

X-Ray Photoelectron Spectroscopy Studies on Activated Carbon Prepared From Rind of *Citrus nobilis*

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The rind of *Citrus nobilis* is waste biomass material. The raw material was carbonized in the inert gas atmosphere and the resulting carbon was activated with 0.1 N nitric acid. The surface studies were made using X-ray photoelectron spectroscopy analysis. The results indicate the concentration of surface oxides. The prepared carbon was used for defluoridation. X-Ray photoelectron spectroscopy studies indicate that the fluoride is adsorbed on activated carbon.

Key Words: X-Ray photoelectron spectroscopy, Activated carbon, *Citrus nobilis*, Defluoridation.

INTRODUCTION

Now a days activated carbons are using for many purposes like odour control, defluoridation in drinking water¹, dyes removal² and toxic elements removal in waste water³ and in various chemical processes⁴.

X-Ray photoelectron spectroscopy is an important surface sensitive tool for the characterization of surface properties of activated carbons which gives vital information from the outer most 3-4 nm surface layers of carbon surfaces *i.e.*, surface groups, metal content and distribution and chemical state of the elements present. From the observed binding energies it is possible to know the molecular environment (oxidation states, bonding atoms) around the elements present in the sample^{5,6}.

In the present study this technique is used to study the changes on surface of the atom after activation and after using this carbon in defluoridation.

EXPERIMENTAL

The rind of *Citrus nobilis* was collected, washed, dried, crushed and carbonized in uniform nitrogen flow in horizontal tube furnace electrically heated at 700 °C for 5 h. The carbon was cooled to room temperature and washed with deionized water until the effluent was clear in colour. Finally the carbon was dried in an oven at 120 °C. The carbon was powdered and the particle size in the range 40-50 µ mesh. The

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carbon was subjected to liquid phase oxidation with 0.1 N HNO₃. After that again the carbon was washed with water, dried in an oven and it was named as CNC (Kaza's carbon).

Method: X-ray photoelectron spectroscopy studies of the prepared activated carbon (CNC) were made using KRATOS AXIS165 under 10⁻⁹ torr vacuum. Pass energy of 80 eV was used in recording the spectra. X-ray excitation source Mg K (1253.06 eV) and hemispherical electron analyzer. The samples were dried at 283 K for 24 h before the analysis. Survey and high resolution narrow beam were recorded for O 1s, C 1s and N 1s photoelectron peaks. The atomic concentrations were calculated from the photoelectron peak areas using Shirley background subtraction⁷ and sensitivity factors were taken from PHI⁸.

50 mL of standard sodium fluoride solution (5 mg/L of F⁻) is pipetted out into conical flask. 0.5 g of prepared CNC is added and is stirred at 120 rpm mechanically 0.5 h. The solution is filtered through Whatmann No. 42 filter paper. The CNC after defluoridation collected, dried and subjected to XPS studies to know whether fluoride is adsorbed on the surface of activated carbon or not.

RESULTS AND DISCUSSION

The X-ray photoelectron spectroscopy (XPS) spectra of CNC indicate the presence of three distinct peaks at 285, 400 and 530 eV which can be attributed due to carbon, nitrogen and oxygen, respectively. The XPS high resolution narrow scan C 1s spectrum is shown in Fig. 1. It shows major peak at 284.6 eV, which corresponds to a non-functionalized carbon *i.e.*, the contribution of C as C *sp*² hybridization and C *sp*³ hybridization, belonging to carbon skeleton of the material and the contribution of aliphatic C *sp*³ that corresponds to hydrocarbons. From the figure the binding energies 284.608, 286.513, 287.294, 289.41 and 291.493 which could be attributed to the presence of C-C/C-H, O-C-O and carboxylic group, O-C=O and transition in aromatic rings, respectively.

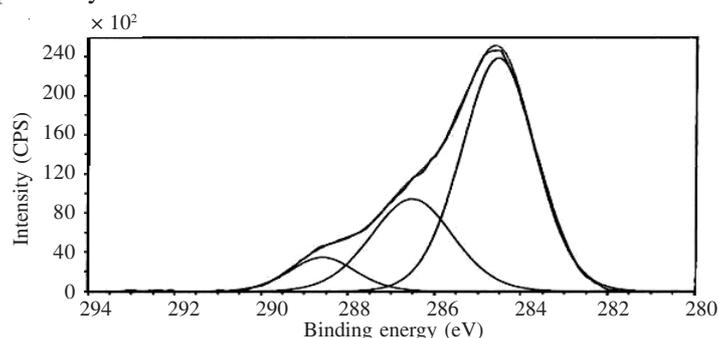


Fig. 1. X-ray photoelectron spectroscopy high resolution C 1s spectra of CNC

The peaks at 286.513 and 287.294 eV regions may also have resulted from the presence of C-N structures. After peak fitting C 1s deconvoluted peaks with B.Es 284.608, 286.513, 288.584 and 286.1 can be attributed to C-C, C-O, C=O and C-OH, respectively.

The surface O 1s peak was observed in the region 529.8-533.4 eV. The O 1s signal not very sensitive to the way in which the oxygen is bond. Papirer *et al.*⁹ suggested that with a first approximation, the 80-90 % peak area of O 1s peak originates from the contribution of surface atoms or atoms of the 3.5-4.0 nm thick outer shell. The high resolution O 1s spectrum is given in Fig. 2. The B.Es 532.05, 531.8 and 533 corresponds to C-OH/C-O-C, C=O and oxygen linked carbon by single bonds, respectively.

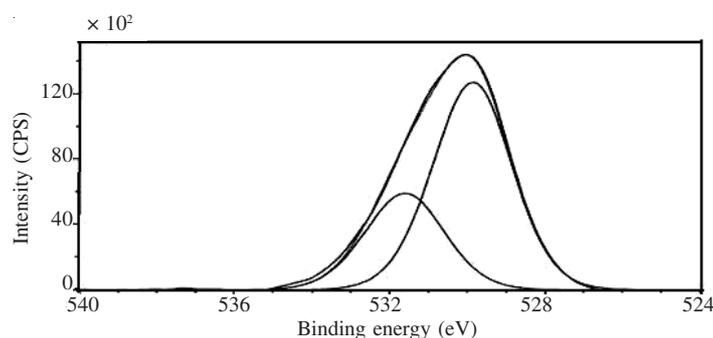


Fig. 2. XPS high resolution O 1s spectra of CNC

The XPS high resolution narrow scan for N 1s region is shown in Fig. 3. The binding energies 398.19, 400.6 and 399.569 can be attributed to the species of pyridine, pyrrole and amino groups attached to aromatic rings, respectively.

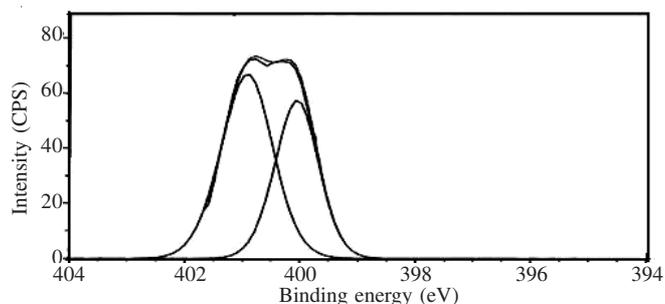


Fig. 3. XPS high resolution N 1s spectra of CNC

X-Ray photoelectron spectroscopy studies on the prepared CNC after using for defluoridation *i.e.*, fluoride loaded CNC were made. The survey and high resolution narrow beam were recorded for C 1s, F 1s and Na 1s photoelectron peaks. The XPS spectra (Fig. 4) indicate the presence of four distinct peak at 685.312, 285.000, 1065.800 and 532.215 eV, which can be attributed due to fluoride, carbon, sodium and oxygen, respectively. The spectra show distinctly carbon, oxygen and sodium peaks of the sample. The deconvoluted C 1s spectra with B.E 284.6 eV correspond to aliphatic carbon. The satellite around 288.9 eV indicating the formation of great

amount of functional groups with C=O double bonds. The C 1s spectrum (Fig. 5) has been resolved into its individual component peaks presenting graphite carbon B.E 284.608 eV. It is found that the C 1s showed peak at 288.9 eV. This new peak is not found in virgin sample and is attributed to due to carbon on which fluoride is adsorbed.

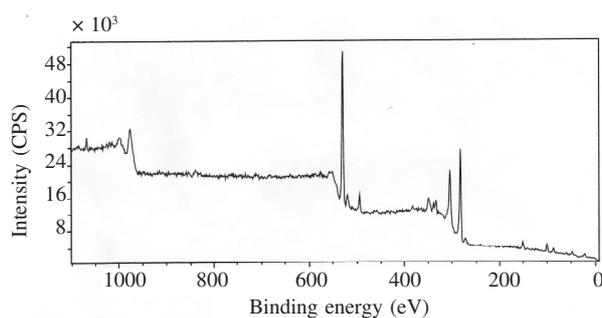


Fig. 4. X-Ray photoelectron spectroscopy scan of CNC

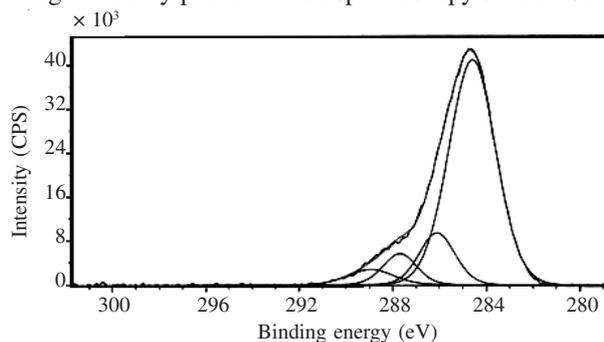


Fig. 5. X-Ray photoelectron spectroscopy high resolution C 1s spectra of fluoride loaded CNC

The XPS spectrum for Na 1s (Fig. 6) with a peak at 1069.8 eV and of F 1s (Fig. 7) with a peak at 685.312 eV. These two peaks clearly indicate the adsorption of sodium and fluoride on activated carbon.

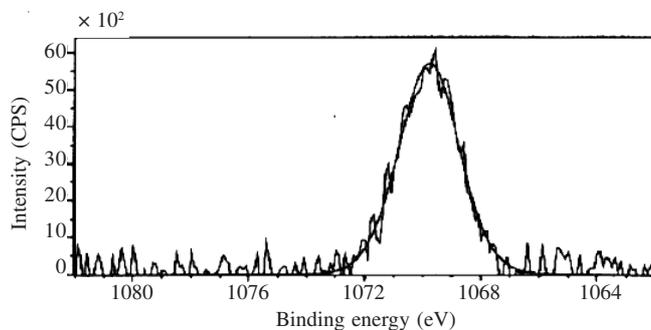


Fig. 6. XPS high resolution Na 1s spectra of fluoride loaded CNC

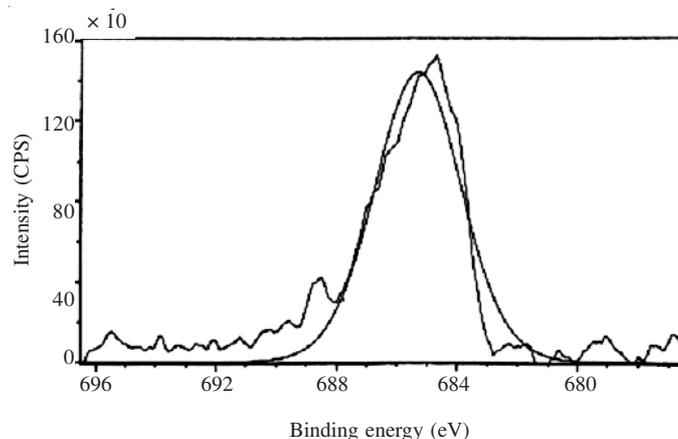


Fig. 7. X-Ray photoelectron spectroscopy high resolution F 1s spectra of fluoride loaded CNC

Conclusion

The prepared activated carbon is cheap, since it can be prepared from biowaste material. X-Ray photoelectron spectroscopy survey indicates that the carbon activated with HNO_3 has more concentration of surface oxides and these group are acidic nature. X-Ray photoelectron spectroscopy analysis also reveals the exact nature of the adsorbent surface, adsorption process. It also confirms that this carbon is capable of removing fluoride from aqueous samples.

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