

PREPARATION AND SORPTIVE PROPERTIES OF PHOSPHORUS-CONTAINING CARBONS

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Introduction

It is known that oxidised activated carbons exhibit selectivity towards lead in the presence of nickel, cadmium and alkaline earth metals [1]. However the presence of copper significantly reduces the amount of lead sorbed. In order to improve the selectivity, novel sorptive carbonaceous material based on phosphorylated phenol-formaldehyde resins has been synthesised. The present paper considers synthetic methods of introduction of phosphorus-containing groups onto the surface of polymer-pyrolised carbonaceous material (PGP-P), its surface characteristics and sorptive properties towards some heavy metals. The sorptive properties of PGP-P carbon were compared to an inorganic phosphorus-containing ion-exchanger (titanium hydroxophosphate) and oxidised activated carbon (Chemviron F400 oxidised activated carbon).

Experimental

Preparation of the carbonaceous sorbent. The carbonaceous sorbent was prepared with 45% yield by a 3-step (200, 500 and 750°C) pyrolysis of a porous spherical phenol-formaldehyde resin [2] phosphorylated by refluxing in POCl₃/toluene solution. The pyrolysis was followed by subsequent washing with water, 0.1M NaOH, water, 0.1 HCl, water and drying until constant weight in vacuo at 120°C.

Analysis of the carbonaceous sorbent. Phosphorus content was determined by digesting a sample of phosphorus-containing carbon (PGP-P) in a mixture of hot perchloric and nitric acids followed by the analysis of the solution obtained by the standard molybdate method [4]. The acidic properties of functional groups were determined by pH-titration with sodium hydroxide in the presence of sodium chloride. The valency and chemical state of phosphorus on the surface of carbon were determined by MAS NMR-P³¹. 85% phosphoric acid was used as a standard. FT-IR spectra were recorded with potassium bromide disks containing 0.2% (wt/wt) of sample.

Metal sorption studies. Sorption isotherms were

obtained in batch mode by contacting various amounts of the sorbents with the metal-containing solutions at constant temperature for 24 hours. The selectivity of the sorbents towards lead was determined by performing mini-column tests using crushed and screened samples, in the size range of 45-90µm. Metal concentrations were determined by AA flame spectrometry.

Results and Discussion

Capacity for Na ⁺ , (mmol/g)	2.1
Phosphorus content, (mmol/g)	2.55
Total area of pores ≥ 4.65Å, (m ² /g)	278.57
Total volume of pores ≤ 2525.7Å, (cm ³ /g)	0.128
Bulk density, (g/cm ³)	0.37

Table 1. Structural and analytical parameters of the PGP-P carbon used.

The nitrogen adsorption isotherm data suggests that the synthesised carbon is predominantly microporous. The mean micropore size is about 7Å. There are also some meso/macropores between 100Å and 1000Å without defined peak. Mercury porosimetry shows the presence of large macropores at 8000Å.

Figure 1 presents the MAS NMR-P³¹ spectrum for the PGP-P carbon. The line at -5.12ppm can be attributed to mono- and/or pyrophosphate groups attached to the carbon surface. The FT-IR spectrum of the PGP-P carbon shows broad peaks between 800 and 1240cm⁻¹ which are attributed to P=O stretching of phosphates and P-O-P asymmetric stretching of pyrophosphates [3].

Ion-exchange properties of PGP-P carbon were compared to those of oxidised F400. The pH titration curves indicate that the PGP-P carbon curve is flat compared to that of F400(oxidised). No well defined inflexions are observed suggesting a polyfunctional nature of PGP-P carbon.

Isotherms of sorption (Figure 2) were performed for the solution containing lead and copper from acetate buffer. The results obtained clearly demonstrate greater sorptive capacity and selectivity for lead over copper on the PGP-P carbon. F400(oxidised) showed no significant difference in copper and lead uptake.

Sorption of lead, copper, nickel and cadmium under dynamic conditions for PGP-P carbon, F400(oxidised) and titanium hydroxophosphate (TiP) are presented in Figures 3, 4 and 5. PGP-P carbon and titanium hydroxophosphate show similar trend in lead removal whereas copper is preferred by F400(oxidised). Nickel and cadmium are not retained by these sorbents.

Conclusions

The PGP-P carbon showed significantly improved sorption selectivity towards lead over copper compared to oxidised carbon. This confirms the potential of phosphorus-containing carbons for medical and industrial applications.

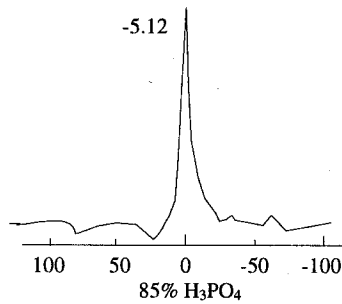


Figure 1. MAS NMR-³¹P spectrum for PGP carbon.

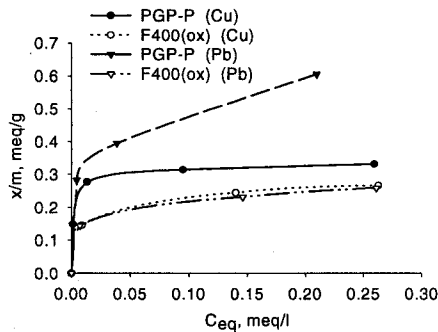


Figure 2. Sorption isotherms for lead and copper on PGP-P and F400(oxidised) carbons.

References

1. Streat, M. and Strelko(jr), V. in *Carbon'96* (European Carbon Conf.), Newcastle upon Tyne, UK, 1996, pp. 260-261.
2. Strelko, V.V., Kartel, N.T., Puziy, A.M., Mikhalovsky, S.V. and Kozynchenko, A.P. Patent of Ukraine No 3396 (1994).

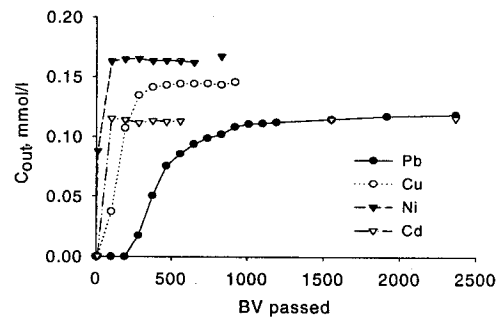


Figure 3. Breakthrough curves for Pb²⁺, Cu²⁺, Ni²⁺ and Cd²⁺ on PGP-P carbon.

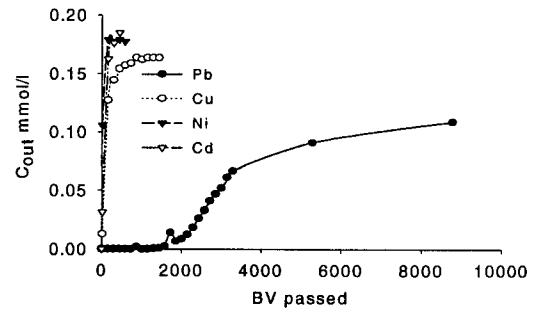


Figure 4. Breakthrough curves for Pb²⁺, Cu²⁺, Ni²⁺ and Cd²⁺ on TiP.

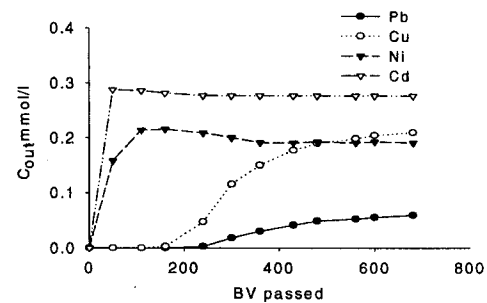


Figure 5. Breakthrough curves for Pb²⁺, Cu²⁺, Ni²⁺ and Cd²⁺ on F400(oxidised).