for removing organic matters. It is hard to achieve long period removal effect to the target pollutants through sorption by itself. Intensified biological degradation cooperated with activated carbon adsorption can improve their removal of organic matters effectively, even some matters not adsorbed by activated carbon can be removed by biology. The key to introduce biological technique lies in an adequate living environment for microbe and to keep its bioactivity. The acclimation and fixation processes of microbe are pivotal to artificial intensify biology. Microbe can be fixed on the surface of activated carbon because there exist priority position, hydrophilic place and existing oxide and emplastic matters (Ma, 2000).

1 Materials and methods

1.1 Water quality and experimental apparatus

The object of this experiment was to evaluate the DBPFP removal effectiveness in water by IBAC. The study was conducted in waterworks in Shenzhen. The water treated in waterworks was collected. The characteristics of the treated water during the experiment period are as follows: low organic matters content (TOC concentration was 0.82—2.36 mg/L, higher in summer and lower in winter), low ammonia nitrogen concentration (0.12—0.55 mg/L), higher DO concentration in treated water, pH value was kept in slightly alkaline, between 7 and 7.8. Fig. 1 shows the complete flow process of water treatment.

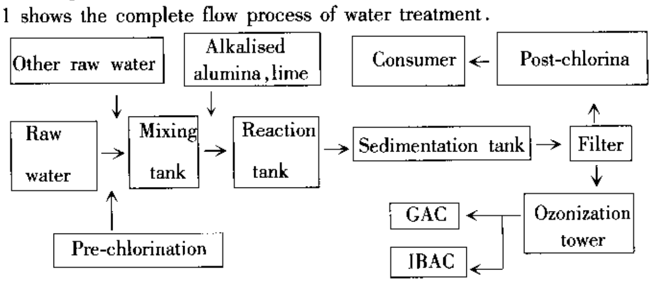

Fig.1 Experimental flow process

In the experiment pre- and post-disinfections by chlorination was adopted, the raw water was treated by conventional processes of coagulant mixing, reaction and sedimentation and filtration in V-filter, then further treatment by ozonization and granular activated carbon (GAC). GAC was packed in two columns with diameter of 10 centimeters and about one meter high. Except for the intensified biological skill adopted in IBAC, the conditions were the same in the two columns. Water flows through the columns downwards with maximum flowrate of 576 L/d and EBCT of 5—25 min. Ozone was dosed in 1.0—2.0 mg/L and contact time 10—15 min. During stable operation GAC was backwashed in cycle of 5—7 d and backwashing cycle time of IBAC was longer than that of GAC. In the course of experiment the average DBPFP concentrations in individual skill is summarized in Table 1.

1.2 Examinations

pH was measured using a pH meter Orion model 868-2.

The UV_{254} was measured by double light beam ultraviolet and visible spectrophotometer at wavelength 254 nm.

THMFP was analyzed using a Hewllet Packard GC/ECD-system with purge and trap injection. The temperature program: 40℃ (3 min), 10℃/min to 160℃.

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Table 1 Average DBPFP concentration in water treatment system

Items	Raw water		Settled outlet		Filter outlet		Ozonized water	
	THMFP	HAAFP	THMFP	HAAFP	THMFP	HAAFP	THMFP	HAAFP
Average value, μg/L	301	330	240	214	180	162	145	128

HAAFP was examined by a Hewllet Packard 6890 GC/ECD after derivation. The temperature program: 50℃ (3 min), 10℃/min to 140℃, 25℃/min to 240℃.

Dissolved organic carbon (DOC) was determined after membrane filtration (polycarbonate 0.45 μm) using a UV-DOC by Phoenix 8000 TOC meter, America. Detector NDR (nonlinear, nondispersive infrared), detetor limitation was 2 μg/L—10000 mg/L.

Microbial dehydrogenase activity (TTC) examination method was the same as Yu (Yu, 1990).

Total bacteria number was enumerated by plane plate count method.

1.3 Acclimation and cultivation of engineering strains

There were 28 strains seperated from raw water by adopting preferential nutrient medium. Different liquid nutrient mediums were necessary for microbial acclimation and cultivation. The object of cultivation and acclimation was to separate those strains can be accustomed to given water quality and be provided with higher activity and finally make them engineering strains with special function.

The seperated 28 strains were elutriated from the slant media by the sterilized water. Different nutrient mediums were added in turn and then parked in shaking table. The acclimation course was finished in the condition of rotation speed 150 r/min, cultivation for 24 h in constant temperature of 37℃.

The acclimated engineering strains would be cultivated continuously for increasing their quantity in special container. Every day nutients were added for their growth. After some days, cultivation stopped when the amount of microbe was enough for the experiment. The GAC column fixed by engineering strains was bachwashed time after time with filtration water before using.

2 Data and results

2.1 Removal of THMFP

THMFP was very difficult to remove in water treatment system. There were some arguments about the THMFP removal rate by GAC in scientific research. Wataru Nishijima (Wataru, 1998) indicated that high THMFP removal was maintained in GAC process even after saturation, which was 32% and 57%, respectively. The high THMFP removal was due to the increase in the subsequent biodegradation by bacteria attached on GAC. Seasonal changes in THMFP removal were not observed in the BAC process. Wang (Wang, 1998) concluded neither fresh GAC nor BAC could remove THMFP effectively. From the data curve in Fig.2, the THMFP removal was limited by GAC when EBCT equaled 10 min. The removal rate decreased while the EBCT prolonged such as in 2300 bed volumens the removal was 10% or so and in 6100 bed volumns it was decreased to only 4%. No obvious change was observed in GAC removal when the EBCT increased to 20 min, it was still 6%—18%. At the same EBCT conditions the removal rate never changed remarkably with IBAC. In time when EBCT equaled 10 min removal rate was 18%—22%, 20 min removal rate was 28%—31%. The THMFP removal rate of biologically intensified GAC increased obviously, while also this process operated stably. GAC removal rate tended to decrease because the pore structure in GAC was blocked up after longtime operation.

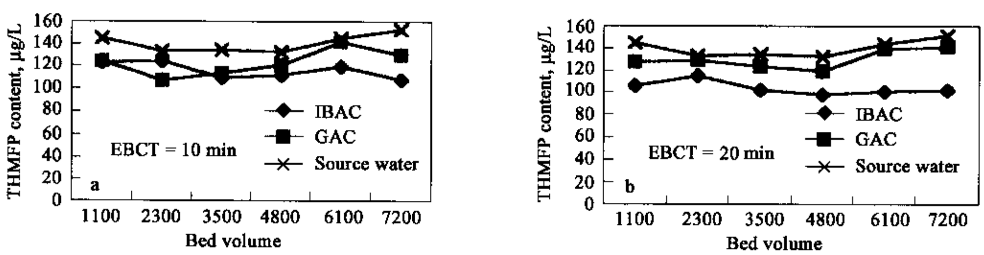

Fig.2 Removal of THMFP vs bed volumes for different EBCTs

2.2 Removal of HAAFP

Since the middle 1980s HAAs in the water was detected, much attention was paid to the change of HAAFP concentration (Akio, 2003). Some differences about the transformation tendency between HAAFP and THMFP were found in experiment. GAC can exert in HAAFP removal through adsorption. While the EBCT equaled 10 min and 20 min, its removal were 13%—25% and 26%—32%, respectively. Obviously prolonging EBCT increased HAAFP removal rate. More impacts were observed with IBAC. At the same conditions the removal was 38%—52% and 68%, respectively. Long EBCT was beneficiary to biological function at the aim of HAAFP removal. Compared with physical sorption of carbon, microbial function seemed to be relatively slow. The extending of EBCT gave long time contact between microbe and organic matters benefited to the degradation of HAAFP. The core of IBAC skill was to control the best environments for microbe. EBCT was one of them. Wang (Wang, 1998) reported 10% HAAFP removal with GAC, 25% removal with BAC. The numerical value was lower than IBAC in the experiment but the description about GAC was identical with the experiment.

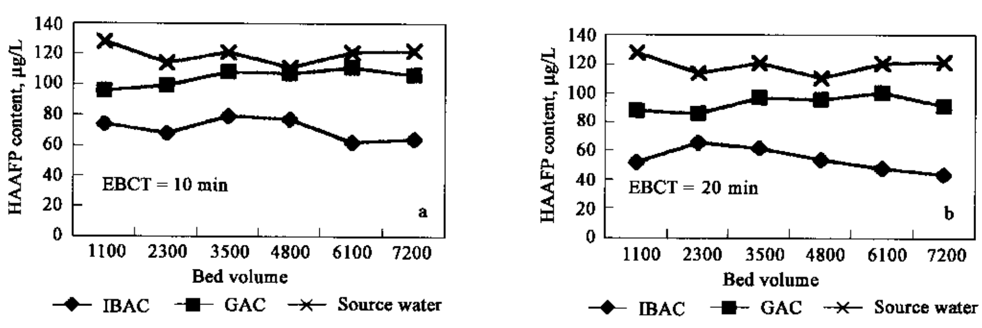

Fig.3 Removal of HAAFP vs bed volumns for different EBCTs

3 Discussion

3.1 Change of biomass

Organic matters were removed by physical sorption simultaneously by biological degradation. The removal rate was depended on the number of biomass and bioactivity directly. Bacteria number attached on activated carbon is shown in Fig. 4 (measurement error 5%). The attached bacteria number on IBAC was up to in magnitude of 10^6. The bacteria number could be omitted in new GAC. When the bed volumes increased to 4800 with GAC the attached bacteria number was up to magnitude of 10^6 also. No remarkable difference was found about biomass in two columns at the end of the experiment. The attached bacteria number which determined biodegradation depended on the factors, such as water quality, backwashing and so on. The removal tendency for DBPFP was not consistence with the change of bacteria numbers in two columns. So biodegradation should be explained not only from the bacteria number but also from the bioactivity.

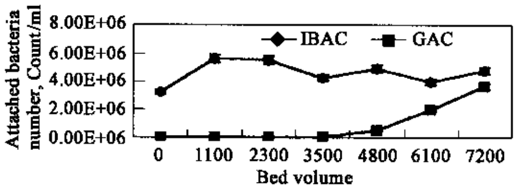

Fig.4 Total bacteria number in GAC and IBAC columns

In the practice work, the methods of bioactivity detection included TTC, micro-respiration rate and ATP detection etc. TTC was a common used method including the advantages of convenient detection and high precision (Shen, 2002). Based on the results in Fig. 5 there was evidence to make sure the bioactivity of intensified strains was higher than that of strains through natural growth. TTC value of bacteria in IBAC was above 200 μg/ml all the time. The bacteria growth in GAC experienced gradual processes to adapt water quality environment so bioactivity increased slowly. Dominant strains were difficult to come into being because strains by natural growth were complex in species. TTC value of GAC was 110 μg/ml. From the conclusion above, explanation of the bioactivity can be accepted that in considerable biomass there existed the difference of DBPFP removal. At the end of operation for GAC, it had nearly lost its physical sorption. At the time, biological function turned into the dominant status. The primary advantage of intensified strains is to enhance the removal target pollutants by microbe and improve bioactivity.

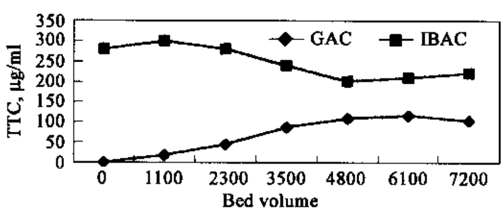

Fig.5 Change of bioactivity in two columns

3.2 Relationship between EBCT and DBPFP

EBCT was an important parameter in removing organic matters by GAC. If the value of EBCT was higher the removal of organic matters was better because increasing EBCT was equivalent prolonging adsorption contact time and reaction time between microbe and organic matters which was beneficiary to the removal of pollutants. But in China economical attention has to be considered. Higher EBCT will cause more investment in waterworks construction and more expenses for drinking water preparation. So the EBCT in waterworks has to be preferred optimally according to that the target pollutants have to be removed.

Similar tendencies about the removal of DBPFP in the two skills were observed, the higher the EBCT value the better the removal rate was obtained, which corresponded the removals of other organic substances using GAC. Because the biodegradation of THMFP was limited, the removal of THMFP changed little along with the EBCT. For instance, while EBCT equaled 25 min THMFP removal was 25% most by IBAC (Fig.6). While increasing EBCT with GAC only 8% removal was observed. The HAAFP removal could be expected in the two skills. Longer EBCT led to little change with GAC but obvious improvement of HAAFP removal happened with IBAC. While EBCT equaled 25 min, the removal rate was 60% in IBAC. The conclusion from this experiment was that the components of THMFP could not easily be adsorbed and degraded; based on the GAC sorption of HAAFP the removal rate increased much through biodegradation by IBAC (Fig.7).

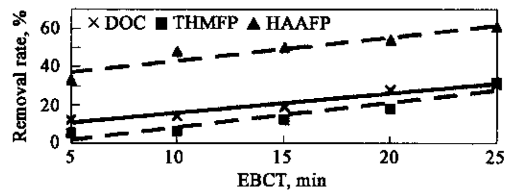

Fig.6 Removal rate of DBPFP with IBAC

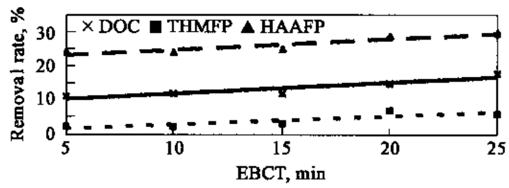

Fig.7 Removal rate of DBPFP with GAC

The statistical results are shown in Table 2. It showed that the linear relation existed between EBCT to DOC and HAAFP in IBAC, function relation was $y = 1.04x + 5.2$, $R^2 = 0.9562$, and $y = 1.24x + 30.6$, $R^2 = 0.9007$, between EBCT and THMFP the linear relation was found in GAC, $y = 0.26x + 0.1$, $R^2 = 0.9782$. The mathematic statistic result fed back the reliable conclusion from experiment. THMFP and HAAFP were DOC components, THMFP removal was mainly determined by EBCT in GAC but none in IBAC; the impact of HAAFP removal was occurred by IBAC. The biodegradation was dominant in HAAFP removal, that is to say the level of degradation led to HAAFP removal. The proportion of THMFP in DOC was determined by different water quality. Jeyong Yoon (Jeyong, 2003) thought the slope of the Korean water THMFP nomalized to DOC, (THMFP/DOC) was 44 ± 20 μg/mg (average ± standard deviatioin); 77 ± 12 μg/mg in U.S. (Amy, 1987). For filtrate water in this experiment it was 160 ± 17 μg/mg.

Table 2 Function relations between EBCT and DBPFP

	Items	Function relation with EBCT	R^2
IBAC	DOC	$y = 1.04x + 5.2$	0.9562
	THMFP	$y = 1.32x - 5.2$	0.8941
	HAAFP	$y = 1.24x + 30.6$	0.9007
GAC	DOC	$y = 0.34x + 8.5$	0.8705
	THMFP	$y = 0.26x + 0.1$	0.9782
	HAAFP	$y = 1.44x + 6.8$	0.7796

3.3 Relationships between UV_{254}, THMFP and HAAFP

The purpose of relativity analysis among manifold matters based on the experiment terms was to provide references for the surrogate measurement of different parameters (Jean, 2003). The UV_{254} level indicated the extent of aromatic and saturated double bond contained in the water treatment. In the selected samples, the relativity between the value of UV_{254} and DBPFP is shown in Fig. 8. The linear relation structures were $UV_{254} = 0.0002THMFP - 0.0185$, $R^2 = 0.855$, $n = 12$ and $UV_{254} = 0.0004HAAFP - 0.0175$, $R^2 = 0.7702$, $n = 12$, respectively. The work of Korshin G (Korshin, 1997) showed that UV_{254} adsorbance indicated the extent of aromaticity and had been considered as a measure of THMFP because the relation between UV_{254} and THMFP was more ideal. The linear relation was present in different regions with the different slope values between the two parameters. The result was uniform to the experiment conclusion but a complementary was necessary. The occurrence of linear relation in water treated by GAC was based on the biodegradation in GAC as a premise. Traditional GAC treatment, especially with fresh carbon, perhaps could not embody the mutual relation. The results indicated there was no relationship between two factors (Fig.8)

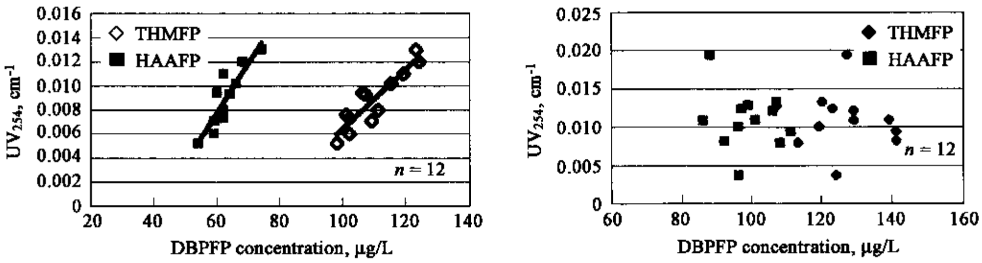

Fig.8 Relationship between UV_{254} and DBPFP in the two skills

3.4 Impact of GAC ageing

The physical sorption and the biodegradation happened simultaneously in BAC. The formation and the attachment of microbe was impacted by GAC which acted as a physical carrier. Commonly GAC needed to be changed after operating for some time. On one hand, physical sorption decreased rapidly and the cost of artificial renewal was relatively high. The lost of carbon itself was unavoidable. On the other hand, the content of metal elements in GAC would increase along the operation. Niquette(Niquette, 1998) showed that the presence of heavy metals or calcium reduced the biodegradation capacity, even the phenomenon of biotoxicosis happened. In fact, compounds and elements adsorbed on GAC were likely to influence the biofilm development, either by occupying the available sites in the case of calcium carbonates or by directly inhibiting the biofilm.

Biodegradation can extend the backwashing cycle time of GAC. In practice, based on the DBPFP transformation, the determination of backwashing cycle time was 15—20 d for IBAC but 5—7 d for GAC. The intensity of backwashing for IBAC was less than that for GAC. Intensified biodegradation can not only increase DBPFP removal and decrease carbon loss but also prolong GAC ageing.

4 Conclusions

No remarkable change of THMFP removal by IBAC was found according to the EBCT change, the removal rates was in the range of 18%—22% and 28%—31% when EBCT were 10 min and 20 min respectively. The removal rate of THMFP by GAC was 4%. There were some differences between HAAFP removal and THMFP removal. HAAFP could be adsorbed by GAC, at EBCT 10 min and 20 min, HAAFP removal rates in the range of 13%—25% and 26%—32% were obtained respectively. Under identical conditions the HAAFP removal rates by IBAC were even higher about 38%—52% and 68% respectively. So intensified biological technique was effective on HAAFP removal.

While discussing biodegradation there were two important guidelines: biomass and bioactivity. The organic substance removal rate was very different with close biomass and distinct bioactivity. There were no remarkable changes of biomass and bioactivity in IBAC but in GAC biomass increased gradually and bioactivity kept in low level compared with IBAC. IBAC skill can not only provide enough bacteria number for degradation of DBPFP but also guarantee high bioactivity through acclimating of engineering strains. This was the fundamental character of IBAC to remove pollutants.

The removal characteristics of THMFP, HAAFP and DOC by GAC with different EBCT (5—25 min) were as follows: THMFP removal rate was relative to GAC and no relationship was found between THMFP removal and IBAC. The changes of HAAFP and DOC removal rates were correlated with IBAC.

The linear relation between UV_{254} and DBPFP with IBAC was found but with GAC there was none.

There were more advantages for IBAC such as long backwashing cycle time and low backwashing intensity which can decrease loss of activated carbon and prolong the GAC ageing.

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