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Advance in nitrobacteria attachment of GAC for water treatment by surface-modified GAC using transition metal and air

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Abstract
When activated carbon (AC) is used in water treatment, it takes tens or even hundreds of days to have a biological function, which consumes a lot of power. To solve this problem, we used surface modified AC(SMAC) instead of AC is prepared by treating the surface with transition metal oxides in the precursor of AC, followed by vapor activation and oxidation with air. The experimental results showed that the microbial biomass attached to SMAC at 25 ℃ and 7 days of the nitrifying microbial culture was 3.53 times higher than AC (0.17× 107 CFU/g).

Keywords: Biological carrier, microbial adsorption, surface modification, water treatment

1. Introduction
Study to purify domestic water and waste water using activated carbon (AC) is now widely progressed worldwide. In particular, it is important to improve the adherence properties of microorganisms by using various methods of surface modified AC (SMAC) [1, 2].
The process of biological reactor by the application of microbial membranes on AC is long, unnecessarily power consuming and insufficient as a biological reactor [2-4].
Hence, this paper presents a study to increase the number of AC surface functional groups during the preparation of AC and to spare time and energy for the normal operation of the biological reactor by applying transition metal oxide treatment which microorganisms can be adhered to a strongly chemically and the method of air oxidation.

2. Method
2.1 Preparation of Modified AC as Precursor of carrier of biological scavenging
Generally, AC is prepared by carbonization and resurrection of horny or wood.
AC as a precursor for biological carrier has must high ion-exchange capacity and covalent binding capacity in favor of microbial attachment to the surface, so it was produced by processes such as carbonization, carbide transition metal treatment, rehabilitation, and air oxidation, unlike the AC production process.

2.1.1 Transient metal oxide treatment on carbide surfaces
The method of treating carbides with transition metal oxide is as follows.
Firstly, the solution of carbide and $Zr(NO_3)_4$ is mixed with a solid-liquid ratio of 1:5, followed by adsorption and ion exchange at 200 rpm for a certain time, and then the solid is separated and dried.
Secondly, the precipitate (2% ammonia solution) and Zr4+ ion-exchanged carbides were added to a solid-liquid ratio of 1:5 and stirred for 30min. The solid was separated, dried at 110 ℃, and calcined at 500 ℃ for 2h to produce the product. The amount of zirconia ZrO_2 supported on carbides was estimated by determining the Zr4+ ion content separated in the ion-exchange adsorption step.
The measured amount of ZrO_2 loaded on AC according to the concentration of $Zr(NO_3)_4$ is shown in Table 1.
As shown in the table, the loading of ZrO_2 on carbides increases with increasing concentration of $Zr(NO_3)_4$ solution, and no significant change is observed above 2.5 mol/L.

Table 1: Amount of zirconia supported on carbides according to $Zr(NO_3)_4$ concentration

Concentration, mol/L	0.5	1.0	1.5	2.0	2.5	3.0
Loading capacity, 10-6mol/g	8.2	14.3	20.4	25.0	25.1	25.2

The loading of ZrO_2 is then maximized. The measured loading of ZrO_2 on carbides with loading time is shown in Table 2.

Table 2: Zirconia loading on carbides as a function of loading time

Loading time, min	10	20	30	40	50	60
Loading capacity, 10-6 mol/g	7.0	12.3	16.8	22.4	24.0	24.0

As shown in the table, the holding time is reasonable for 1 hr. At this time, the ion exchange-adsorption process is fully equilibrated.

2.1.2 Surface functional group modification of AC by air oxidation

Air oxidation is carried out by using air as an oxidant at a given temperature after water vapor resuscitation after coating the carbides with transition metal oxides. The experimental setup is shown in Figure. 1.

The experiments were carried out by adding 10 g of steam-revived AC after coating the carbide with transition metal oxide in an alumina crucible, varying the air inlet velocity and oxidation temperature.

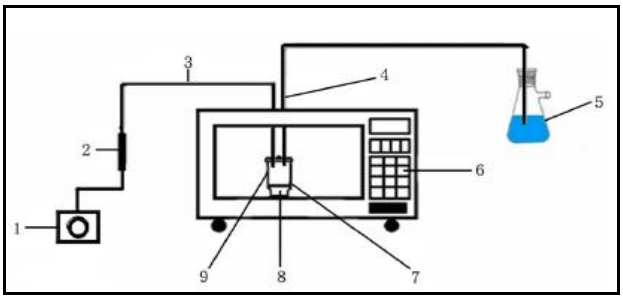

Fig 1: Experimental setup for oxidative modification of AC with air

(1-Compressor, 2-Gas Flow Control Valve, 3-Gas Guide, 4-Gas Drain Tube, 5-Gas Collection Vessel, 6-Electric Furnace Control Panel, 7-Sample, 8-Reactor Stack, 9-Alumina Crucibles)

The surface functional groups of AC and modified AC were determined by infrared absorption spectroscopy and ion exchange capacity by NaOH method. The main factors affecting the degree of modification of AC are oxidation time and oxidation temperature.

First, the change of the ion exchange capacity of AC with oxidation temperature was considered, and the results are shown in Table 3. The oxidation time was set at 1 hr.

Table 3: Change of ion exchange capacity of modified AC with oxidation temperature

Oxidation temperature ℃	150	200	250	300	350
Ion exchange capacity, mmol/g	1.6	2.5	4.1	4.5	4.7
Extraction rate, %	90	82	65	47	41

As shown in Table 3, with the increase of oxidation temperature, the ion exchange capacity of modified AC increased but the yield decreased.

Therefore, the oxidation temperature was set to 250 °C, where the product of ion exchange capacity and yield was maximized.

Next, the change of ion exchange capacity of modified AC with oxidation time was investigated.

The results are shown in Table 4. The oxidation temperature was set at 250 °C.

Table 4: Change of ion exchange capacity of modified AC with oxidation time

Oxidation temperature, ℃	150	200	250	300	350
Ion exchange capacity, mmol/g	1.6	2.5	4.1	4.5	4.7
Extraction rate,%	90	82	65	47	41

As shown in Table 4, with the increase of oxidation time, the ion exchange capacity of modified AC increased but the yield decreased.

Hence, the oxidation time was set at 60 min, considering both the ion exchange capacity and the yield of the modified AC. In addition, functional group analysis was carried out with a Nicolet 6700 Fourier transform infrared spectrometer to characterize the ion exchange properties of AC and modified AC.

The most important factor in the preparation of bioactive carbon is how the surface functional groups of modified AC are formed. This is due to the different adhesion properties of microorganisms depending on these surface groups. The IR absorption spectra of AC and modified AC are shown in Fig. 2 and 3, and the functional group analysis results of AC and modified AC are given in Tables 5 and 6.

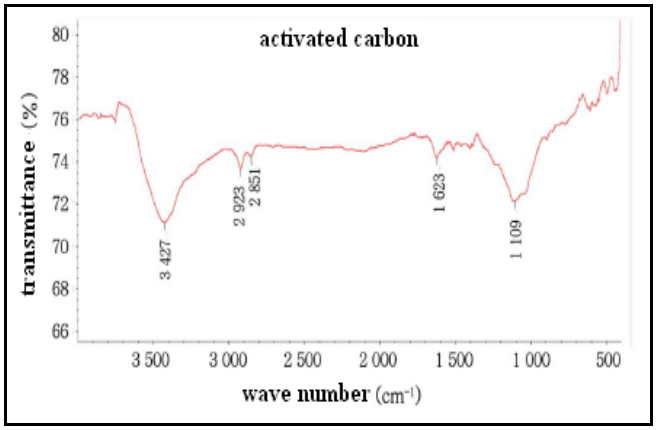

Fig 2: Infrared absorption spectrum of AC

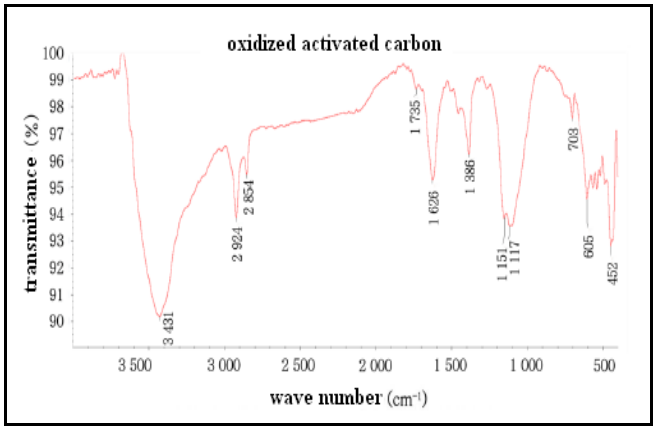

Fig 3: Infrared absorption spectra of modified AC

Table 5: Functional analysis of AC

Wave number, cm-1	Functional group	Oscillating shape
3427	-OH group in phenol	O-H stretching vibration
2923	CH_3 group in aliphatic compounds	CH_3 symmetric stretching vibration
2851	-CH_2-group in aliphatic compounds	CH_2 symmetric stretching vibration
1623	N-H group of primary amide	N-H strain oscillation
1109	Lactone C-O-C group	C-O-C asymmetric stretching

Table 6: Functional analysis of modified AC

Wave number, cm-1	Functional group	Oscillating shape
3432	-OH group in phenol	O-H stretching vibration
2924	CH_3 group in aliphatic compounds	CH_3 symmetric stretching vibration
2855	-CH_2-group in aliphatic compounds	CH_2 symmetric stretching vibration
1735	C=O group in lactone	C=O stretching vibration
1626	N-H group of primary amide	N-H strain oscillation
1386	COO-group of carboxylate	COO-symmetric stretching
1151,1117	lactone C-O-C group	C-O-C asymmetric stretching
703	Ar-OH group in phenol	O-H out-of-plane vibration
605	Ar-OH group in phenol	O-H out-of-plane deformation vibration
452	C-O-C group in ether	C-O-C strain oscillation

As shown above, the variety of surface functional groups in the modified AC increased significantly.

2.2 Preparation of biological carrier

In 100 ml Erlenmeyer flasks, 20 g of SMAC and conventional AC were added to 100 ml of nitrifying microbial culture, and incubated for 7 days at 25 °C in a thermostatic incubator after inoculation with isolated nitrifying microorganisms.

After incubation, the SMAC was washed with distilled water, and biological carrier was obtained.

3. Results and Discussion

The amount of attached biomass was measured by spraying denitrifying the bacterial culture, perfusing the nutrient solution for 7 days to form a biofilm, and then placing 1g of the carrier before and after incubation in sterile water, followed by counting the number of highly agitated and detached cells by plate culture [5, 6].

Table 7: Comparison of microbial biomass.

Division	Microbial biomass (1×107 CFU/g)
SMAC	0.6
AC	0.17

4. Conclusion

The above-said method helps establish a new surface treatment method for AC, which can enhance the water purification ability of AC by increasing the microbial attachment rate, and pretreat the AC before it, thus making it possible to produce biological carrier with a low time and energy consumption. The microbial biomass attached to SMAC is 0.6×107 CFU/g, 3.52 times higher than that of AC. This suggests that microbial biomass can reduce the bio-acclimation period to less than one-third as it determines the bio-acclimation period.

Further studies on the modification of AC surfaces by microorganisms suitable for purification are needed.

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