Studies on Evaluation and Utilization of Activated Carbon (Part 3)

High Temperature Batch Reactivation of Activated Carbon with a 50 mm ϕ Fluidized Bed Reactor

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High temperature reactivation of activated carbon used in phenolic wastewater treatment was investigated by using a 50 mm ϕ fluidized bed reactor.

The spent carbon could not be regenerated merely by heating at 700°C in nitrogen. Most of the phenols adsorbed on the carbon were found to be decomposed into such gaseous products as hydrogen and methane but some carbonized into substances that adhered to the carbon.

In the steam reactivation at high temperatures, the spent carbon could be regenerated by raising the temperature and by extending the period of reaction. When the spent carbon was treated with steam at 800°C for 10 min its specific surface area was fully restored while its methylene blue adsorption capacity was only partly restored, and the original adsorptive power of the carbon for phenolic wastewater treatment was practically restored.

Both sulfur and ash, which had accumulated on the carbon by adsorption, could not be removed even by high temperature reactivation.

Activated carbon particles suffered but slight from pulverization due to steam reactivation at high temperatures.

Since linear relations were observed between bulk density and other properties of the reactivated carbon, its properties could be predicted from its bulk density.

1. Introduction

Generally, activated carbons used in liquid phase adsorption cannot be regenerated by simple heat treatment¹⁾. Most of the industrial regeneration processes of spent carbon involve high temperature reactivation²⁾. Although air oxidation in an aqueous medium, electrolytic oxidation and biological oxidation have also been proposed, none of them has been applied practically^{3),4)}.

Thermal analyses of the various adsorbates on the activated carbon have suggested that such substances as phenol, lignin, humus, etc. cannot be removed by simple heat treatment, and that the spent carbon adsorbing them should be reactivated at high temperatures with an activating gas such as steam⁵⁾. The following aspects of the problem have already been clarified by some fundamental experiments: increasing the amounts of adsorbates makes regeneration difficult^{6),7)}; repeated high temperature reactivation treatments result in pulverization of activated carbon particles^{8),9)}; some kinds

of inorganic compounds, especially alkali metal compounds, cause a decrease in high temperature reactivation yield and effect changes in pore size distribution^{10),11)}. But these findings are still not sufficient to show how the spent carbon is reactivated.

In high temperature reactivation, the decreases in reactivation yield, particle size and strength of activated carbon always take place along with other undesirable phenomena, which are said to be largely dependent on the kinds of activated carbon used and adsorbates found thereon. Thus, a suitable reactivation procedure must be investigated for the kind of activated carbon used and composition of the waste in question.

In this report, high temperature reactivation of activated carbon used in the treatment of phenolic wastewater was investigated by using a 50 mm ϕ fluidized bed reactor.

The spent carbon that had adsorbed phenol was regenerated practically with an aqueous sodium hydroxide solution, and this was applied to the process for recovering pure phenol¹²⁾. When the organics in the wastewater are found in mixtures, a regeneration process using caustic soda should be avoided, because the subsequent treatment of the spent caustic soda is very difficult.

Received September 8, 1977.

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2. Experimental

2.1 Spent Activated Carbon

Commercially available activated carbon made from coal was used in these studies. The phenolic wastewater used contained phenol and its derivatives (103 ppm as phenol, 170 ppm as total organic carbon) and was obtained from a fluid catalytic cracking plant (FCC). 1.2 l of the wastewater was treated with 1 g of the activated carbon which was sieved to 16 to 32 mesh sizes (Tyler) before use. The activated carbon after treatment was left on a sheet of filter paper for 24 hrs for drying before storing in a sealed bottle. Its drying weight loss was 6.7%, according to the test method described in JIS K 1474.

From the drying weight loss and the volume of the phenolic wastewater treated, the composition of the spent carbon was calculated as follows:

Activated carbon	: 83.0 wt%
Moisture	: 6.7
Phenols	: 10.3

Assuming that the activated carbon would adsorb the various contaminants other than phenols in the wastewater, the above value (83.0%) for the activated carbon may be somewhat larger than the net value.

The properties of the virgin and spent activated carbon are listed in **Table 1**. Values of their bulk densities and strengths were determined at their wet base.

Table 1 Properties of Virgin and Spent Activated Carbons

Properties	Virgin	Spent
Specific Surface Area (m ² /g)	1,226	817
Methylene Blue Adsorption Capacity (mg/g)	334	106
Bulk Density (g/ml)	0.448	0.572
Strength (%)	90.0	93.0
Sulfur (%)	0.18	0.56
Ash (%)	1.82	1.09

The spent carbon tested with a thermobalance in Section 3.1 was different from the others only in the length of air drying period involved in its preparation, and its drying weight loss was 15%.

2.2 Procedure

A fluidized bed reactor of 50 mm ϕ in inner diameter was used¹³⁾. The temperature was controlled with an electric furnace.

30.0 g of the spent carbon (wet base) was placed in the reactor. While the reactor was heated up to the selected temperature (750~850°C) in 10 min, the spent carbon was fluidized with nitrogen gas.

After attaining the temperature, the fluidizing gas was changed from nitrogen to steam (2 gH₂O/min) which acted as an activating reagent. When the scheduled reactivation period was over, the fluidizing gas was changed fast to nitrogen. The reactivated carbon was then drawn into the flask installed at the bottom of the reactor. After cooling down to room temperature, the carbon was taken out of the flask and weighed and its properties were determined.

2.3 Determination of Various Properties of Activated Carbon

Specific surface area was measured by the BET method (nitrogen adsorption), methylene blue adsorption capacity was determined as described in our previous report¹⁴⁾, and bulk density was calculated from the weight and the volume of the carbon filled most tightly in a 10 ml graduate. Sulfur and ash contents were measured by the methods of JIS K 2541 and JIS K 1474, respectively; the ash was measured as ignition residue.

Strength was measured with an Activated Carbon Tester made by Nigorikawa Rikagaku Kikai Co., Ltd. The procedure was as follows. 10 g of activated carbon (16~32 mesh) was put into a rotary pot with ten steel bells (10 mm in diameter). The pot then was rotated at a rate of 90 rpm for 30 min. Strength was given by the following equation:

$$\text{Strength (\%)} = \frac{\text{Weight of the portion left above 32 mesh sieve (g)}}{\text{Weight of the sample fed (g)}} \times 100$$

It was a modified method described in former JIS K 1412. Strength of the virgin carbon was 99.0% by the method of JIS K 1412 and was 90.0% by our method.

Thermal analysis of activated carbon was carried out by using a thermobalance MTG-11 made by Shimadzu Seisakusho Ltd..

2.4 Determination of Adsorption Properties

Adsorption isotherms and adsorption rates were determined as described in the previous report¹⁴⁾.

2.5 Analysis of Gas Evolved in Thermal Cracking of Spent Activated Carbon

Composition of the gases evolved in the thermal cracking of the spent carbon was analyzed gas chromatographically.

3 Results and Discussion

3.1 Thermal Analysis of Spent Activated Carbon

The weight decrease in the spent carbon by heat treatment was measured at the heating rate of 20°C/min in an atmosphere of nitrogen, and the

Fig. 1 T. G. Curves of Spent and Virgin Activated Carbons in Pure N_2

methylene blue adsorption capacity¹⁴⁾ of the carbon thus treated was measured. The results are shown in **Fig. 1**.

The rate of vaporization of pure phenol adsorbed on activated carbon is known to be very slow⁵⁾, and the vaporization of substances adsorbed in sewage treatment is known to occur continuously and gradually⁶⁾.

The weight decrease in the spent carbon occurs in three steps. The first may be due to the vaporization of moisture, and the second due to the vaporization of phenols and the other adsorbates, and the third due to the decomposition of the adsorbates. Thus the organics in the phenolic wastewater from the FCC plant are considered to consist of two types of substances, one that vaporizes readily and the other that decomposes.

The amount of adsorbates on the carbon was estimated from these experimental results to be about 15% by weight (dry base).

Methylene blue adsorption capacity (MB) increased with the weight decrease. MB of the spent carbon was 106 mg/g, and it increased slightly when all the moisture was driven out, but it increased to 197 mg/g after rapid vaporization of the adsorbates, and finally to 222 mg/g after decomposition of the adsorbates at 700°C. The value 222 mg/g was considerably smaller in comparison with 334 mg/g of the virgin carbon. These results meant that the spent carbon that adsorbed considerably large amounts of adsorbates could not be regenerated completely by a simple heat treatment in an atmosphere of nitrogen^{6),7)}.

3.2 Composition of Liquid and Gaseous Products Obtained in Thermal Cracking of Spent Activated Carbon

15.0 g of the spent carbon (wet base) was put into a 70 ml stainless steel flask. The atmosphere in the flask was replaced with nitrogen and the flask was placed in an electric furnace maintained at 800°C. The gaseous products after condensibles were separated in a water-cooled trap were col-

Table 2 Composition of Thermal Decomposition Products

Spent Activated Carbon (g)	15.0(wet base)
Residue of Thermal Decomposition (g)	12.5
Liquid Product of Thermal Decomposition (g)	1.81
Gaseous Product of Thermal Decomposition (ml)	635
Phenols in Liquid Product (g as Phenol)	0.33
Composition of Gaseous Product (vol%)	
H_2	44.80
O_2	0.54
N_2	26.81
CH_4	6.16
CO	21.00
CO_2	0.43
C_2H_6	0.08
C_2H_4	0.07
C_3H_8	0.03
C_3H_6	0.08
C_4	0
H_2S	0
SO_2	tr
(total 100.00)	

lected over water saturated with sodium chloride.

Analytical data for these products are listed in **Table 2**.

As shown in **Table 2**, 1.81 g of liquid substance and 635 ml of gaseous substances were obtained from 15.0 g of the spent carbon (wet base). The solid residue was assumed to consist of the original activated carbon and small amounts of carbonized adsorbates. The liquid phase contained 0.33 g of phenols, and this meant that about 80% of the phenols on the carbon might have decomposed into gaseous or carbonized substances and adhered onto the carbon, because 1.55 g of phenols was thought to have been adsorbed on 15.0 g of the spent carbon (wet base).

Although hydrogen was the main constituent of the evolved gases, considerable amounts of carbon monoxide, methane and carbon dioxide were also found. The contents of hydrocarbons whose carbon numbers are not less than 2 were less than 0.1% by volume.

From the experimental result that large amounts of hydrogen, carbon monoxide and carbon dioxide were formed, it might be reasonable to consider that the reaction of carbon with steam (the main reaction in reactivation of spent carbon) proceeded simultaneously with thermal decomposition of the adsorbates. Under such conditions, the temperature of the spent carbon containing a large amount of moisture could have raised so quickly that the carbon might have reacted with steam to some extent¹⁵⁾ before the moisture in the carbon was

Table 3 Reactivation Conditions and Results

Ex. No.	TS-0 Virgin	TS-0' Spent	TS-1 Spent	TS-2 Spent	TS-3 Spent	TS-4 Spent	TS-5 Spent	TS-6 Spent	TS-7 Spent	TS-10 Spent
Feed (g)	—	—	30.0	30.0	30.0	30.0	30.0	30.0	30.0	36.5
Temperature (°C)	—	—	800	800	800	750	750	850	850	800
Period (min)	—	—	0	10	15	10	15	10	15	10
Yield (wt%)	—	—	100	92.3	87.1	96.4	94.4	83.6	74.0	93.4
Yield (vol%)	—	—	99.1	96.5	94.5	96.9	94.7	92.5	93.8	102
Bulk Density (g/ml)	0.448	0.572	0.491	0.467	0.456	0.491	0.488	0.443	0.389	—
Specific Surface Area (m ² /g)	1,226	817	1,186	1,204	1,276	1,129	1,225	1,343	1,640	1,210
Methylene Blue Adsorption Capacity (mg/g)	334	106	255	305	339	272	287	341	402	298
Strength (%)	90.0	93.0	90.5	91.6	90.5	91.1	99.7	87.5	85.6	—
Sulfur (%)	0.18	0.56	0.26	0.24	0.25	0.24	0.24	0.24	0.20	—
Ash (%)	1.82	1.09	1.66	2.59	3.15	2.92	4.06	3.82	3.64	—

removed from the reaction system.

A small amount of sulfur dioxide was found in the evolved gases, so some means to remove this poisonous substance should be considered in industrial applications.

3.3 High Temperature Reactivation

Reactivation conditions and results are listed in **Table 3**. Reactivation yield by weight was calculated as follows:

Yield (wt %)=

Amount of reactivated carbon
obtained(g) × 100

{Amount of the spent carbon
fed (g, wet base) × {(Thermal
decomposition yield (wt %)/
100)}

where, thermal decomposition yield means the ratio of the amount of the solid product remained after decomposition at 850°C in an atmosphere of nitrogen to the feed amount of the spent carbon used. The good reliability of these calculations was shown by experiment TS-10, as shown in **Table 3**.

In the experiment TS-10, 36.5 g of the spent carbon (wet base) was prepared by treating the phenolic wastewater with 24.3 g of the virgin activated carbon (dry base) and air drying the mixture. The carbon was reactivated at 800°C for 10 min, and 22.7 g of reactivated carbon resulted. The yield here calculated was 93.4% by weight, which was approximately equal to that of experiment TS-2 whose reactivation conditions were the same as those of experiment TS-10.

Reactivation yields decreased with increasing temperature and with increasing time of reaction as shown in **Fig. 2**.

3.3.1 Effect of Reactivation Temperature on Properties of Reactivated Carbon

The effect of reactivation temperature on the properties of reactivated carbon is shown in **Fig. 3**.

The specific surface area (S) of the reactivated carbon increased with increasing temperature, and this tendency was greater in the case of reactivation

Fig. 2 Effect of Reactivation Temperature on Yield

Fig. 3 Effect of Reactivation Temperature on Properties of Reactivated Carbon

carried out for 15 min. Restoration of S was comparatively easy. S of the reactivated carbon became approximately equal to that of the virgin carbon by reactivation at 750°C for 15 min or 800°C for 10 min. The yields in these cases were 94.4 and 92.3% by weight, respectively. The yield was larger for reactivation carried out at the lower temperature.

Restoration of MB was a little more difficult than that of S. Reactivation at 800°C for 15 min or at 850°C for 10 min was necessary for complete rege-

neration of MB. The yields under these reactivation conditions were 87.1 and 83.6% by weight, and again the yield was larger with lower temperature reactivation.

The bulk density of the spent carbon decreased by reactivation. It decreased to 0.491 g/ml by a simple heat treatment in an atmosphere of nitrogen at 800°C, but it was still larger than that of the virgin carbon (0.448 g/ml). Bulk density was recovered by reactivation at 800°C for 15 min.

Strength of the activated carbon hardly decreased by reactivation.

The sulfur content of the activated carbon increased through treatment of the phenolic wastewater. Considerably more severe reactivation conditions would be necessary for complete removal of the sulfur. When such conditions were applied, the reactivation yield would be as low as 80~70%, as shown in **Fig. 4**. Thus a small amount of accumulation of sulfur should be allowed, and the sulfur content of the activated carbon, as a result, might increase by repeated uses and reactivations. Further investigations would be necessary to clarify the effect of accumulated sulfur on adsorption performance of the activated carbon.

Ash in the spent carbon could not be removed by reactivation, as shown in **Fig. 5**, but it was considered to be accumulated on the activated carbon as in the case of sulfur.

Generally, the ash in the activated carbon existed in the form of a salt or oxide⁶⁾, and it might not be

removed merely by heating at 750~850°C for 10~15 min. The effects of accumulated ash on adsorption performance and reactivation should also be clarified.

3.3.2 Relationships between Properties of Reactivated Carbons and Reactivation Yields as well as Bulk Densities

Fig. 6 shows the relationships between reactivation yields by weight and properties of reactivated carbons.

Fig. 6 Relationships between Reactivation Yields and Properties of Reactivated Carbons

The properties of reactivated carbons were improved with decreasing reactivation yield. As mentioned above, S and MB were regenerated favorably at lower temperatures and at longer times of reaction. The reactivation yields required for the regeneration of the individual properties varied depending on the kinds of properties concerned.

for S	91~94 wt%
for MB	84~87 "
for bulk density	85 "
for strength	90 "

Fig. 7 shows the relationships between bulk densities and other properties of reactivated carbons.

Bulk density is often used practically as an index for estimation of regeneration effect¹³⁾. This was approximately correct in this study, because the bulk density of the reactivated carbon was almost linearly related to other properties.

The regression lines showing each relationships in **Fig. 7** was calculated statistically.

Fig. 4 Removal of Sulfur by Reactivation

Fig. 5 Removal of Ash by Reactivation

3.3.3 Particle Size Distribution

Fig. 8 shows the distribution of particle sizes of virgin, used and reactivated carbons.

The activated carbon appeared to coagulate partially by coming in contact with the phenolic wastewater as shown in **Fig. 8**, but it was clear that such

Fig. 7 Relationships between Bulk Densities and Properties of Reactivated Carbons

coagulation would result from the mere attaching of the activated carbon particles to the others. Portions of the activated carbon particles in the range from 24 to 32 mesh sieve increased a little by reactivation, but those under 32 mesh did not. Thus, within the limitations of this reactivation study, pulverization of activated carbon was not significant, but the decrease in the radii of the activated carbon particles might progress by the process of repeated reactivation^{8),9)}.

3.4 Optimum Reactivation Conditions and Treatment of the Phenolic Wastewater with the Reactivated Carbon

Reactivation conditions required for a complete regeneration of fundamental properties such as *S* and *MB* varied according to the kinds of properties considered. Comparatively severe conditions were necessary for regeneration of *MB* that consequently gave lower reactivation yields. Steaming at 800°C for 10 min was here considered to be the optimum reactivation conditions. The conditions resulted in complete regeneration for *S*, but not for *MB*, and gave the reactivation yield of 92.3% by weight.

The adsorption isotherm and adsorption rate of the carbon reactivated under the above optimum conditions were measured in the treatment of the phenolic wastewater and the results obtained are shown in **Figs. 9** and **10** along with those of the virgin carbon. Freundlich's constants *K* and *n*^{14),17)} are calculated and shown in **Fig. 9**. *D_i*¹⁴⁾,

Fig. 8 Particle Size Distribution

Fig. 9 Adsorption Isotherm for Phenols

Fig. 10 Adsorption Rate for Phenols

an intraparticle diffusion constant (radius of the carbon particle assumed as 0.038 cm) and K_v^{14} , an apparent adsorption rate constant, are shown in Fig. 10.

From these figures, it is evident that the carbon is practically regenerated under the above conditions to be applicable to the phenole wastewater treatment.

4 Conclusions

High temperature batch reactivation of activated carbon used in the treatment of phenolic wastewater was investigated by using a 50 mm ϕ fluidized bed reactor. The results were as follows:

1) The spent carbon was not regenerated sufficiently by a simple heat treatment at 700°C in nitrogen.

2) Most of the phenols adsorbed on the carbon decomposed into gases such as hydrogen and me-

thane or carbonized into substances that adhered to the carbon.

3) Linear relationships were observed between bulk density and other properties of the reactivated carbon during reactivation: thus, properties of the reactivated carbon could be predicted from its bulk density.

4) When the spent carbon was treated with steam at 800°C for 10 min, its specific surface area was fully restored, while its methylene blue adsorption capacity was partially restored. But it was confirmed that the adsorption performance of the carbon in the phenolic wastewater treatment was recovered practically completely.

Acknowledgement

The authors gratefully acknowledge the valuable advice and encouragement of Dr. T. Shibusawa, Director and General Manager, Dr. T. Amemiya, former director, and Dr. H. Miyake of Research and Development Center, Maruzen Oil Co., Ltd.

The authors also wish to express their appreciation to Maruzen Oil Co., Ltd. for permission to publish this work.

References

- 1) Yanai, H., "Kasseitan Dokuhon", 56, 219, (1976) Nikkan Kyogyo Shinbunsha.
- 2) Shumaker, T. P., Chem. Process (Chicago), **36**, (5), 45¹(1973).
- 3) Gitchel, W. B., Meidl, J. A., Burant, W. Jr., Chem. Eng. Progr., **71**, (5), 90 (1975).
- 4) Urano, K., Kagaku Kogaku, **37**, (7), 877(1973).
- 5) Suzuki, M., *ibid.*, **40**, (8), 408 (1976).
- 6) Urano, K., Nihon Kagaku Kaishi, **1972**, (5), 975.
- 7) Urano, K., Huruya, T., *ibid.*, **1975**, (5), 921.
- 8) Akamatsu, I., Ueshima, H., *ibid.*, **1973**, (7), 1333.
- 9) Akamatsu, I., Kobayashi, T., Ueshima, H., *ibid.*, **1975**, (3), 550.
- 10) Walker, P. L., Rushinko, F. Jr., Austin, L. A., Advances in Catalysis, **11**, 133 (1959).
- 11) Mine Safety Appliance Res. Corp., EPA Project, #17020 DAO (1970).
- 12) Himmelstein, K. J., Fox, R. D., Winter, T. H., Chem. Eng. Progr., **69**, (11), 65(1973).
- 13) Kudo, K., Terada, K., Yokogawa, A., Mitooka, M., Shirao, M., Ishibashi, K., Noda, Y., J. Fuel Soc. Japan, **55**, (593), 749 (1976).
- 14) Terada, K., Kudo, K., Yamamoto, Y., Mitooka, M., Yokogawa, A., Bull. Japan Petrol. Inst., **19**, (2), 179 (1977).
- 15) Baba, A., Terui, A., Honda, H., Yoshida, Y., Tachikawa, S., Suzuki, M., Kawamura, N., "Sekitan Kagaku Kogyo", 161, (1960) Sangyo Tosho.
- 16) Culp, R. L., Culp, G. L., "Advanced Wastewater Treatment", 163, (1971) Van Nostrand Reinhold Co.
- 17) Keii, T., "Kyuchaku", 26, (1965) Kyoritsu Shuppansha.

要 旨

活性炭の評価ならびに利用に関する研究 (第3報)

50 mm ϕ 流動床炉による活性炭の高温回分式再生

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石油類の接触分解装置から排出されるフェノール類含有廃水処理に使用した活性炭を、50 mm ϕ 流動床炉によって回分式高温再生した。使用した活性炭は石炭を原料として製造された市販品である。

窒素気流中における使用済活性炭の熱分析の結果、使用済活性炭は水分の他に 15% 程度の熱分解性吸着質を吸着していることがわかった。熱処理 (窒素ふん囲気下, 700°C) によるメチレンブルー吸着力の回復は、新炭の値に対し約 70% であった (Fig. 1)。

流動床による工業的再生を想定して、使用済活性炭を 800°C に急熱して分解生成物の組成を調べた。活性炭上のフェノール類は、加熱によって約 20% が脱離し他は分解もしくは活性炭上に炭化沈積すると思われた。分解ガスの主成分は水素、一酸化炭素、メタン等であり、炭素数 2 以上の炭化水素は少なかった。それらの分解ガス組成から、水分を多量に含有する使用済活性炭を急熱すると、水性ガス反応も同時に起こることが認め

られた (Table 2)。

水蒸気による高温再生によって、比表面積、メチレンブルー吸着力などの活性炭の基礎的な性状はほぼ完全に回復された。廃水処理によって吸着された無機化合物もしくは硫黄化合物に基づく活性炭上の灰分および硫黄分は、再生によって除去することは困難でありある程度蓄積するものと思われた (Table 3)。

再生炭のかさ密度と比表面積およびメチレンブルー吸着力とはほぼ直線関係にあることが認められ、再生炭の性状はそのかさ密度から推定され得ると思われた (Fig. 7)。

再生による活性炭粒子の粒径減少が認められたが、微粉化にまでは至らなかった (Fig. 8)。

水蒸気による 800°C、10 分間の再生によって 92.3 wt% の収率で得られた再生炭の比表面積はほぼ 100% 回復していたが、メチレンブルー吸着力は約 90% の回復を認めたに過ぎなかった。しかしながら、廃水中のフェノール類に対する吸着等温線および吸着速度を測定したところ、実質的にはほぼ完全に吸着能力を回復していることが認められた (Figs. 9, 10)。

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Keyword

Activated carbon, Adsorption capacity, Batch reactivation, Phenolic wastewater