Studies on Evaluation and Utilization of Activated Carbon (Part 5)

Treatment of Phenolic Wastewater by Simultaneous Application of Activated Carbon and Activated Sludge

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The treatment of phenolic wastewater by simultaneous application of granular activated carbon and activated sludge [(AC+AS)Method] was investigated by comparing it to the conventional method using activated sludge alone (AS Method) and this Method followed by activated carbon [(AC after AS)Method].

The (AC+AS)Method was found to be more effective for shorter operation periods than either the AS Method or (AC after AS)Method.

The activated carbon once used could be regenerated by aerating in the copresence of activated sludge.

The treatment efficacy or power of the (AC+AS)Method decreased appreciably for repeatedly used activated carbon only in the second run, but thereafter the decrease was very small.

1. Introduction

Activated sludge, sometimes followed by activated carbon[1,2], has been employed widely in water treatment.

Recently, powdered activated carbon in the presence of activated sludge has been studied for its performance in water treatment and some synergetic effect of the combination has been reported, but its details have not been clarified.

In this paper, the performance of a simultaneous use of both granular activated carbon and activated sludge for phenolic wastewater has been investigated. The good performance of granular activated carbon is well known, but the performance of such a simultaneous use of granular activated carbon and activated sludge has not been investigated because of the difficulty in separating them from each other.

Here, it should be noted that granular activated carbon which can be attracted to a magnet (magneto-sensitive activated carbon) has successfully been prepared, and that such magneto-sensitive activated carbon can readily separated and recovered from a mixture of activated carbon and activated sludge.[4]

2. Experimental

2.1 Apparatus

A 2l bottle with a second opening at its lower part was used. A magnetic agitator was equipped just below the surface of the phenolic wastewater in the bottle so that it could be aerated sufficiently by agitation. An air inlet tube was set at 10 cm above the water surface.

2.2 Activated Carbon, Phenolic Wastewater and Activated Sludge

Magneto-sensitive activated carbon[4] M-AC used was prepared as follows: propane deasphalted asphalt (8 parts by weight) mixed homogeneously with red mud (2 parts by weight) was treated with 60% oleum (1.5 parts by weight at 70°C for 1.5 hrs in the presence of 1,1,2-trichloroethane (80 parts by weight). The granular particles thus precipitated was separated and washed with distilled water, and particles of 16—32 mesh sieves were activated with steam at 850°C for 30 min. The overall yield of activated carbon M-AC was 50% based on the raw asphalt used.

The specific surface area determined by the

Table 1 Properties of Activated Carbons

<table>
<thead>
<tr>
<th>Activated Carbon</th>
<th>Specific Surface Area (m²/g)</th>
<th>Methylene Blue Adsorption Capacity (mg/g)</th>
<th>Particle Size (mesh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-AC</td>
<td>952</td>
<td>194</td>
<td>16—32</td>
</tr>
</tbody>
</table>

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BET method and methylene blue adsorption capacity of the activated carbon are listed in Table 1.

The phenolic wastewater was prepared by adding pure phenol to FCC (Fluid Catalytic Cracking) wastewater from which hydrogen sulfide and ammonia were stripped. The FCC wastewater, containing 37 ppm phenols and 70 ppm total organic carbon, was stored in a refrigerator and filtered before adding phenol. The phenolic wastewater samples were prepared just before performing the tests. The final concentration of phenols was about 300 ppm.

The activated sludge from a sewage treatment center (Miyashiro-machi, Saitama-ken) was used after acclimatization that was carried out as follows: 20 l of the sludge was mixed with 200 l of the FCC wastewater and the mixture was agitated vigorously. The sludge was used for experiments after it was agitated at least for 7 days adding pure phenol (10,000 ppm in distilled water) continuously at a rate of 5 ml/min.

2.3 Procedure

The activated sludge (AS) was first washed with the phenolic wastewater three times in a separatory funnel in order to replace the coexisting water with the phenolic wastewater, and then it was allowed to settle for 1 hr. Measured volumes of the settled AS and phenolic wastewater were put into the 2 l bottle. The total volume of AS (apparent volume) and phenolic wastewater was 1.0 l in every experiment, and the ratio of AS to the whole volume 1.0 l (SV, %) was used as the index of the amount of AS used. A definite amount of activated carbon was added, and the mixture in the bottle was agitated at a rate of 350 rpm and then air was blown into it at a rate of 500 ml/min. The product water layer was filtered to remove the activated carbon particles and AS immediately after it was drawn off from the lower opening of the bottle, and the concentrations of phenols and total organic carbon (TOC) were determined. COD<sub>mn</sub> was also measured for some of the product water samples.

2.4 Analysis

Concentration of phenols was measured as phenol spectrophotometrically (λ<sub>max</sub> : 270 mÅ) using a spectrophotometer Type 323 (Hitachi Co., Ltd.).<sup>6</sup> Preliminary experiments indicated that analytical data were nearly equal to those determined by the method described in JIS K 0102.

TOC was measured with a TOC meter Type 102 (Toshiba-Beckman Co., Ltd.). COD<sub>mn</sub> was determined in accordance with the method described in JIS K 0102.

3. Results and Discussion

3.1 Effect of Amount of Activated Carbon on Treatment Performance

The treatment performance for phenols was examined for a constant amount of AS (SV=20%) and various amounts of activated carbon M-AC (100~1,000 mg). The results are shown in Fig. 1.

In the case of treatment with M-AC alone (AC Method), it is evident from Fig. 1 that the concentration of phenols decreased with increasing amount of M-AC added, but the equilibrium concentration reached within 2 hrs was as high as 180 ppm. The phenols remained in considerably high concentration also after treatment with AS alone (AS Method).

On the contrary, concentrations of the remaining phenols after simultaneous treatment with M-AC and AS ((AC+AS)Method) were found to be considerably lower than those obtained either by AC Method or AS Method alone, and they decreased with increasing amount of M-AC added. Concentrations of phenols observed after treatment for 6 hrs by these three methods were as follows:

- **AC Method** (M-AC : 1,000 mg) : 180 ppm
- **AS Method** (SV : 20%) : 220 ppm
- **(AC+AS) Method** (M-AC : 1,000 mg) : ≤0 ppm
  (SV : 20%)
3.2 Effect of SV on Treatment Performance

The treatment performance for phenols and TOC at a constant amount of M-AG and various amounts of SV (10~70%) was examined. The results are shown in Fig. 2 (removal of phenols) and Fig. 3 (removal of TOC).

It is evident here that phenols could also be effectively removed by the (AC+AS) Method. The concentration of remaining phenols is found, from Fig. 2, to be decreasing with increasing SV, while the removing ability does not increase much at SV levels higher than 50% which is considered to be optimum. SV 50% corresponded to MLSS 1,500—2,500 ppm (MLSS: Mixed Liquor Suspended Solids).

As shown in Fig. 3, the removal of TOC proceeded similarly to that of phenols shown in Fig. 2, but it was not complete and 20~30 ppm of TOC remained after treatment for 4 hrs. Some of the reasons may be that any organic substance in water cannot be removed completely by treatment with activated sludge, that the total treatment period (4 hrs) may be too short to accomplish a complete removal, and that there may be some substances which can hardly be adsorbed by activated carbon and can hardly be digested by activated sludge.

Considering the above results, the treatment conditions of (AC+AS) Method in the succeeding experiments were fixed as follows:

- Amount of Activated Carbon: 1,000 mg
- SV: 50%

Changes in the concentrations of phenols, TOC and COD₅ in the treatment under the above conditions are shown in Fig. 4.

3.3 Comparison of Treatment Performance between (AC+AS) Method and Conventional Method

In the more advanced wastewater treatment plant, the wastewater is treated by the AS Method which is generally followed by the AC Method. This process involving the two methods in such arrangement will be referred to as the (AC after...
Three modes of treating systems were used and the results obtained were evaluated. Two of the systems were AS Method and (AC+AS) Method. The third was the (AC after AS) Method, in which the wastewater was treated by AS Method and the product water, after the removal of the sludge, was then retreated with activated carbon M-AC for 6 hrs. In the case of (AC after AS) Method, the term “treatment time” meant the time required for treatment with the AS Method. The results are shown in Fig. 5 (removal of phenols) and Fig. 6 (removal of TOC).

Curve (1) in Figs. 5 and 6 was obtained for the treatment with the AS Method, curve (2) with the (AC+AS) Method, and curve (3) with the (AC after AS) Method. Curve (3) means the concentration level of phenols or TOC by treating the wastewater with AS and further with M-AC for 6 hrs.

It is natural that (AC+AS) Method (curve (2)) and (AC after AS) Method (curve (3)) were more effective than the AS Method (curve (1)). It appears that the (AC after AS) Method was the most effective within a treatment time about 1.5 hrs, but in that period considerably high concentrations of the contaminants still remained, and 5 hrs or more was necessary to remove them sufficiently. That is, the total treatment time required in the (AC after AS) Method was equal to the sum of that required in activated sludge treatment and that required in M-AC treatment.

On the other hand, only 3 hrs were necessary to remove the phenols to less than 20 ppm and TOC to less than 40 ppm by the (AC+AS) Method. The treatment time was considerably shortened by a simultaneous application of activated sludge and activated carbon.

From the above discussion, treatment with the (AC+AS) Method is found out to be superior to the (AC after AS) Method, a conventional method now being used.

Such contaminants as phenols and TOC are removed from the wastewater and concentrated on the active sites of M-AC, and the contaminants concentrated on M-AC may be digested by the activated sludge; consequently the active sites of M-AC may be regenerated by the sludge. The activated sludge itself may naturally show its own treatment effect (curve (1)) as well as the activated carbon M-AC (curve (3)). The high treatment efficacy of (AC+AS) Method may be due to the digestive effect of the sludge, the adsorption effect of the carbon, and such additional effects as mentioned above which are shown by applying the sludge and the activated carbon simultaneously. The regenerative effect of the activated sludge on the activated carbon will be discussed further in the following sections.

The less treatment efficacy, within about 1.5 hrs, of the (AC+AS) Method than that of the (AC after AS) Method may be due to the fact that M-AC required about 1.5 hrs for adsorption to exert sufficiently its adsorptive power as already shown in Fig. 1.

If a considerably longer treatment time is ap-
plied, the AS Method as well as (AC after AS)-Method will likely remove the phenols or TOC to nearly the same level as that attained with the (AC+AS)-Method. However, the former methods are less satisfactory than the latter, (AC+AS)-Method, from an industrial and economical viewpoint.

3.4 Effect of Activated Sludge on Regeneration of Activated Carbon

1.0 l of the phenolic wastewater was treated with 1.0 g of M-AC for 6 hrs, and then the M-AC used was aerated in the mixture of AS and distilled water (SV=50%) for 16 hrs.

The treatment efficacies of used and regenerated M-ACs were examined with the AC Method and the (AC+AS)Method, and they were compared with those of virgin M-AC. The results are shown in Fig. 7 (removal of phenols) and Fig. 8 (removal of TOC).

From the figures, the treatment efficacy of the used M-AC was found to be very small, but that of the regenerated M-AC was considerably large, especially for TOC, it being nearly equal to that of the virgin M-AC except that its adsorption rate was somewhat smaller. Similarly, it is evident also that the treatment efficacy of the (AC+AS)Method with the regenerated M-AC was considerably larger than that with the used M-AC.

From these results, it can be concluded that activated carbon M-AC can be regenerated by aerating it together with AS, and this fact may be the reason for why the treatment efficacy of the (AC+AS)Method with the used M-AC was slightly larger than that of the AS Method. That is, the M-AC once used may be regenerated a little by aerating it with AS even in the phenolic wastewater.

Next, the change in the treatment efficacy of the (AC+AS)Method was examined by treating the phenolic wastewater four times using the same M-AC repeatedly. In the first step, the wastewater was treated with the (AC+AS)Method for 4 hrs, and the M-AC used in the treatment was recovered, and then a new feed of the wastewater was treated again with the (AC+AS)Method using the recovered M-AC and newly added AS. These procedures were repeated three times.

The treatment power of the (AC+AS)Method using the same M-AC repeatedly was larger than that of the AS Method, and it removed with every treatment about 50% of what could be removed by the virgin M-AC as shown in Fig. 9.

From these results, it may be reasonable to suppose that two processes, the adsorption of phenols or TOC by M-AC and regeneration of M-AC by AS, should proceed simultaneously. In addition, the following expectation may be possible: if the treatment or the aeration was continued for a longer time so that M-AC could be kept together with AS in the water containing lower concentrations of phenols or TOC, the treatment power of the (AC+AS)Method in the next run would be larger, and it would be continued further.

Since the M-AC used was made from a mixture of...
of a asphalt (80%) and red mud (20%), it contained considerable amounts of such metals as aluminum and iron that brought about the difference in its composition from that of the common activated carbon. Next, the treatment efficacy of the (AC+AS) Method with a commonly activated carbon was examined, and its high treatment efficacy was confirmed. However, it was difficult to separate the carbon from its mixture with AS, while the M-AC was recovered easily from such a mixture by using a magnetic separator such as a magnetic belt

4. Conclusions

The treatment of phenolic wastewater by simultaneous application of granular activated carbon and activated sludge (AC+AS) Method was investigated. The activated carbon was made from a mixture of asphalt and red mud, and it could be attracted to a magnet (magneto-sensitive activated carbon, M-AC).

1) The treatment with the (AC+AS) Method was more rapid and effective than either of the treatment with activated sludge (AS) alone or with the AS treatment followed by M-AC treatment, a conventional method commonly used in wastewater treatment plants.

2) The M-AC used in the treatment could be regenerated by aerating it in the presence of AS.

3) In the treatment with the (AC+AS) Method using the same M-AC repeatedly, the treatment efficacy or power decreased a little only in the second treatment, but henceforward no appreciable decrease was observed.

References

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要 旨
活性炭の評価と利用に関する研究（第5報）
活性炭活性汚泥同時使用によるフェノール類含有廃水の処理
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活性炭を直接利用することによって活性炭との混合系から容易に分離・回収された。

活性炭の添加量および活性炭の使用量を種々変化させて、それぞれの最適使用条件を検索した。その結果、活性炭添加量としては、活性汚泥使用量に対して50%が適当であることがわかった。

活性炭と活性炭との同時使用による方法（AC+AS法）は、活性汚泥単独処理法（AS法）および通常の活性汚泥処理法である活性汚泥処理後活性炭処理法（AC after AS法）のいずれよりも優れた処理方法であることが確認された（Fig. 5）。

使用活性炭は、活性汚泥の中でかんぱん・ばらつきすることによって再生されることが明らかになった（Fig. 7）。

同一の活性炭を繰り返し使用した場合、（AC+AS法）の処理能力は2回目の処理においては低下した。しかし、それ以降においては処理能力の低下はほとんど認められなかった（Fig. 9）。

Keyword
Activated carbon, Activated sludge, Phenolic wastewater