Pak. j.. sci. ind. res., vol. 37, no. 3, March 1994

ADSORPTION OF PALLADIUM IONS BY MODIFIED CARBONS FROM RICE HUSKS

M. R. MOSTAFA

Chemistry Department, Hail T T Junior College, Hail, Kingdom of Saudi Arabia

(Received January 12, 1993; revised November 13, 1993)

Steam activated carbon of high surface area does not show any Palladium ions adsorption. Treatment of this carbon with HF acid increases to a great extent the gas adsorption capacity expressed as nitrogen surface area as well as the adsorption capacity of Palladium ions from aqueous solution. HHB was loaded in different amounts on to these carbons. The acid sites represent the active fraction of the surface on which the adsorption of Palladium ions proceed. The uptake of Palladium ions by HHB treated carbons is related to the total number of HHB molecules loaded on the carbon surface.

Key words: Activated carbon, Surface modification, Adsorption of palladium.

Introduction

Activated carbon is effective for the removing and recovering of valuable components from wastes and ore extracts; firstly because it provides a large interfacial area at which such substances may accumulate [1], secondly, differences in adsorptive behaviour can be explained in terms of relative pore size distributions [2] and thirdly to varying surface properties of the carbon depending on its method of preparation [3]. Recent research has centred on information about the nature and behaviour of activated carbon and about the adsorption process [4-6]. In many applications it was found that the chemistry of the carbon surface is the controlling factor which decides the uptake of metal ions from aqueous solutions.

The investigations reported on the adsorption of Palladium ions by activated carbon prepared from agricultural byproduct as an adsorbent being few [7]. The object of the present study is to prepare activated carbon from rice husks. HF as an oxidant was used to create more acid sites on the carbon surface. 2-Hydroxyimino-3-($\bar{2}$-hydrazonopyridyl)-butane (HHB) was reported to react with Mn^{11}, Co^{11}, Ni^{11}, Cu^{11}, Cd^{11}, Hg^{11} and Co^{111} to form metal complexes [8]. Thus HHB was loaded onto the carbon surface to study its effect on the adsorptive properties of the prepared carbons. The adsorptive properties of the investigated carbons were determined from the adsorption of nitrogen at 77K and the adsorption of Palladium ions from aqueous solutions at 303K.

Experimental

Materials. 2-Hydroxyimino-3-($\bar{2}$-hydroazonopyridyl)-butane (HHB compound) was prepared by boiling an ethanolic solution of 2-hydrazinopyridine with 2, 3-butane dions monoxime (1:1) under reflux for 1 hr. On cooling, the formed pale yellow crystals was removed by filteration, washed with ethanol then recrystallised from hot absolute ethanol and finally dried in vacuo [8].

Non-modified carbon, sample C, was prepared by carbonizing dried rice husks at 873 K in nitrogen followed by activating in steam at 1173 K to 26% burn off [6]. Treatment with HF acid was carried out as follows: weighed amount of carbon sample C was added to weighed amount of 10% HF in order to obtain acidcarbon ratios of 0.1, 0.2, 0.3, and 0.4 respectively. The mixture was refluxed for 6 hrs on water bath. The solution was then concentrated to one half of its volume, cooled, filtered and washed with CO_2 - free distilled water until neutral. Symbols C_1, C_2, C_3 and C_4, represent the acid treated carbons and indicates acid-carbon ratios of 0.1, 0.2, 0.3 and 0.4 respectively.

Carbon sample C and HF acid treated carbon sample C_1 was loaded with HHB in order to obtain carbons containing 0.1, 0.2, 0.3 and 0.4 m. mole HHB per gram carbon. This was achieved by impregnating 5 g of the carbon sample with 50 ml chloroform containing the appropriate amount of HHB. The suspension was heated under reflux for 2 hrs, dried in vacuum and then stored in stoppered 30 ml hypo-vials. Symbols CI, CII, CIII and CIV represent HHB non-acid treated carbon, While symbols C_1I, C_1II, C_1III and C_1IV represent HHB acid treated carbons respectively. Only carbon samples collected between 150-250 mesh were selected for the adsorption measurements.

Techniques. The surface area was measured from the nitrogen adsorption at 77 K using a conventional volumetric apparatus. Adsorption of Palladium ions from aqueous solution was obtained by shaking 0.5 g of carbon sample with 50 ml of Palladium chloride solution in stoppered glass bottles thermostated at 303 K. Various Palladium ions concentrations were used and the solutions were left for 24 hrs to reach equilibrium. Initial and equilibrium concentrations were determined colorimeterically [9] using Spectronic 20.

The surface acidity of carbon sample C and HF acid treated carbons was determined by calorimetric titration method. The technique adopted was essentially the same as described before [10]. IR analysis for HHB loaded carbon sample CIV before and after the adsorption of Palladium ions was carried out using a Perkin Elmer 883 infrared spectrophotometer.

Results and Discussion

Nitrogen adsorption isotherms for all the carbon samples investigated are type II of BDDT classification (11) with closed hysteresis. Representative adsorption-desorption isotherms are shown in Fig. 1. The specific surface areas were calculated by the application of the BET equation [12], adopting a value of 16.2 Å² for the molecular area of nitrogen. The S_{BET} areas are given in column 2 of Table 1. The data obtained from nitrogen adsorption allowed the determination of two other surface parameters namely the total pore volumes and the mean pore radii of the carbon samples. The former is the volume of liquid nitrogen (ml/g) adsorbed near saturation i.e. at P/P° close to 1.0, the later parameter was obtained from the relationship [13]:

$$\bar{r}\ (\text{Å}) = \frac{2V_T\,(\text{ml/g}) \times 10^4}{S\ (\text{m}^2/\text{g})}$$

V_T is the total pore volume, S is the surface area and $\bar{r}$ is the mean pore radius. The total pore volumes and the mean pore radii are given in columns 3 and 4 of Table 1 respectively.

Columns 2, 3 and 4 of Table 1 reveals that the treatment of carbon sample C with HF acid causes a considerable increase in both surface area and total porosity. The increase was found to go parallel with the amount of HF acid used in the treatment. However, the pore dimension exhibit slight variation upon the acid treatment. Steam activated carbon sample C, is characterized by its high silica content (42%), which may cause the partial blocking of porosity. As the acid-carbon ratios increase the silica content continues decrease to reach 18% for carbon sample C_4 (Table 1). HF dissolves a fraction of silica as $H_2[SiF_6]$ which leads to an increase of both surface area and the total porosity. On the other hand loading of carbon C and acid treated carbon sample C_1 with different amounts of HHB causes a slight variation in the surface area. The most important variation has been found in the pore size. Continuous pore widening is shown with the increase of the loading amount of HHB from 0.1 to 0.4 (Table 1).

The adsorption of Palladium ions from aqueous solutions by acid treated carbons exhibit L-curves according to Giles classification [14] Fig. 2. The isotherms were found to obey the Langmuir adsorption equation where satisfactory straight lines are obtained by plotting C/X vs C, where C is the equilibrium concentration and X is the amount of Palladium ions adsorbed /g carbon. Figure 3 shows the linear Langmuir plots for these set of carbons. The monolayer capacity (m. mole/g) was calculated from the plots and is listed in column 5 of Table 1.

Figure 4 shows the adsorption isotherms of Palladium ions on carbon sample C modified by loading with different amounts of HHB. The mutual effect of HHB loading and HF acid treatment on the adsorption of Palladium ions is shown in Fig. 5. The isotherms are typically class H according to Giles classification [14]. This type of curves is produced by hard adsorption including the cases of chemisorption. The monolayer capacity was taken at the knee bend (point B) and is listed in Table 1.

Inspection of Table 1 reveals that, non-modified steam activated carbon sample C does not show any meassurable Palladium ions adsorption. This particular carbon sample is characterized by its surface basicity [4]. Basic sites may retard the adsorption of Palladium ions or at least are inert sites for the adsorption of metal ions. On the other hand, treament of this carbon sample with HF acid causes appreciable increase in the uptake of palladium ions from aqueous solution. Moreover the

Table 1. Adsorptive Properties and Surface Acidities of the Carbons Used.

Sample	S_{BET} (m²/g)	VT (ml/g)	$\bar{r}$ (A°)	Monolayer capacity (m.mole/g)	Surface acidity (m.mole/g)
C	425	0.38	18.0	Nil	Nil
C_1	510	0.47	18.5	0.23	0.28
C_2	620	0.59	19.0	0.31	0.36
C_3	680	0.66	19.4	0.39	0.48
C_4	720	0.72	20.0	0.47	0.60
CI	420	0.42	20.0	0.09	-
CII	405	0.50	24.6	0.19	-
CIII	402	0.57	28.4	0.29	-
CIV	388	0.65	33.4	0.38	-
C_1I	500	0.49	19.4	0.28	-
C_1II	496	0.56	22.6	0.36	-
C_1III	490	0.66	26.8	0.44	-
C_1IV	484	0.73	30.0	0.57	-

Table 2. Carbon, Ash and Silica Contents of HF Non-Treated and HF Treated Carbon Samples.

Sample	Carbon wt (%)	Ash wt (%)	SiO_2 wt (%)
C	51.4	47.8	46.0
C_1	60.2	39.2	37.6
C_2	68.6	29.8	28.2
C_3	74.8	23.6	22.4
C_4	79.0	19.4	18.0

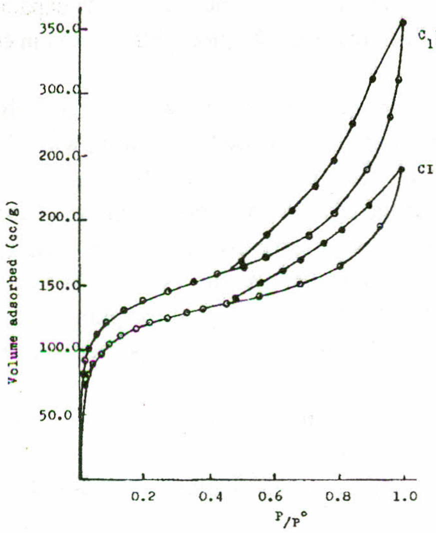
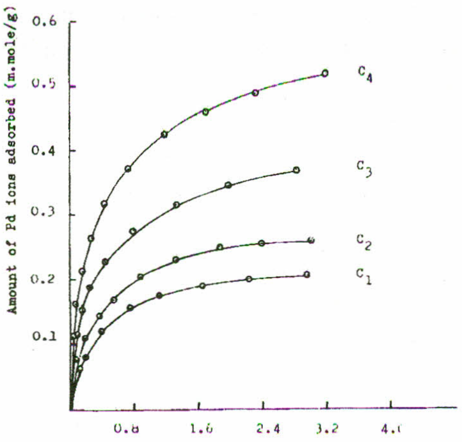
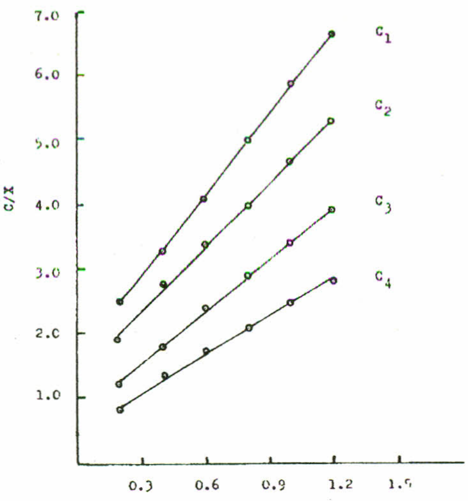


Fig. 1. Representative nitrogen adsorption isotherms at 77K.



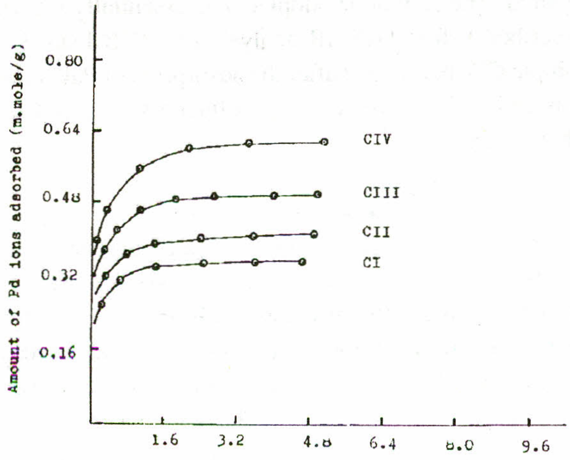
Equilibrium concentration (m.mole/L)

Fig. 2. Adsorption isotherms of Pd ions on acid treatd carbons.



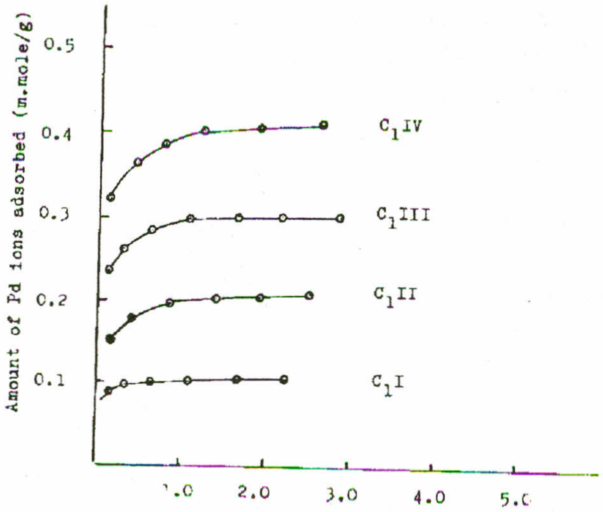
Equilibrium concentration (m.mole/L)

Fig. 3. Langmuir plots of HF acid treated carbons.



Equilibrium concentration (m.mole/L)

Fig. 4. Adsorption isotherms of Pd ions on HHB non-acid treated carbons.



Equilibrium concentration (m.mole/L)

Fig. 5. Adsorption isotherms of Pd ions on HHB acid treated carbons.

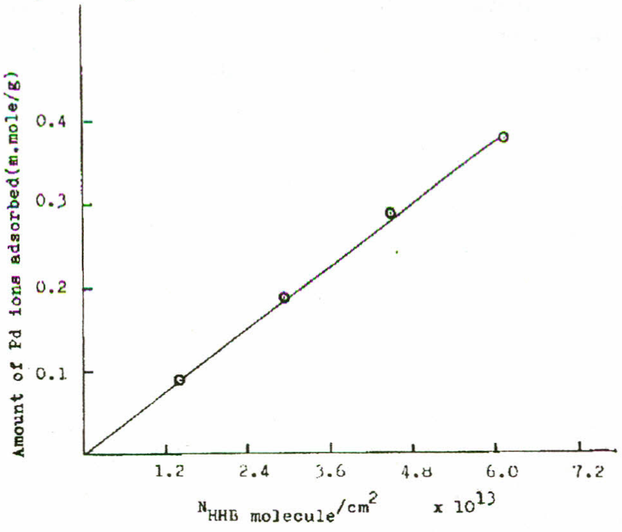


Fig. 6. Amount of Pd ions adsorbed as a function of the number of HHB molecules per unit area.

amount of Palladium ions adsorbed has been found to increase with the increase of the severity of the acid treatment. HF acid may create acid centres on the carbon surface. The acidity values of the acid treated carbons are listed is column 6 of Table 1. These valuess indicate at least a general trend which is the adsorption capacity increase with the increase of the surface acidity. Acid centres seems to be the active fraction of the surface on which the adsorption of Palladium ions proceed.

It has been also found that, loading of carbon sample C with HHB considerably increases the uptake of Palladium ions. The relation between the number of HHB molecules per unit area (N_{HHB} molecule/cm^2 as a function of the amount of Palladium ions adsorbed (m.mole/ g carbon) is shown in Fig. 6. The plot is fairly linear indicating that the total number of HHB molecules are active for the adsorption of Palladium ions.

From the above mentioned discussion the adsorption of Palladium may proceeds through the chemisorption of Palladium ions by HHB molecules loaded on the carbon surface. IR spectrum of HHB treated carbon sample CIV before the adsorption of Palladium ions shows three bands at 1608, 1578 and 1518 cm^{-1} assigned to γ (C=N) pyridine [15], (C=N) imine (16) and (C=N) oxime modes respectively. The bands at 3180 and 930 cm^{-1} are assigned to γ (NH) and γ (NO) modes respectively. The spectrum of the same carbon sample after the adsorption of Palladium ions indicates that the band at 1578cm^{-1} γ (C=N) imine is shifted to lower wavenumber (15 cm^{-1}) and the band at 1608 cm^{-1} γ (C=N) pyridine is shifted to higher wavenumber (20 cm^{-1}) suggests the participation of these groups in the chemisorption of Palladium ions.

References

1. O. P. Mahajan, A. M. Youssef and P. L. Walker, J. Separation Science and Technology, **13,** 487 (1978).
2. O. P. Mahajan, C. Moreno-Castilla and P. L. Walker, J. Separation Science and Technology, **15**(10), 1733 (1980).
3. A. M. Youssef, Ext. Abstr. Programe Bienn. Conf. Carbon 15th, 234, England (1981).
4. A. M. Youssef, M. R. Mostafa and E. M. Dorgham, Bull. Soc. Chem. Fran., **6,** 741 (1989).
5. H. Oda and C. Yokokawa, Carbon, **21,** 485 (1983).
6. A. M. Youssef, M. R. Mostafa and E. M. Dorgham, Afinidad, **XLVII,** 425 (1990).
7. H. U. Foresterling, Carbon, **28,** 1, 27 (1990).
8. K. M. Ibrahim, M. M. Bekheit and G. M. Abu El-Reash, Tran. Met. Chem., **16,** 189 (1991).
9. J. Minczewski, M. Krasicko and Z. Marczenko, Chem. Anal., **15,** 43 (1970).
10. K. Tanabe and T. Yamaguchi, J. Res. Inst. Catal., **14,** 93 (1966).
11. S. Brunauer, L. S. Deming, W. S. Deming and E. Teller, J. Am. Chem. Soc., **62,** 1723 (1940).
12. S. Brunauer, P. H. Emmett and E. E. Teller, J. Am. Chem. Soc., **60,** 930 (1938).
13. P. H. Emmett and T. W. Dewitt, J. Am. Chem. Soc., **65,** 1253 (1943).
14. C. H. Giles, T. H. MacEwan, S. N. Nakhwa and D. Smith, J. Am. Chem. Soc., 3973 (1960).
15. S. Burman and D. N. Sathyanaryana, J. Coord. Chem., **11,** 219 (1982).
16. G. C. Percy and D. A. Thornton, Inorg. Nucl. Chem. Lett., **7,** 599 (1971).