4-1-2 Development of Odor Management Techniques Based on the pH Diagnostic Method for Activated Carbon Used in Deodorizing Equipment

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ABSTRACT

The Bureau of Sewerage, Tokyo Metropolitan Government, has introduced the deodorizing equipment with activated carbon (AC) etc. in order to prevent odor emission from sewage treatment facilities. The deodorizing performance of deodorizing equipment used to be judged by reference to the result of odor measurements by the triangular odor bag method; however, it was difficult to quickly assess the current deodorizing performance due to the cost and time required about two weeks from sampling to reporting. Thus, we developed the pH diagnostic method to quantitatively evaluate the deodorizing performance of AC. Using this method, deodorizing performance can be assessed easily and directly. Utilizing the pH diagnostic method has allowed us to use AC for a longer period compared with conventional replacement cycle, and to comply with the odor standards while reducing the maintenance cost.

KEYWORDS: pH diagnostic method, odor prevention, deodorizing equipment, activated carbon

INTRODUCTION

In Japan, odors emitted from sewage treatment facilities are regulated based on such as the odor index as set out in the Offensive Odor Control Law. The subjects of regulation are exhaust ports of deodorizing equipment, smokestacks of sludge incinerators, effluent outlets, and boundaries of sewage treatment facilities. The Bureau of Sewerage, Tokyo Metropolitan Government (hereinafter, the “Bureau”) provides sewerage services in the metropolitan area of Tokyo, so that many sewage treatment facilities are close to residential areas and offices (Figure 1). Thus, in particular, odor prevention is important to ensure comfortable living environment of citizens.

For odor prevention, the Bureau’s sewage treatment facilities are equipped with, the deodorizing equipment using deodorants such as activated carbon (AC), humic deodorant and impregnated carbon depending on odor concentration and component. About 70 percent of the deodorizing equipment in wastewater treatment plants (WWTPs) uses AC. AC has numerous fine pores, and its mechanism of removal of odor substances is physical adsorption. Since AC has high adsorbability of odor components (e.g. hydrogen sulfide, methyl mercaptan, methyl sulfide, methyl disulfide and ammonia) emitted from sewage facilities, AC is suitable for deodorant of such components. The deodorizing performance of AC, however, gradually decreases according to the adsorption of odor substances and, in particular, greatly declines when it comes close to saturation level. Thus, it is necessary to maintain AC in good condition by replacing (includes regeneration) it in advance so that we can comply with odor standards.

Figure 1. Deodorizing equipment of Shibaura Wastewater Reclamation Center (for deodorizing odorous gas from reaction tank) is close to offices.

The time for replacement of AC used to be decided by the results of odor measurements by the triangular odor bag method at exhaust ports of the deodorizing equipment and by the replacement records (replace after a certain period of use, referring to the inlet odor concentration). The triangular odor bag method is one of sensory test methods used for measurement of odor index, which is a Japan's unique method that the Tokyo Metropolitan Research Institute for Environmental Protection developed by improving the ASTM Syringe Method. It is, however, difficult to accurately evaluate the deodorizing performance from a result of a single odor measurement because the concentration of odors emitted from sewage treatment facilities significantly differ depending on installation site, temperature and weather (Kawase, 2011). For instance, when the inlet odor concentration temporarily increases, the outlet odor concentration also increases. Results of odor measurement remain indirect data for evaluation of the deodorizing performance, and thus are unlikely to be used as direct index. In addition, in Japan, odor measurement by the triangular odor bag has to be done by certified olfactory measurement operators. Therefore, the odor measurement is generally demonstrated by inspection institutes or companies which have the certified operators. Usually, it takes about two weeks from sampling to reporting so that it is difficult to measure frequently because of the cost. For these reasons, we used to carry out early replacement of AC in order to comply with the odor standards.

Under these circumstances, there was a strong need for development of a maintenance method that allows us to quantitatively and easily assess the deodorizing performance in order to accurately and quickly decide the timing for replacement of AC. Generally, one of the indexes of the deodorizing performance of AC is the adsorption capacity (defined as an equilibrium adsorption capacity of organic solvent vapor measured as an increase in the weight of AC through saturation test using vapor of a single organic substance). This does not correspond to the development needs because it is necessary to outsource the analysis due to complexity of procedure and requirement of organic solves such as toluene and benzene. On the other hand, the main component of odors that are emitted from WWTPs is hydrogen sulfide. Therefore, we focused on changes in pH of AC as an easily measurable evaluation index of the deodorizing performances because the hydrogen sulfide is oxidized after the adsorption removal by AC and then becomes sulfuric acid. Thus, we developed the low-cost pH diagnostic method that it is easy to assess the deodorizing performance of AC by quantitative evaluation of the relationship between the deodorizing performance and pH of AC.

MATERIALS AND METHODS

Determination of evaluation indexes for deodorizing performance of AC
Most of deodorizing equipment in Tokyo is composed of double cartridges filled with AC. Schematic diagram of deodorizing equipment is shown in Figure 2. The odor substances transmitted to the bottom of the deodorizing equipment are first removed by the AC filled in the lower cartridge and deterioration of the AC in the lower cartridge starts. Then, the removal of odor substances becomes to be carried out by the one in the upper cartridge. For this reason, the gradual deterioration of the AC filled in the lower cartridge starts from its bottom, which finally leads to complete loss of its deodorizing performance.

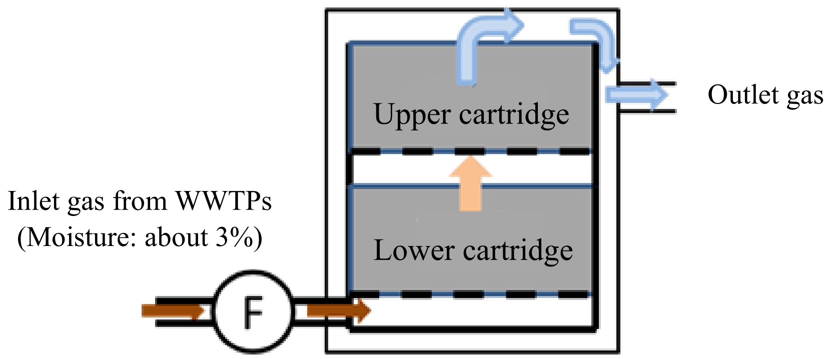

Figure 2. Schematic diagram of deodorizing equipment

Therefore, the replacement of AC is carried out following the procedure as shown in Figure 3. First, the AC is removed from the lower cartridge, then the upper cartridge is transferred to the position of the lower cartridge, finally a cartridge filled with new (or renewed) AC is set to the position of the upper cartridge.

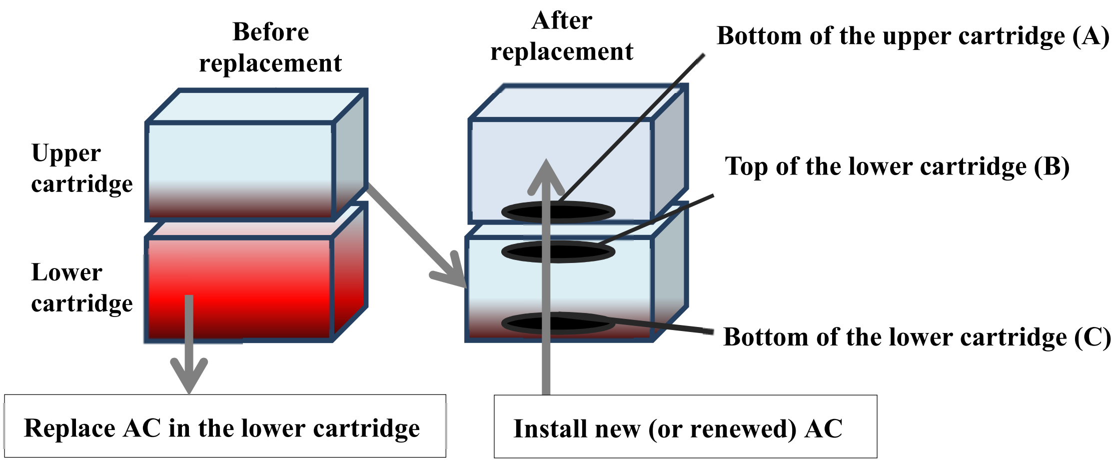

Figure 3. Procedure of AC replacement

Selection of deodorizing equipment to be surveyed
Most of deodorizing equipment in WWTPs deodorizes odors emitted from wastewater treatment facilities not from biosolid treatment facilities. In this study, we decided to survey the deodorizing equipment using AC for both upper and lower cartridges in the wastewater treatment facilities.

Specifications of the deodorizing equipment and survey period are shown in Table 1. In order to sample and analyze the AC with various deterioration conditions, we carried out surveys in FY 2011 on the deodorizing equipment of the rapid filtration system of the influent wastewater in the Shibaura Wastewater Reclamation Center (WRC) where the deodorizing performance deteriorates relatively earlier, and on the one of the grit chamber in the east train of the same center where the deodorizing performance gradually deteriorates. In addition, in FY 2012, the same survey was carried out for the deodorizing equipment of reaction tanks in the Ukima WRC. Table 2 shows the maximum concentration for each odor component that flows into the deodorizing equipment surveyed. Table 3 shows the specification of AC filled in the cartridges.

Table 1. Specifications and survey periods of the deodorizing equipment surveyed

WWTP	Facility	Air volume (m^3/min)	AC cartridge	Linear velocity (m/sec)	contact time	Survey period
Shibaura WRC	Influent wastewater rapid filtration	415	1.4×1.4×0.6 m high 12 × 2 layers	0.3	Approx. 4 sec.	Sep 2011 - Feb 2012
	East train grit chamber	140	1.0×1.0×0.6 m high 8 × 2 layers	0.3	Approx. 4 sec.	
Ukima WRC	Reaction tank	440	1.6×1.4×0.7 m high 12 × 2 layers	0.3	Approx. 4 sec.	Jul 2012 - Feb 2013

Table 2. Maximum concentrations of influent odors (unit: ppm)

WWTP	Facility	Hydrogen sulfide	Methyl mercaptan	Methyl sulfide	Methyl disulfide
Shibaura WRC	Influent wastewater rapid filtration	39	0.45	0.024	0.039
	East train grit chamber	0.45	0.032	0.0048	0.0085
Ukima WRC	Reaction tank	0.077	0.084	0.054	0.024

Table 3. Specification of the AC used in the deodorizing equipment

Item	Specification
Material	Wood-based adsorbent (coconut shell) is used as a standard material
Particle size	Particles within 4-8 meshes should be 95 % or more
Adsorption capacity	Benzene adsorption capacity should be 30 wt % or more
Bulk density	Approximately 410 kg/m^3 (new carbon)

Surveyed samples

The samples of AC with different stages of deterioration were taken from three parts: the bottom of the lower cartridge where the deodorizing performance of AC is expected to significantly decrease (Figure 3 C), the top of the lower cartridge where the deterioration is expected to gradually progress with the duration of use (see Figure 3 B), and the bottom of the upper cartridge (see Figure 3 A). Those samples were taken monthly during the survey period as shown in Table 1. The samples of the top and bottom of cartridges were taken using a shovel and a zone sampler (see Figure 4), respectively. Gaseous samples were collected into odor-free bags in odor to measure odor index of exhausted gas from deodorizing equipment.

Figure 4. Zone sampler

Measurement items and methods

The main component of odors emitted from wastewater treatment facilities is hydrogen sulfide. We assumed that pH of AC was decreased due to conversion of H_2S to H_2SO_4 by being oxidized after adsorption to AC, and sulfur in AC was accumulated due to adsorption of H_2S which was a sulfur-containing substance. Thus, we measured adsorption capacity, pH and total sulfur of the AC sample and surveyed the relationships between adsorption capacity (one of indexes for deodorizing performance), and pH and total sulfur. In addition, odor indexes at the exhaust and intake ports (conventionally measured items) were measured.

Adsorption capacity was measured according to JIS (Japanese Industrial Standards) K 1474 as the equilibrium adsorption capacity of toluene, which was calculated from the increase in the amount of the sample when its quantity became constant by letting air containing 1/10 toluene steam into AC by 2 L/min.

Total sulfur (T-S) was measured according to JIS M 8813. The sample was heated in oxygen stream up to about 1,350°C to oxidize and gasify sulfur, and gaseous sulfur was collected in H_2O_2 water. Then sulfur in H_2O_2 water was titrated with 0.1 mg/L sodium hydroxide.

The pH measurement method was based on JIS K 1474 (hereinafter, "JIS method"); Figure 5 shows the schematic diagram of the measurement procedure. The AC was put in a beaker with distilled water. The beaker was boiled for five minutes on an electric stove, and cooled down. And the pH of water was measured with a pH meter. Required time to measure each sample with this method is nearly 20 minutes, which is easy and quick enough to access with the conventional analytical instruments in WWTPs.

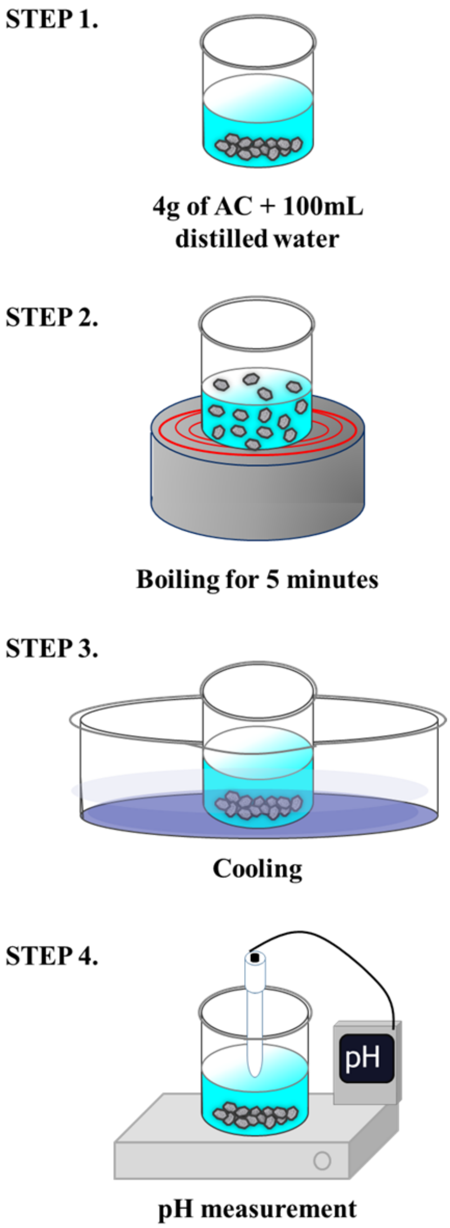

Figure 5. Schematic diagram of pH measurement of AC (JIS method)

Odor index was measured in accordance with triangular odor bag method. In the triangular odor bag method, the sensory test is conducted by at least 6 members of the panel. Each panel is given 3 bags; 1 with a sample in it and 2 without sample (odor-free air) and asked to choose the odorous bag. If the panel can tell the correct bag, the odor is then diluted and the test is continued until it becomes impossible to identify the bag with odor. In order to ensure the accuracy of the measurement, it is important to take account of psychological influences of panel members and olfactory fatigue.

RESULTS AND DISCUSSIONS

Relationships between adsorption performance of AC, and total sulfur or pH
Figures 6 and 7 show the relationships between adsorption capacity of AC, pH or total sulfur respectively. The adsorption capacity is one of indexes for the deodorizing performance of AC and the large adsorption capacity means the high deodorizing performance. The specification criteria of the adsorption capacity before use is 30 wt % or more (table 3).

There was a high correlation between pH and adsorption capacity, and pH rapidly decreased when adsorption capacity decreased (Figure 6). pH was high (8-10) and alkaline when the adsorption capacity was about 30 wt %, while pH was low (≤ 2) and highly acidic when it was 20 wt %.

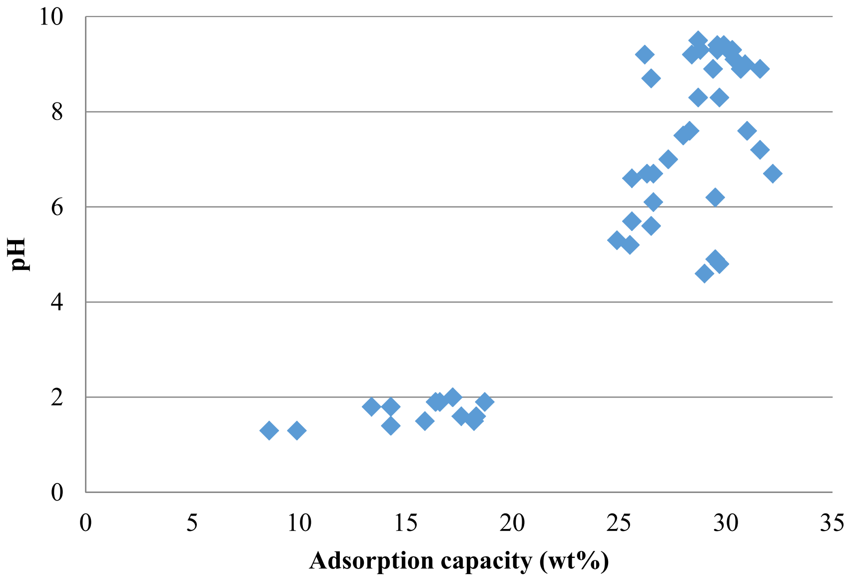

Figure 6. Relationship between adsorption capacity and pH

Moreover, there was an inverse correlation between the adsorption capacity and total sulfur. When the adsorption capacity decreased, total sulfur increased in a linear manner (see Figure 7). The total sulfur was low (i.e. only 0-1 wt %) when the adsorption capacity was about 30 wt %, while the total sulfur was high (i.e. 4-8 wt %) when the adsorption capacity was 20 wt % or less.

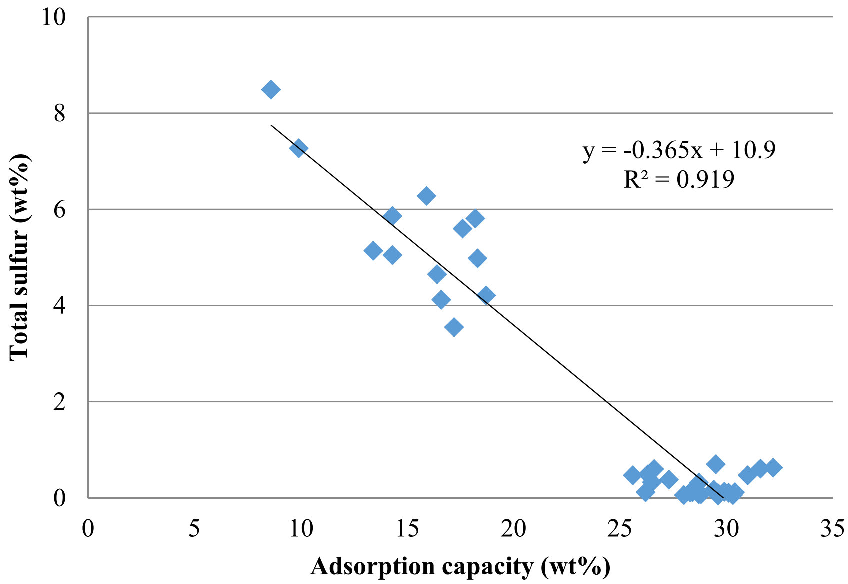

Figure 7. Relationship between adsorption capacity and total sulfur

As for an adsorption of hydrogen sulfide, it is known that the oxidation reaction occurs in the presence of air (oxygen) or moisture (humidity), and then that hydrogen sulfide is partially oxidized on the surface of AC and converted to sulfur or sulfuric acid (Shoda, 1994). Figure 8 shows the relationship between pH and total sulfur. When total sulfur was less than 1 wt %, the pH was over 6; however, when total sulfur increased to 4 wt % or more, the pH decreased to 2 or less. These results proved that it was reasonable to assume that the adsorption of hydrogen sulfide – a main component of odors emitted from sewage facilities – to AC lead to the increase in total sulfur and the decrease in pH. In addition, it became clear that the adsorption capacity of AC can be evaluated by pH or total sulfur. The evaluation of adsorption capacity and total sulfur requires special analysis equipment, cost and time. However, pH can be inexpensively and easily analyzed. For this reason, we decided to use pH as an index for evaluation of the adsorption capacity of AC.

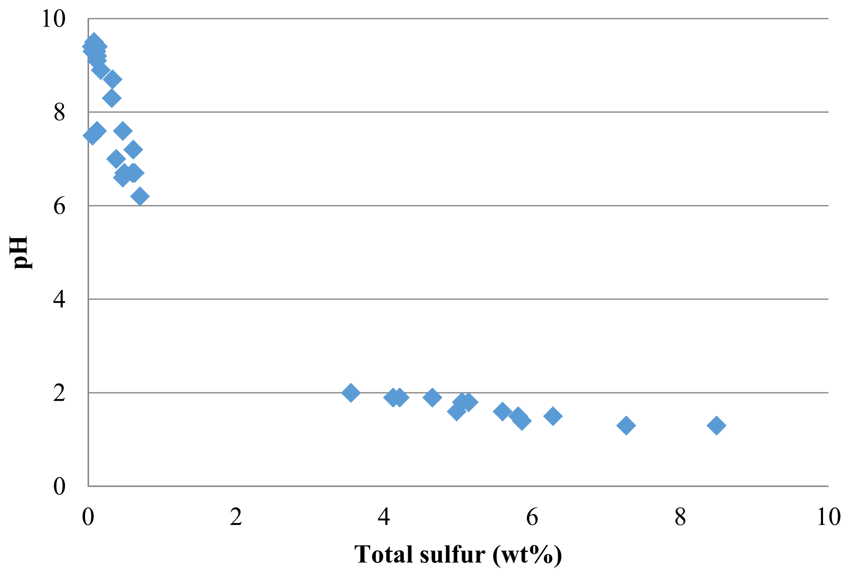

Figure 8. Relationship between total sulfur and pH

Establishment of the pH diagnostic method

Sampling points

It is important for appropriate replacement of AC in the deodorizing equipment to collect AC samples from proper position in the equipment. The deterioration in the deodorizing performance of the AC begins from the bottom of the lower cartridge, through which odor substances first pass, and moves up towards the upper cartridge. The most efficient and economical replacement timing is when the lower cartridge has completely deteriorated and the deterioration of the upper cartridge has hardly progressed. That is, cartridges can be replaced at more appropriate timing if the deodorizing performance of AC located in the middle part (A or B in Figure 3) of the double-layer deodorizing equipment can be grasped. Thus, we decided to collect the AC in the middle part. In this study, in the middle of the deodorizing equipment, the pH of the bottom of the upper cartridge (A in Figure 3) and the pH of the top of the lower cartridge (B in Figure 3) were almost the same values; therefore, it was concluded that sample for pH measurement should be collected from the former because of easiness sample collection.

Evaluation criteria

The evaluation criteria for assessment of deterioration of AC were set in order to decide easily whether it is necessary to replace AC. As shown in Figure 9, the evaluation criteria are: “normal” (pH 6 to pH 10), “caution needed” (more than pH 2 to less than pH 6), and “deteriorated” (pH 2 or less). The reason for setting from pH 6 to pH 10 as “normal” is that when the pH is 6 or more the adsorption capacity is 25 wt % or more, that is, the deodorizing performance is sufficiently retained.

On the other hand, the reason for setting pH 2 or less as “deteriorated” is the fact that when the adsorption capacity is 20 wt % or less, the pH becomes highly acidic – pH 2 or less.

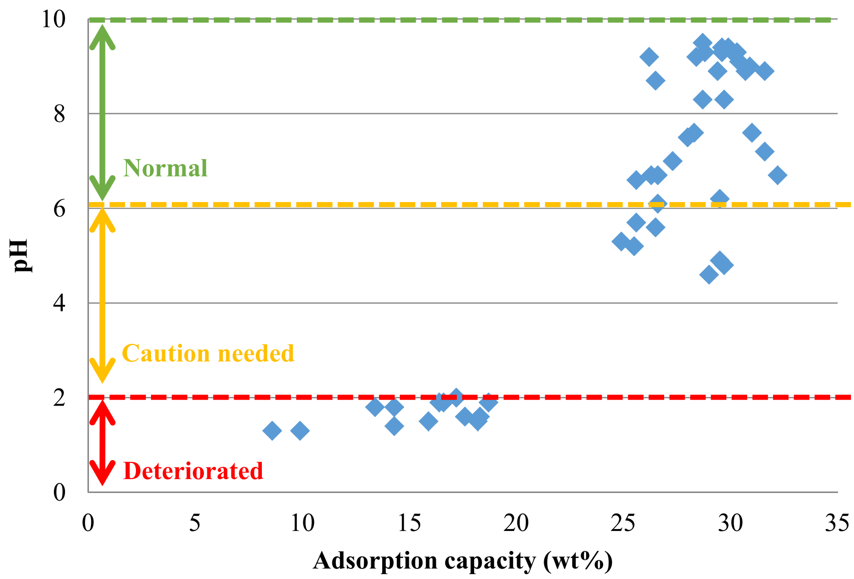

Figure 9. Evaluation standards of the deterioration status of AC using pH diagnostic method

The simplified assay method

In the JIS method as shown in Figure 5, it is necessary to boil samples for 5 minutes and cool them. In cases where there are multiple samples, the assay work may take a few hours because it takes about 20 minutes per sample. Therefore, we further considered a simplified assay that can shorten measurement time. This is a method to agitate the AC in a beaker with distilled water for five minutes or more by a stirrer and a stirring bar, excluding the boiling and cooling steps as mentioned above (Figure 5). Figure 10 shows comparison of the results of the measurements of pH in the JIS method and the simplified assay method. The pH measured in this simplified assay method showed a significantly high positive correlation with the JIS method. As a result, it was concluded the simplified assay method was able to substitute for JIS method especially in case of high pH. Therefore we decided to apply the simplified assay method to evaluation of “normal”. If the pH measured by the simplified assay method is pH 7 or more, this is evaluated as “normal,” and the JIS method is not carried out. On the other hand, if the pH measured by the simplified assay method is less than pH 7, this is an indication of deterioration, and the JIS method is carried out. As a result, the simplified assay method can shorten measurement time for 8 minutes from 20 minutes.

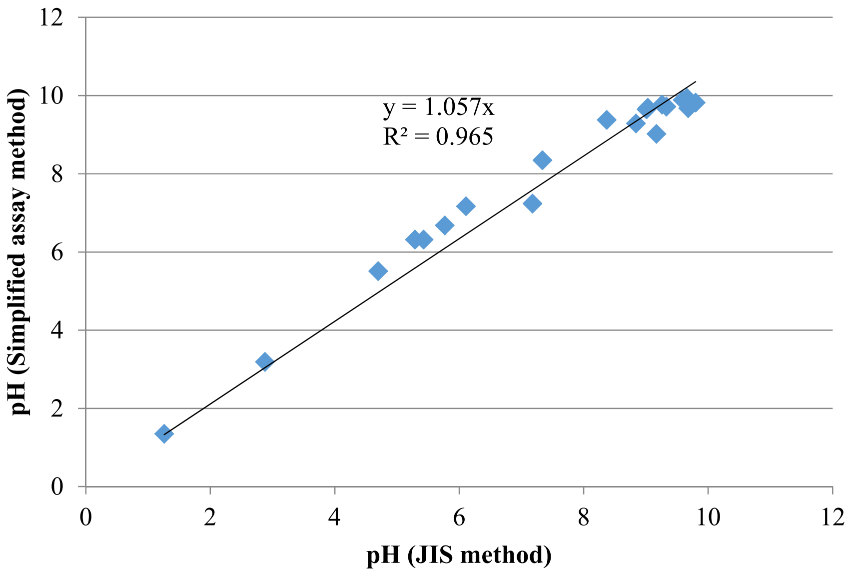

Figure 10. Correlation JIS and simplified assay methods in the measurement method for pH of AC

Outline of the pH diagnostic method and its utilization

The procedure of the pH diagnostic method is shown in Table 4. Compared with the conventional method of replacing AC based on the odor measurement, the pH diagnostic method has a massive advantage in allowing us to significantly reduce time required for conducting collection and analysis of AC. As for the conventional diagnosis of the deodorizing performance based on odor measurements, it is necessary to demonstrate by inspection institutes or companies which have the certified operators. For this reason, it takes about two weeks and many costs. In addition, there are disadvantages that measurement results differ depending on inlet odor concentration of the deodorizing equipment. On the other hand, the pH diagnostic method is easy and cost-friendly to analyze. Additionally, it takes only about two hours per sample from AC collection to pH measurement to quantitatively diagnose the deodorizing performance. The pH diagnostic method can evaluate the deodorizing performance to “normal,” “caution needed” or “deteriorated”. If the AC is evaluated as “deteriorated,” decide whether it is necessary to replace the AC.

Table 4. The procedure of the pH diagnostic method

Step	Procedure
1.	Collect AC from the bottom of the upper cartridge using a zone sampler (see Figure 4).
2.	Measure the pH of the collected AC by the pH simplified assay method (see Figure 5).
3.	If the pH is pH 7 or more, the AC is evaluated as “normal” and the JIS method is not carried out.
4.	If the pH is less than pH 7, the JIS method is carried out.
5.	Classify the deodorizing performance as “normal,” “cautious” or “deteriorated.”
6.	If a sample is evaluated as “deteriorated,” decide whether it is necessary to replace AC.

APPLICATION TO ACTUAL MANAGEMENT

In FY 2012, for our 74 deodorizing equipment in 11 WWTPs and 5 pumping stations, the pH diagnostic method was used for the management of the deodorizing performance of AC. Here are two examples of the utilization of the pH diagnostic method.

First, the deodorizing performance was evaluated as “caution needed” by the pH diagnostic method at the deodorizing equipment for the reaction tanks of the west system at the Morigasaki WRC in May 2012. In addition, the odor index that was measured in January 2012 was almost the odor standard (see Table 4(a)). (Odor measurements are carried at exhaust ports of the deodorizing equipment of each WWTP at least twice a year including summer when the inlet odor concentration increase). For this reason, the AC was replaced six months earlier than the original scheduled date – after the summer in 2012. Consequently, The WWTP was able to comply with the odor standard in summer when the inlet odor concentrations usually increase.

On the other hand, the deodorizing performance was evaluated as “normal” at the deodorizing equipment of the grit chamber at the Kosuge WRC in August 2012. In addition, the odor index of air at the exhaust port of the deodorizing equipment was considerably lower than the odor standard (see Table 4(b)). Thus, we concluded that the AC sufficiently retained its deodorizing performance, so that the replacement of AC was postponed, originally planned in FY 2012, to the next fiscal year. The AC of this deodorizing equipment had been used to replace every three years, however, by adopting the four-year cycle replacement, the cost of AC replacement was reduced by about 30 percent.

Table 5. Examples of utilization of the pH diagnostic method
(a) An example of acceleration of replacement schedule

WWTP	Facility to be deodorized		pH	The deterioration status	Odor index	Odor standard (odor index)
Morigasaki WRC	West system reaction tank	No.1	4.1	Caution needed	21	27
		No.2	3.9	Caution needed	21	
		No.3	4.2	Caution needed	26	

(b) An example of extension of replacement cycle

WWTP	Facility to be deodorized	pH	The deterioration status	Odor index	Odor standard (odor index)
Kosuge WRC	Grit chamber	9.4	Normal	Less than 12	24

Moreover, the pH diagnostic method was used the management of replacement of AC at WWTPs and pumping stations also in FY 2013, as well as FY 2012. The cost was reduced by postponing the replacement of AC used for deodorizing equipment at WWTPs, which were evaluated as “normal,” to the following fiscal year.

By extending the AC replacement cycle based on the quantitative evaluation of deodorizing performance of AC using the pH diagnostic method, both reduction in cost and compliance with odor standards was achieved. Thus, the management of AC replacement by the pH diagnostic method was able to promote odor prevention.

CONCLUSION

We have developed the pH diagnostic method in order to evaluate the deodorizing performance of activated carbon (AC) used for deodorizing equipment. The advantages of the pH diagnostic method lie in the fact that the method makes it possible to evaluate the deodorizing performance of AC easily and quickly at low cost. By utilizing the evaluation based on the pH diagnostic method, the AC replacement cycle was extended by about 1 year for some deodorizing equipment in FY 2012 and FY 2013, thereby reducing the cost of the replacement work. Furthermore, the conventional earlier replacement can be shifted to the replacement by means of the evaluation based on quantitative analysis, thereby achieving both cost reduction and thorough compliance with laws and regulations.

In the future, we are planning to verify the applicability of the evaluation based on this method in terms of the deodorizing equipment in biosolid treatment facilities, because it is considered that the principle of the method is applicable if the main odor substance arising from sludge treatment systems is hydrogen sulfide. In addition, there were only a small number of samples that were evaluated as “caution needed” based on the pH diagnostic method. For this reason, we are trying to enhance the accuracy of the evaluation criteria by shortening the time intervals between schedules for sampling of AC and increasing the amount of data within the range of “caution needed.”

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