COLLECTION OF MERCURY FROM AQUEOUS SOLUTIONS WITH CARBONACEOUS MATERIALS

Hideko KOSHIMA and Hiroshi ONISHI
University of Tsukuba, Sakura-mura, Ibaraki-ken 305

The effect of pH on the collection of mercury(II) and methylmercury was investigated with nine commercially available carbonaceous materials. Specific surface area and C, H, O, N, and S in these materials were determined. Activated carbon (powder, granular, or felt) was the best adsorbent for mercury. Satisfactory recoveries were also obtained with carbon black from solutions of pH 1 to 14. In spite of the small specific surface area of anthracite, it gave fair recoveries of mercury.

1 Introduction

Activated carbon is a good adsorbent for mercury in aqueous solutions\(^{1,2}\). The purpose of the present work is to obtain data on the collection of mercury(II) and methylmercury with other commercially available carbonaceous materials, that is, carbon black, graphitized carbon black, graphite, glassy carbon, and coal. In general, activated carbon owes a large portion of remarkable adsorption properties to its porous nature. It has been reported that oxygen-containing functional groups, e.g., carboxyl group, are present on the surface of activated carbon and carbon black\(^{3,4}\). In this work, specific surface area was measured by the N\(_2\)-BET method. The contents of carbon, hydrogen, nitrogen, and sulfur were determined by the methods of organic elemental analysis. The oxygen content was determined by 14 MeV neutron activation\(^{5}\).

In the presence of oxidizing agents, low recoveries of mercury(II) with activated carbon were obtained\(^{6}\). Consequently the effect of reducing agents on the collection of mercury was also examined.

2 Experimental Section

2.1 Materials and reagents

Nine commercially available carbonaceous materials (Table 1) were used after drying at 110°C for 2 h. As reported previously\(^{2}\), activated carbon was heated at 350°C for 2 h (for purification) before collection of mercury. Before drying, activated carbon felt was cut to 5×5 mm and anthracite was ground to pass 200 mesh. Glassy carbon was 200 to 325 mesh.

Standard mercury(II) and methylmercury solutions were prepared as described before\(^{2}\).

2.2 Apparatus

Mercury was determined by electrothermal atomic absorption (Nippon Instruments Co. Ltd., Rigaku Mercury SP\(^{2}\)).
Specific surface area was measured by using an instrument (Sibata Chemical Apparatus Mfg. Co. Ltd., Rapid surface area apparatus, Model SA-1000) which is based on the N₂-BET method. Before the measurement, the materials were heated in nitrogen at about 140°C for 2 h to remove adsorbed gases.

The oxygen content was determined by 14 MeV neutron activation (Kaman Sciences, Neutron generator, Model 1 A-711, 160 kV, 2.5 mA). Gamma activity due to ¹⁶N was counted integrally in the energy region between 4.8 and 6.4 MeV with a 2 x 2 in NaI(Tl) detector. Oxygen standards were prepared by mixing reagent-grade sucrose with pure graphite (Union Carbide, spectroscopic powder, SP-1C).

2.3 Procedure

Basic procedure was previously described for the collection of mercury¹). Fifty mg of a carbonaceous material was added to 50 ml of solution containing 4 or 16 ng of mercury. The pH of the solution was adjusted with hydrochloric acid or sodium hydroxide. The amount of mercury added to the solution depended on the initial mercury content of the carbonaceous material (<0.1 to 140 ng Hg/g). In the case of granular carbon and felt carbon, the solutions were mixed mechanically. The pH of the filtrate was measured with a pH meter.

<table>
<thead>
<tr>
<th>Carbonaceous material¹</th>
<th>Specific surface area² m²/g</th>
<th>Element, %</th>
<th>Total</th>
<th>Ash%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon, powder Merck, No.2186</td>
<td>803</td>
<td>92.7</td>
<td>0.7</td>
<td>4.8</td>
</tr>
<tr>
<td>Activated carbon, powder Merck, No.2186, 350°C, 2h</td>
<td>871</td>
<td>91.7</td>
<td>0.6</td>
<td>5.9</td>
</tr>
<tr>
<td>Activated carbon, granular Kanto Chemical Co.</td>
<td>1050</td>
<td>90.0</td>
<td>0.3</td>
<td>5.8</td>
</tr>
<tr>
<td>Activated carbon, felt Toyobo, KF-1500</td>
<td>1320</td>
<td>84.8</td>
<td>0.8</td>
<td>12.6</td>
</tr>
<tr>
<td>Carbon black Mitsubishi Kasei, MA 600</td>
<td>123</td>
<td>97.1</td>
<td>0.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Graphitized carbon black Mitsubishi Kasei, No.4000B</td>
<td>82</td>
<td>99.7</td>
<td>&lt;0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Graphitized carbon black Supelco, Carbopack B</td>
<td>91</td>
<td>99.5</td>
<td>&lt;0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Graphite Chuetsu Kokuen, CX-600</td>
<td>15</td>
<td>97.5</td>
<td>0.1</td>
<td>1.8</td>
</tr>
<tr>
<td>Glassy carbon Tokai Carbon, GC-20</td>
<td>2</td>
<td>99.0</td>
<td>&lt;0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Anthracite Yamabishi Kogyo</td>
<td>5</td>
<td>89.2</td>
<td>2.9</td>
<td>3.8</td>
</tr>
</tbody>
</table>

a After drying at 110°C for 2 h.
b Ignition residue after heating at 800°C.
c Results of measurement on standard samples:
  NPL M11-02 Graphitized carbon black 73.4 m²/g (certified value 71.3±2.7 m²/g)
  NPL M11-04 Meso-porous silica 247 m²/g (certified value 286.1±3.5 m²/g).
3 Results and Discussion

3.1 Specific surface area and elemental analysis of carbonaceous materials

As shown in Table 1, specific surface area values were about 1000 m²/g for all the materials of activated carbon (powder, granular, and felt), and about 100 m²/g for carbon black and graphitized carbon black. The oxygen content of the materials of activated carbon was 5 to 13 %, that is, 4 to 11 oxygen atoms per 100 carbon atoms. Two materials of graphitized carbon black had high carbon contents. Anthracite was not porous, but it contained appreciable amounts of oxygen, hydrogen, and nitrogen.

3.2 Collection of mercury with carbonaceous materials

The effect of pH on the collection is shown in Fig. 1. Collection of mercury(II) with activated carbon powder (b) from hydrochloric acid solution was previously reported. Quantitative recoveries were obtained with all the materials of activated carbon (powder (b), granular (c), and felt (d)) from solutions of pH 0 to 14. Carbon black (e) was also a good adsorbent in solutions of pH >1. Two materials of graphitized carbon black, (f) and (g), showed similar specific surface area but different mercury collection behavior. Recoveries of mercury(II) and methylmercury with graphitized carbon black (f) were similar to those with graphite (h). In spite of the small specific surface area of anthracite (j), fair recoveries of mercury(II) and methylmercury were obtained. On the basis of collection behavior of mercury(II) and methylmercury, the carbonaceous materials used in the present work can be divided into two groups. With Group I (activated carbon and carbon black) mercury(II) and methylmercury show the same collection behavior, while with Group II (graphitized carbon black, graphite, glassy carbon, and anthracite) they show different collection behavior.

In the preceding experiment, buffer solutions were not used. When sodium tetraborate (0.01M) - hydrochloric acid or sodium hydroxide solutions (pH 6 to 13) were used, the recoveries of mercury(II) obtained with activated carbon powder (b), carbon black (e), and graphite (h) were the same as those obtained without buffer solutions. Recoveries of mercury(II) from the solutions adjusted to ionic strength 0.1 and 1 (sodium perchlorate, pH 6 to 8) were almost the same as (b), (e) and (h) in Fig. 1.

3.3 Effect of reducing agents

The effect of reducing agents was investigated in order to obtain information on the mechanism of the collection of mercury(II). The recovery of mercury(II) (4 ng) from 1M hydrochloric acid solution with graphite increased from 4 % in the absence of tin(II) chloride to about 40 % in the presence of more than 0.3 mmol of tin(II) chloride (50 ml of solution and 50 mg of graphite). But hydroxylammonium chloride and L-ascorbic acid were not effective in 1M hydrochloric acid. Positive effect was obtained in the presence of tin(II) chloride (0.1 mmol) or sodium borohydride (0.5 to 2 mmol) with graphite from solutions of pH 12. These results indicate that mercury is collected with carbonaceous materials more favorably in the presence of the strong reducing agents than in the absence.
Fig. 1 Collection of mercury with carbonaceous materials

solution, 50 ml; carbonaceous material, 50 mg; mercury, 4 or 16 ng

- mercury(II)
- methylmercury
Acknowledgment

The authors wish to thank the Radioisotope Center of this university for help in the activation analysis. The elemental analysis was made by the Chemical Analysis Center of this university.

(Presented at the 30th Annual Meeting of the Japan Society for Analytical Chemistry, Kyoto, October, 1981)

References


Keyword phrases

collection of mercury with carbonaceous materials from aqueous solutions; electrothermal atomic absorption; mercury(II) and methylmercury.

(Received July 31, 1982)