

THIN SECTIONING OF CARBONACEOUS ADSORBENT SPHERES FOR VISUALIZATION BY LIGHT MICROSCOPY AND SCANNING ELECTRON MICROSCOPY

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Abstract

Three different types of Rohm and Haas carbonaceous adsorbent spheres (XE-340, XE-347 and XE-348) were prepared for light and scanning electron microscopy by embedding in resin and by thin sectioning. Spurr's low viscosity resin, because of its penetrating and wetting ability, contributed to the production of the most uniform and artifact free thin sections. In addition to thin sectioning, gas adsorption surface area measurements were made on batches of each type of sphere.

There was an apparent relationship between the surface area measurements of 417.8 m²/g for XE-340, 583.4 m²/g for XE-347 and 752.9 m²/g for XE-348 and the microstructural appearances of the internal morphologies of each type of sphere.

Key Words: Scanning electron microscopy, light microscopy, ultramicrotomy, carbonaceous adsorbent spheres, XE-340, XE-347, XE-348, surface area, gas adsorption.

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Introduction

Ambersorb XE-340 is one of many synthetic carbonaceous adsorbents developed by the Rohm and Haas Company to remove organic chemicals from liquid or gaseous environments. These adsorbents are hard black spheres whose respective total surface areas range from 400 m²/g to 700 m²/g and whose modes of action are similar to activated carbon (Anonymous, 1977).

Although a model for the adsorption process of these spheres has been theorized and some internal features have been elucidated (Neely and Isacoff, 1982), to date the internal cross-section morphology as a result of ultramicrotomy has not been visualized.

A comparative microscopical evaluation of the spheres' internal morphological characteristics would provide visual data to enhance an overall understanding of the modes of action during adsorption. Therefore, in this paper, ultramicrotomy was used to obtain thin sections for light microscopy (LM) and scanning electron microscopy (SEM) visualization of the internal morphologies of XE-340, XE-347, and XE-348 carbonaceous adsorbent spheres. In addition, gas adsorption was used to measure the surface areas of these spheres.

Materials and Methods

Ultramicrotomy

Carbonaceous adsorbent spheres (XE-340) from the same container were placed in separate molds (1.5 cm long x 0.5 cm wide x 0.2 cm deep) into which an embedding mixture had been poured. The mixture was composed of Epon 812 (10 ml), Araldite 506 (6 ml), dodecyl succinic anhydride (DDSA; 10 ml), nadic methyl anhydride (NMA; 9 ml), and dimethyl amino ethylphenol (DMP-30; 20 drops). Following polymerization in a 60°C oven for 24 hours the hardened blocks were removed from the molds, trimmed, and thin (50 nm) sections were cut with a Sorval MT2B ultramicrotome equipped with a glass knife.

In addition to Epon 812, Spurr's "One Shot" low viscosity embedding resin mixture was also used. First the spheres were put into the Spurr's resin mixture for

24 hours to allow for maximum penetration. Then the spheres were transferred to the flat molds, polymerized, trimmed, and sectioned as described above.

Light Microscopy (LM)

Sections obtained by microtomy were placed into drops of water on the surface of glass slides, which were then put on a slide warmer. Heat caused the water to evaporate, leaving the sections affixed to the slides.

The sections were then examined using a Zeiss Ultraphot camera microscope and photographs were taken using Polaroid type 55 film.

Scanning Electron Microscopy (SEM)

Microtomed sections, having been put onto 2.5 mm diameter copper grids, were allowed to dry for one hour on a slide warmer. The drying caused the sections to adhere to the grids which were then mounted on aluminum stubs using carbon paint, sputter coated with gold/palladium, and then examined with a Zeiss CSM 950 SEM at 10 or 15 kV accelerating voltage and 16-22 mm working distance. Electron micrographs were taken using Polaroid type 52 film.

Surface Area Measurements

The surface areas of three samples of activated carbon spheres were measured using a Micromeritics 2100E gas adsorption instrument. Approximately 0.3 g of each of the samples was placed in each of the three adsorption tubes. The tubes were attached to the instrument and evacuated at 110°C for more than 24 hours to remove all residual vapors. Nitrogen gas was used as the adsorbent; adsorption was carried out at liquid nitrogen temperature.

Complete isotherms were obtained for each sample with at least 16 data points between $P = 0$ and the saturation pressure, P_s . However, only data from the region where the volume adsorbed is a linear function of the pressure ratio P/P_s was used in the surface area analysis. In the present calculations we used data from the linear region $0.01 < P/P_s < 0.3$. The analysis uses the BET adsorption isotherm equation to obtain the volume of nitrogen vapor required for monolayer coverage of the surface. The surface area covered by a single nitrogen molecule was taken as 16.2 \AA^2 .

Results and Discussion

The external appearance and general size range of XE-340 spheres (Fig. 1) was similar to both XE-347 and XE-348 spheres. However, light micrographs of ultramicrotome cross-sections of XE-340 spheres (Figs. 2a-d) reveal a diversity of internal differences, and microtomed cross-sections of XE-347 (Fig. 3), and XE-348 (Fig. 4) spheres show different morphologies than XE-340.

The samples described above had been embedded in Epon and were found to be somewhat brittle. Because of this, we switched to Spurr's resin for the remaining samples and found the brittleness to be significantly reduced.

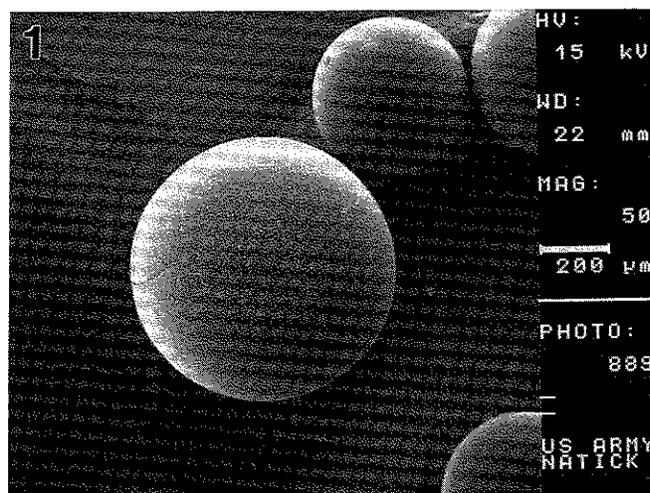


Figure 1 (above). Scanning electron micrograph showing different sizes of Rohm and Haas XE-340 carbonaceous adsorbent spheres with similar external features. Bar = 200 μm .

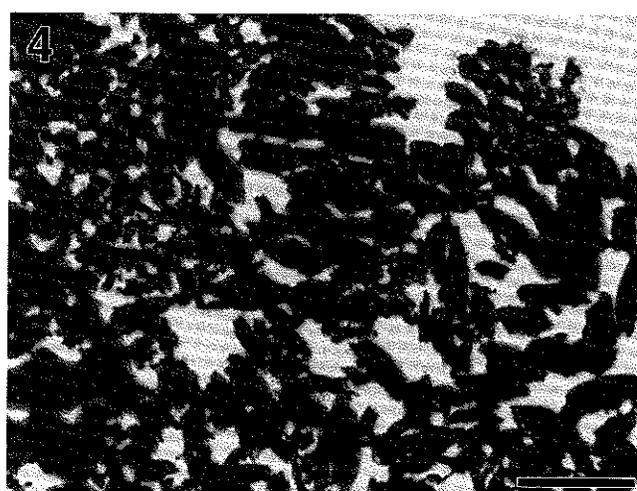
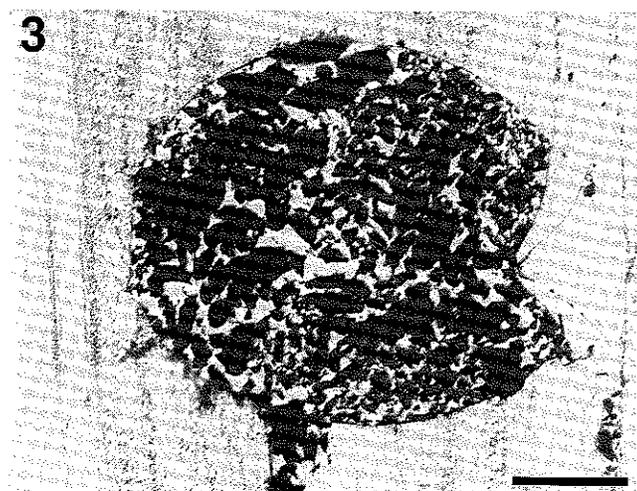
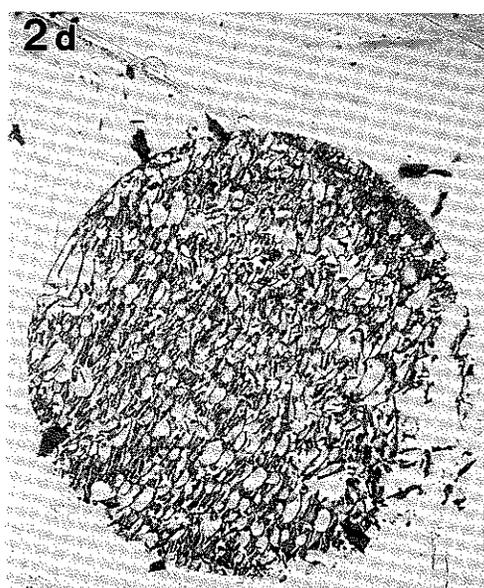
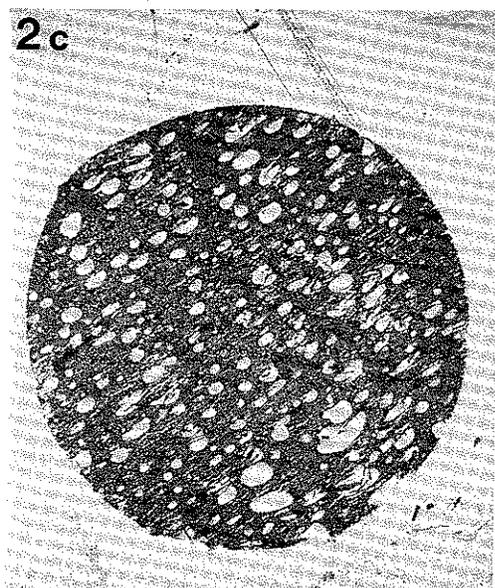
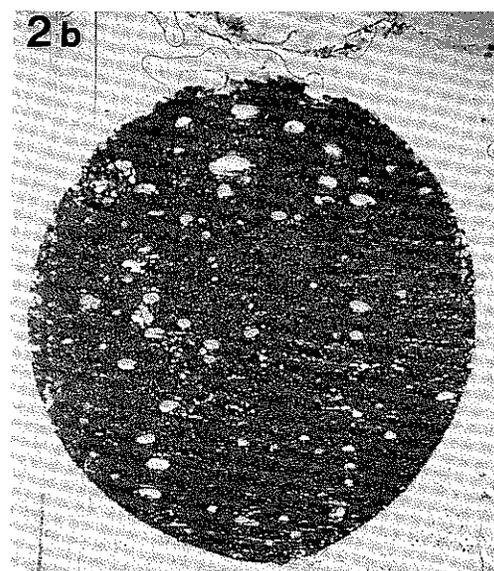
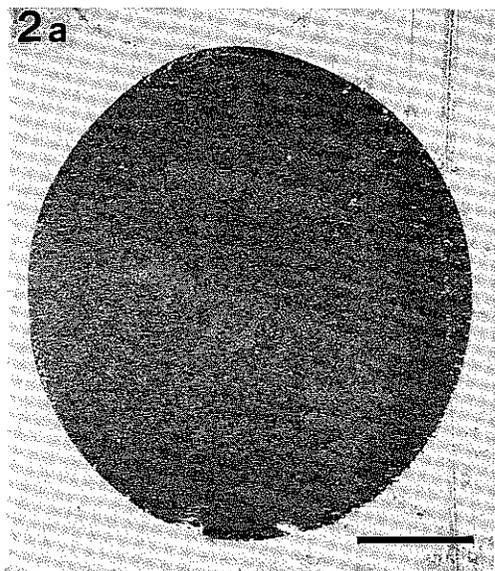
Figure 2. Light microscopy photomicrographs of microtomed thin sections (at identical magnifications) through XE-340 spheres. Each of the spheres (a, b, c, d) were from the same batch. Bar = 200 μm .

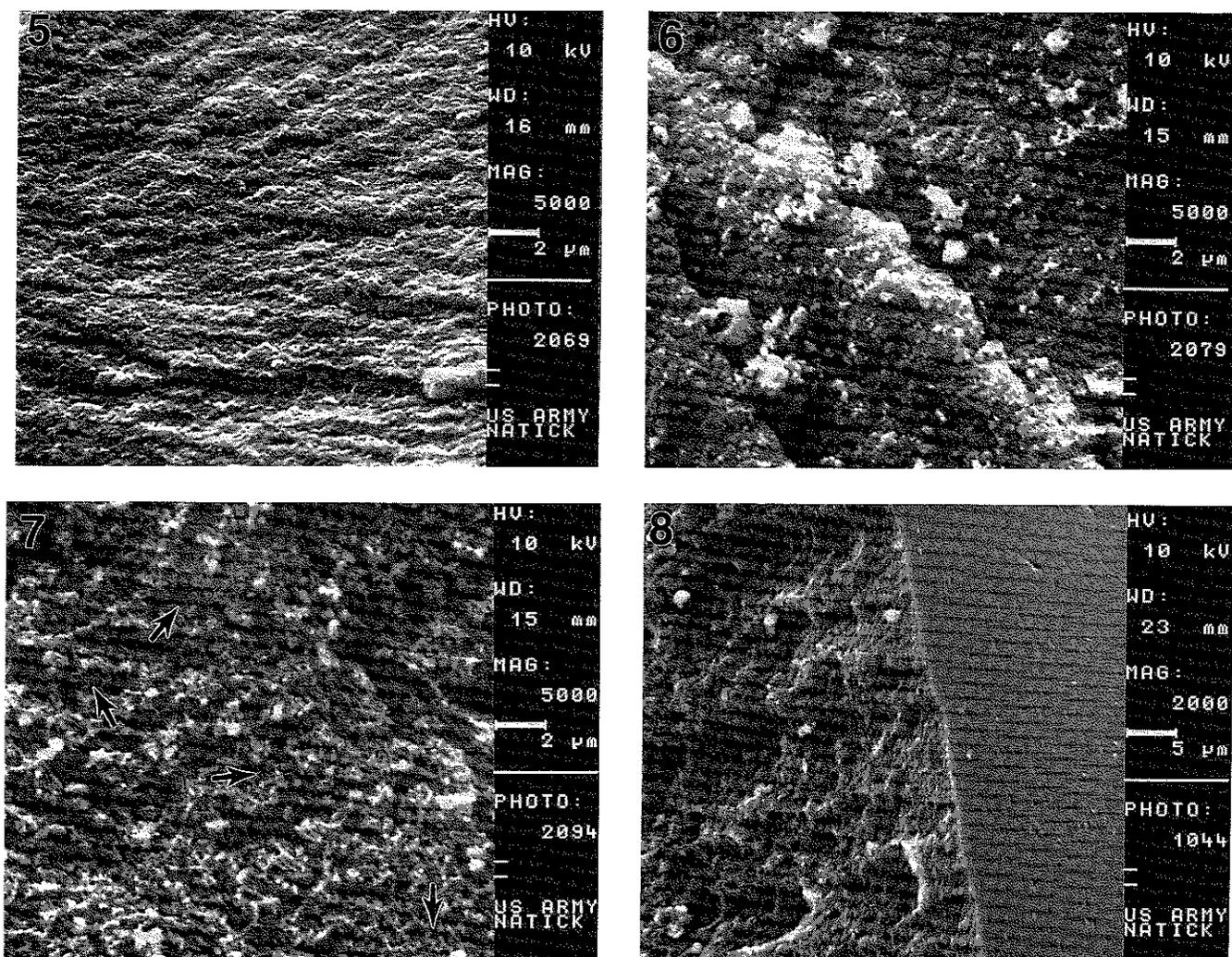
Figure 3. Light microscopy photomicrograph of microtomed thin section through a Rohm and Haas XE-347 carbonaceous adsorbent sphere showing structure similar to XE-340 but with somewhat larger lamellae. Bar = 200 μm .

Figure 4. Light microscopy photomicrograph showing lamellae of Rohm and Haas XE-348 carbonaceous adsorbent sphere. These were similar in appearance to those in Figure 3. Bar = 40 μm .

Scanning electron micrographs of the surface of microtomed cross-sections do show differences in the spheres' morphologies. XE-340, which appears to have the most uniform particle distribution (Fig. 5), has a surface area of $417.8 \text{ m}^2/\text{g}$. XE-347, which appears to have a less even distribution of particles (Fig. 6) has a surface area of $583.4 \text{ m}^2/\text{g}$. The surface of the cross-section of XE-348 (Fig. 7) appears to have a mesh-like appearance, very different from the others, and a surface area of $752.9 \text{ m}^2/\text{g}$, which is higher in value than the others.

Thin Sectioning of Carbonaceous Adsorbent Spheres





Figures 5-7. Scanning electron micrographs of interior surface of XE-340 (Fig. 5), XE-347 (Fig. 6), and XE-348 (Fig. 7) spheres from thin sections. Arrows indicate mesh-like structures. Bar = 2 μ m.

Figure 8. Scanning electron micrograph of fractured XE-340 sphere. Left side of photo shows the large surface area of the sphere's interior, whereas the exterior is relatively smooth. Bar = 5 μ m.

Conclusions

The methods described in this paper were suitable for obtaining thin sections to study the morphology of carbonaceous adsorbent spheres by light microscopy and scanning electron microscopy. Gas adsorption measurements of surface area as related to visualization of the spheres' internal structures showed their comparative similarities and differences whose further study could provide information to better understand their relative adsorption capabilities.

Acknowledgement

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References

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Discussion with Reviewers

Reviewer I: Were there any spheres which were found to have been fractured during the manufacturing process? It might be useful to compare the internal structure of such spheres with those which were embedded and then sectioned.

Thin Sectioning of Carbonaceous Adsorbent Spheres

Authors: The SEM photo (Fig. 8) is one such example. It shows an XE-340 sphere whose interior on the left side of the photo has a very large surface area compared with the outer part of the sphere seen on the right. A microtomed section of this particular sphere might appear similar to Fig. 2c.

R.F. Antrim: Are the artifacts resulting from the embedding and sectioning techniques?

Authors: Since the sections have, for the most part, retained their spherical appearance, formation of artifacts due to embedding and sectioning seems unlikely. However, we did notice that sectioning was much easier with Spurr's resin than with Epon and that the Epon sections tended to be more brittle.

J.D. Fairing: Please comment further on the penetration and wetting by resins.

Authors: Spurr's low viscosity resin was used to maximize penetration and wetting of the spheres. When Epon was used a large number of spheres floated on the resin's surface after 24 hours; however, most of the spheres sank to the bottom of Spurr's resin. Because of this we assumed complete penetration and wetting had taken place.

Reviewer IV: Do you have any data showing pore size distribution within the spheres?

Authors: Figures 9, 10, and 11 show the pore size distribution data for XE-340, XE-347, and XE-348 spheres. In XE-340 (Fig. 9) 70% of the pores are < 20 Å. In XE-347 (Fig. 10) 85% of the pores are < 20 Å. Finally, in XE-348 (Fig. 11) approximately 82% of the pores are < 20 Å.

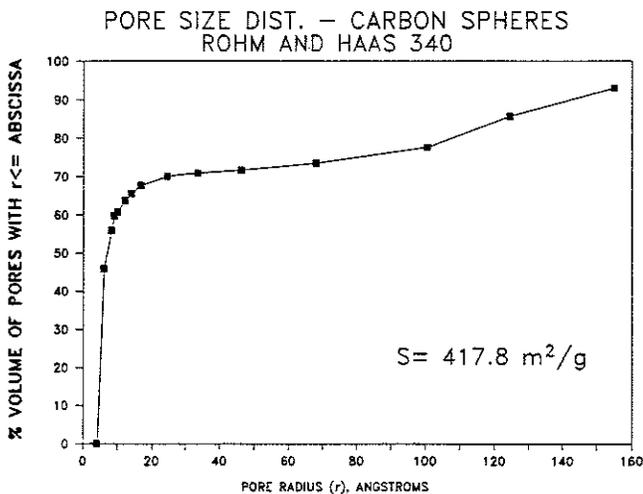


Figure 9. Pore size distribution of Rohm and Haas XE-340 spheres. Surface area (S) = 417.8 m²/g.

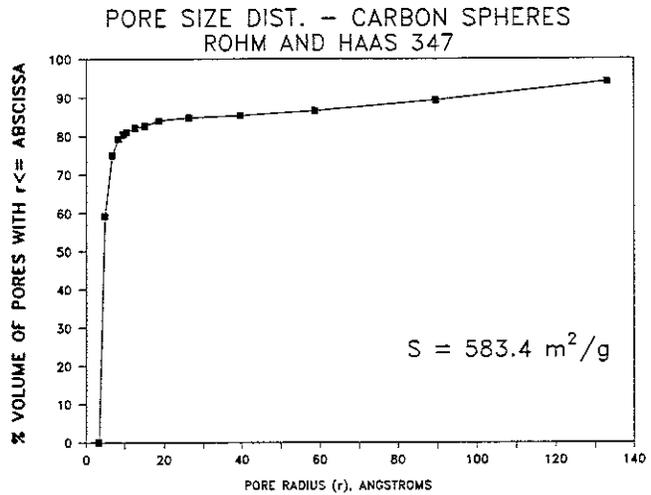


Figure 10. Pore size distribution of Rohm and Haas XE-347 spheres. Surface area (S) = 583.4 m²/g.

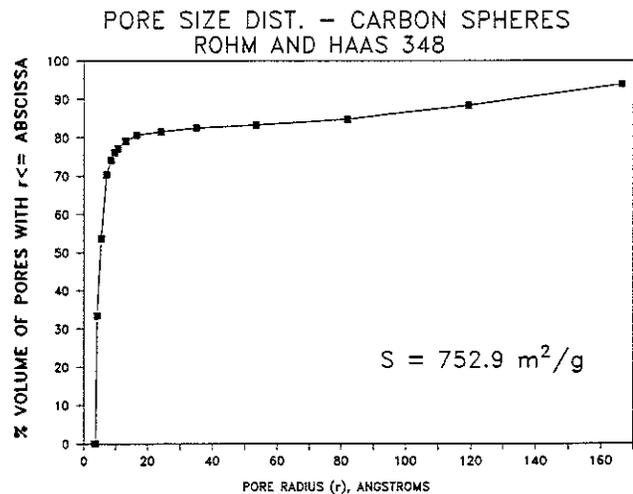


Figure 11. Pore size distribution of Rohm and Haas XE-348 spheres. Surface area (S) = 752.9 m²/g.