
Polymer coating for hemoperfusion over activated charcoal

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Plasma polymerization (glow discharge) was used to make a polymeric coat with hexamethyldisiloxane on the surface of activated charcoal granules. These samples were examined with ESCA and SEM for

surface chemical analysis, coat thickness, and uniformity, and for changes in surface topography. The effects of the coat on adsorptive capacity and release of fine particles were examined.

INTRODUCTION

Activated charcoal is commonly used for impurity and toxin removal because of its high adsorptive capacity. Although it has been known as an oral antidote in medicine for a long time, its use for removal of exogenous metabolites from the blood was first reported in the 1960's.¹ Later on, charcoal hemoperfusion became a focus of interest because its use was more economical in comparison to other techniques such as dialysis and ultrafiltration. Major problems associated with the use of activated charcoal in hemoperfusion are the release of carbon fines (leading to emboli formation) and damage to blood cells, particularly platelets. In order to overcome these complications, charcoal granules have been microencapsulated^{2,3} in, or coated with, biocompatible polymers.^{4,5} In this study, glow discharge technique was used to coat charcoal granules in a similar manner to that reported earlier by Ozdural et al.⁶ The superiority of this technique over the others arises from the fact that there is no need for solvents or catalysts for polymerization. Polymerization is initiated with an electrical discharge and therefore it is possible to make a coat with no impurities due to solvent or polymerization initiators. Another characteristic of this technique is that it is possible to make a thin and tenacious coat, which preserves the original properties of the substrate. In this study, after microscopic investigations, the coated charcoal granules were examined for their adsorptive capacity and release of fines.

MATERIALS AND METHODS

In this study, Nuchar WV-G (mesh size 12×40) activated charcoal, obtained from Westvaco Division, USA, was used. The choice was based upon the higher adsorptive capacity of Nuchar in comparison with Norit RBXS-1 (Gambro, Germany),⁷ a clinically used activated charcoal for hemoperfusion. Nuchar was washed, dried and brought to constant weight. It was then brought in contact with pure hexamethyldisiloxane (HMDS) gas under vacuum. Deposition of polymer was achieved through application of electrical discharge by using a 13.56 MHz RF generator in a capacitively coupled system which has been previously described in detail.^{8,9} Adsorption tests were carried out by using the system illustrated in Figure 1. Coated and uncoated charcoal samples were transferred to the glass column (1 cm \times 10 cm, with mesh at both ends), washed with ethanol (100 mL) and then with isotonic phosphate buffer (pH 7.4, 100 mL) by running the solutions through the column with the aid of a peristaltic pump at a rate of 10 mL/min. Creatinine (MW = 113) or vitamin B₁₂ (MW = 1355) solutions were put into the reservoir and flowed through the column with the same rate. The concentration of creatinine solution was determined as follows; 0.5 mL samples were drawn from the reservoir, and to these solutions, distilled water (2.5 mL), NaOH (1 mL, 0.75 N) and saturated picric acid (1 mL), were added. After 45 minutes, the amount of colored creatinine-picric acid complex was determined spectrophotometrically at 500 nm. The concentration of vitamin B₁₂ was determined by drawing 1 mL samples from the reservoir and measuring the absorbance at 525 nm.

Experiments to determine release of fines were carried out by using the system shown in Figure 2. Ethanol (100 mL) was pumped (with a rate of 10 mL/min) through the column which contains the charcoal granules (3 g) and was filtered through Millipore (Pore size: 0.45 μ , size: 25 mm, Sartorius). The fines were then counted by light microscopy.

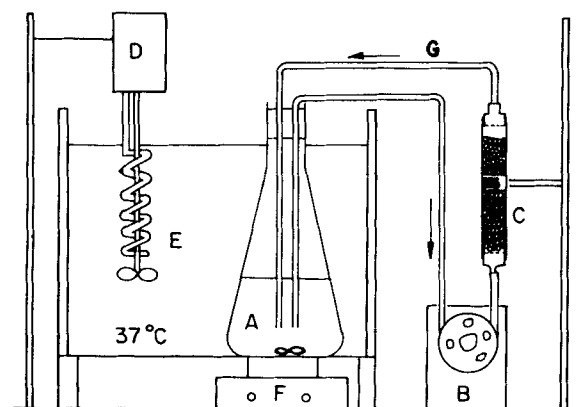


Figure 1. Adsorption System (a) Solution; (b) Peristaltic pump; (c) Charcoal column; (d) Heater-Stirrer; (e) Constant temperature bath; (f) Magnetic Stirrer; (g) Silicone tubing

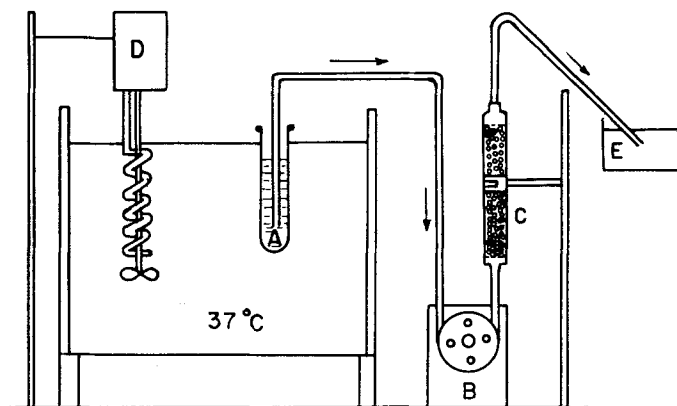


Figure 2. System for fines release experiments

RESULTS AND DISCUSSION

In the coating process of activated charcoal, one critical point is the calculation of the amount of deposited polymer. It is critical, because (a) the amount of deposited polymer is not very high, and, (b) the moisture content of the highly adsorptive charcoal must be taken into account. In order to be able to have an accurate measurement of the weight gain, the untreated charcoal granules were subjected to low pressure (0.5 mm Hg) for long periods until a constant weight was obtained. This weight was used as the untreated weight. Weighing was performed immediately after coating, before appreciable moisture adsorption could take place. These precautions kept the error margin within 2%. It was observed that the extent of surface coverage by the coat depends very much on the amount of polymer deposited.¹⁰ When the weight increase was about 28% (by application of 20 W, 50 mL/min, 60 min for discharge power, monomer flow rate, and discharge duration, respectively), a uniform and "snowing" type coat covering the surface was obtained (Figure 3). On the other hand, when the increase was about 17% (by application of 20 W, 50 mL/min, 5 min for discharge power, monomer flow rate, and discharge duration, respectively), the deposition was not quite detectable by SEM examination (Figure 3). It is thought that in the latter case, the deposition is more as monomer adsorption in the pores than polymer deposition on the external surface of the charcoal granules. A discharge of 5 min is not sufficient to polymerize all the adsorbed monomer. ESCA examination of these samples showed that the intensity of Si peaks increases 3 times when the sample has 28% weight increase and 1.6 times when it has 17% weight increase (Figure 4). Since uncoated charcoal samples are known to contain 4.85% Si, which was determined by X-ray fluorescence analysis, 3 times this value yields 14.5% Si. This then corresponds to approximately 30% increase in the weight of charcoal through HMDS deposition ($(\text{MW HMDS}/\text{MW Si}) \times (14.55 - 4.85) \approx 30$). On the other hand, in the second case, the increase in the Si content corresponds to 8.6% polymer

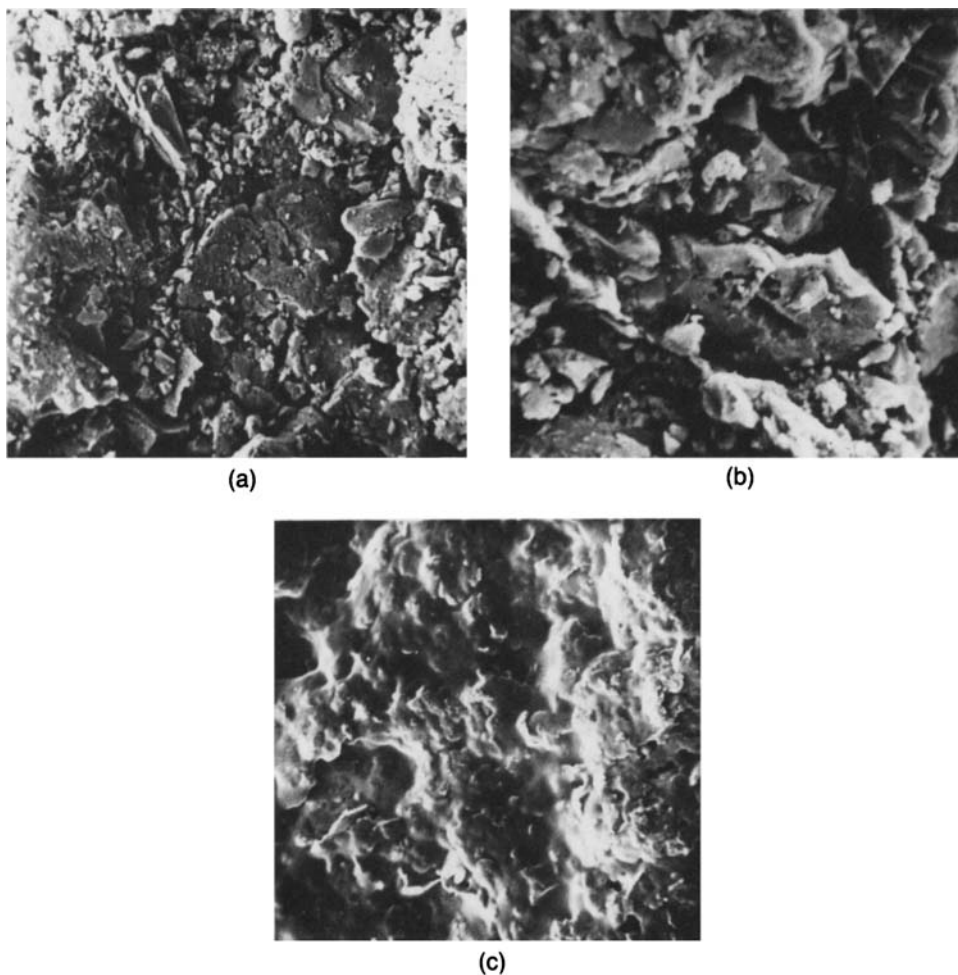


Figure 3. Scanning electron micrographs ($\times 1800$ original magnification) (a) Charcoal; (b) Coated charcoal (discharge duration = 5 min); (c) Coated charcoal (discharge duration = 60 min) (charcoal samples were coated by application of, monomer flow rate = 50 mL/min, power = 20 watt.)

deposit. Even this much of deposition was not detectable with SEM. Therefore, in order to polymerize all the adsorbed monomer, discharge duration was kept long enough (1 h) without changing the other parameters, and these coated granules were used in the other experiments.

The thickness of polymer coats, which were prepared on aluminum foil by using the same polymerization parameters, were determined from SEM results and found to be in the micrometer level. These coats were found to be insoluble in common organic solvents.

The results of the adsorption of creatinine and vitamin B₁₂ are presented in Figures 5 and 6. Here one important point is the hydrophobic nature of the silicone coat. It was observed that when coated charcoal granules were

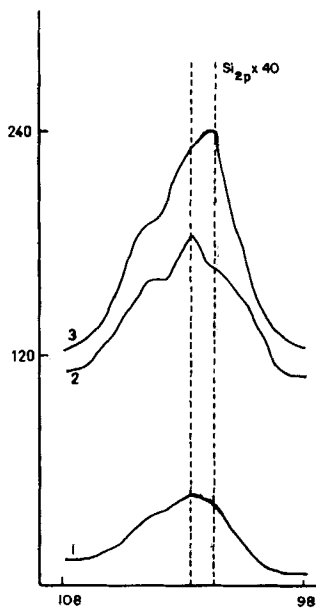


Figure 4. ESCA, Si_{2p} intensities (1) Charcoal; (2) Coated charcoal (discharge duration = 5 min); (3) Coated charcoal (discharge duration = 60 min) (charcoal samples were coated by application of, monomer flow rate = 50 mL/min, power = 20 watt.)

brought in contact with aqueous solutions, the granules could not be wetted and they floated. Only after treatment with ethanol did the granules become wettable. In Figure 5 it is seen that while uncoated charcoal can remove

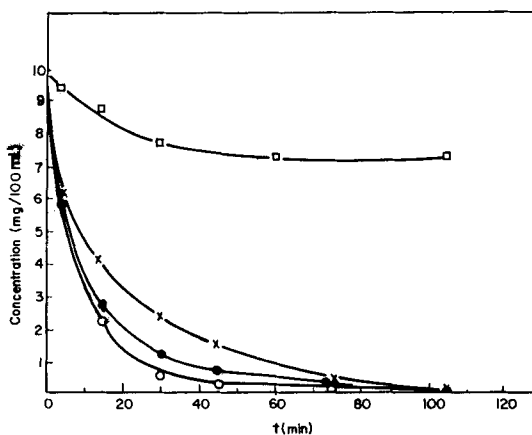


Figure 5. Creatinine Adsorption (○) Charcoal; (□) Coated charcoal (discharge duration = 60 min, without ethanol treatment); (x) Coated charcoal (discharge duration = 60 min, after ethanol treatment); (●) Coated charcoal (discharge duration = 5 min, after ethanol treatment); (charcoal samples were coated by application of, monomer flow rate = 50 mL/min, power = 20 watt.)

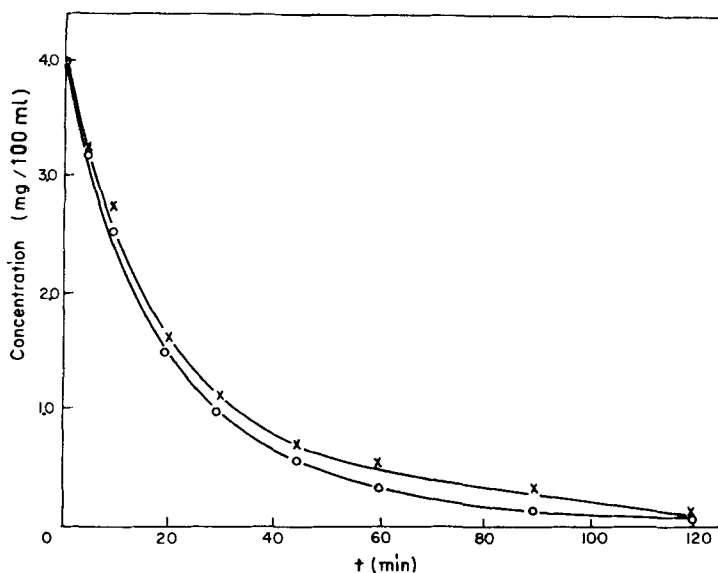


Figure 6. Vitamin B₁₂ Adsorption (○) Charcoal; (x) Coated charcoal (60 min discharge, after ethanol treatment)

10 mg creatinine in 75 min, coated, but ethanol-untreated, granules were not able to do the same in a much longer time, and became saturated after adsorption of approximately 3 mg of creatinine. It seems that the hydrophobic, non-wettable coat prevented a real contact between the chemicals and the granules, leading to the observed decreased adsorptive capacity. Charcoal granules which have a thinner coat (coated by application of glow discharge for 5 min) have more adsorption capacity than the samples which have thicker coat (coated by application of glow discharge 1 h) (Figure 5), after both samples were treated with ethanol. These results show that the presence of the coat does not alter the adsorptive capacity of charcoal. Substantial decreases of up to 50% in adsorptive capacity have been reported for solution coated charcoal samples.¹¹ These can be explained as follows: In

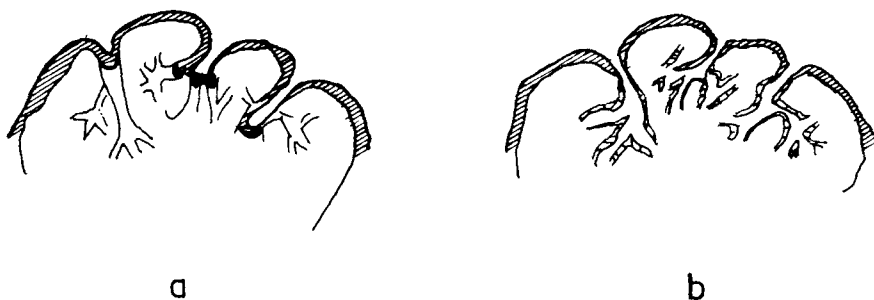


Figure 7. Effect of coating on the pores (a) Coat from solution-blocks the pores; (b) coat from gas phase-cover the surface

the case of solution coating, the solution fills the pores (probably not the micropores) and the excessive polymer deposited blocks them, thus decreasing the activity of micropores. In the case of electrical discharge polymerization, it is thought that since the monomer is adsorbed from the gas phase, it can not collect in sufficient quantity to block the pores (Figure 7).

Experiments on release of fines showed that the washed and dried charcoal granules are not completely free of fines. Between 4500–7000 particles were counted on 1 cm² area, while 750–1200 particles were observed with the coated samples, leading to 80–85% reduction in fine release.

CONCLUSION

Adsorption tests done by creatinine and vitamin B₁₂ showed that glow discharge polymerization of HMDS on the surface of charcoal granules did not alter the adsorptive capacity of charcoal because of its very thin nature, even in the case of a 28% weight increase. ESCA examination showed that plasma polymerized hexamethyldisiloxane was present on the surface by having a greater intensity in Si peak for the coated samples. It was observed that the coat was effective in preventing the release of fines from the charcoal granules.

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