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EFFECT OF OXIDATIVE MODIFICATION OF ACTIVATED CARBON ON SURFACE CHEMISTRY, POROSITY AND TARTRAZINE ADSORPTION

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Abstract— The surface chemistry and pore structure of porous activated carbons determine their application. Activated carbons (ACs) were modified by oxidization and degassing. The effect of oxidation and degassing on the textural properties such as surface area, pore size, pore volume, and surface chemistry was thoroughly examined by using elemental analysis, Fourier transform spectroscopy, SEM analysis, surface acidity/basicity and pH_{ZPC} measurements. The micropore volume and surface area decreases with oxidation treatment and increases on degassing. The adsorption capacity of the oxidized samples for tartrazine dye is poor than the untreated activated carbons.

Key words: Oxidative modification, pore size, porous activated carbon, surface acidity, tartrazine

I. INTRODUCTION

Contamination due to release of large number of toxic chemicals into the environment is the major undesirable features. Many governments have established strict standards for clean air and water. So the development of improved methods for the controlled release of toxic contaminants and designing of new materials to remove a wide range of contaminants is necessary. Adsorption is extremely attractive for this purpose because of their ease of operation. Tartrazine is an azobenzene artificial yellow water soluble acidic dye. It is known to cause allergic reactions such as asthma and urticaria (1, 2). Neurobehavioral parameters of human beings have also been affected by tartrazine (3). It may cause thyroid tumors and chromosomal damage.

Several adsorbents such as bottom ash and De-oiled soya (4) chitosan-coated bentonite (CCB) beads (5) polystyrene anion exchange resins (6) and activated carbons prepared from different sources (7-10) have been used for the removal of tartrazine from aqueous solution. Adsorption of tartrazine by activated carbons prepared from different sources has been intensively investigated, but relatively less work is reported related to modified carbons. In this research paper, we examine how the pore size and surface chemistry through oxidation and degassing affects the AC in the adsorption of tartrazine.

II. EXPERIMENTAL

Preparation of modified activated carbons

Oxidation with nitric acid was carried out by treatment of commercial activated carbon with nitric acid solution. About 400 ml of 50% nitric acid was added to 10 g AC and the mixture was placed on a water bath maintained at about 80°C. When about 10 ml of the acid is left, the contents are diluted with distilled water and then filtered. The sample is then washed exhaustively with hot distilled water and dried at 120°C.

Oxidation with hydrogen peroxide included the addition of about 10 g of carbon sample in a stoppered reagent bottle containing 700 ml of a 3 N solution of hydrogen peroxide. The mixture was placed for about 48 hrs with intermittent shaking. The treated sample was then filtered off, washed with distilled water and dried at 110°C.



Degassing of oxidized activated carbons has been carried out by the elimination of carbon oxygen surface groups formed during oxidation at 950°C. Temperature controlled tube furnace was used for degassing. In this quartz tube furnace, 5g of a carbon sample was placed in a thin layer of about 5 inches in length. The tube furnace is then connected to a Hyvac.Cenco vacuum pump capable of giving vacuum to an order of 3×10^{-3} mm of Hg. Appropriate voltage is then applied to set its temperature at desired level. To avoid reformation of the carbon-oxygen complexes, degassed sample is allowed to cool in vacuum. The cooled sample is then transferred to stoppered bottles flushed with nitrogen.

BET Surface Area and Pore Size distribution

Nitrogen adsorption-desorption isotherms were measured at 77 K by using a Quantachrome Instruments Nova 2200e Surface area and Pore size analyzer. From these isotherms BET surface area, total pore volume and average pore radius of a particular activated carbon sample is determined. The activated carbon samples were degassed for 6 h at 320°C before the analysis. Approximately 0.10 g of sample is used for this analysis. The surface area is determined using the BET equation, while the total pore volume is directly calculated from the volume of nitrogen held at the highest relative vapour pressure ($p/p_0 = 0.99$). Pore size radii are determined by Dubinin-Astakov equation. All calculations are done using NovaWin software provided with the analyzer.

Elemental Analysis

Elemental analysis was performed using a Flash 2000 CHNS-O Organic Elemental Analyzer. Determination of carbon, hydrogen, nitrogen and sulfur is carried out in CO₂, H₂O, N₂ and SO₂ forms, respectively. The analyzer uses a combustion process to break down substances into simple compounds which are then quantified. The sample of approx. 1 mg AC is prepared in a tin paper (CHNS analyses) or silver (O analysis). The combustion of the sample at 1800°C (pyrolysis at 1070°C in the case of O analysis) release gases which undergo a cycle of treatment (oxidation and reduction) in a tube reactor. The eluted gases are conveyed to the thermal conductivity detector TCD that generates electrical signals (processed by the Eager 300 software) for the Nitrogen, Carbon, Hydrogen, and Sulfur percentages contained in the sample.

Scanning electron micrograph (SEM)

The Scanning Electron Microscopy is a technique of electronic microscopy based on the electrons-material interactions. The interaction of the electrons provided by SEM with the material initiates a number of reactions inside the sample which results in the generation of signals which can give information about the sample. The surface morphology and pore structure of ACs were analyzed by Hitachi S-4300

scanning electron microscope (SEM) at accelerating voltages of 10–20 k. Prior to analysis, samples were dried and then coated with ultrathin coating of gold with Fine coat ion sputter (JFC 6100).

Fourier Transform Infrared Spectrometer (FTIR) Analysis

Perkin Elmer-Spectrum RX-1 Fourier Transform Infrared Spectrometer was used to measure the infrared spectrum of the ACs and to identify their chemical functionality. The ACs were dried at 150°C prior to IR evaluation. The spectra were recorded as KBr pellets in the 4000 - 500 cm⁻¹ spectral range. The KBr pellets are prepared by mixing and grinding the activated carbon with KBr (mass ration1:100) in a pestle mortar and then pressing the resulting mixture under pressure of 8×10^4 N in hydraulic press.

Base neutralization capacity (Surface acidity and basicity)

1g each of a carbon sample was placed in contact with 100 ml of 0.1 N sodium hydroxide solutions in a stoppered bottle. The contents were placed on a water bath at 80°C for 6 h. The mixture was then cooled and an aliquot volume of supernatant liquid was titrated against standard hydrochloric acid solution. The amount of alkali neutralized gives the surface acidity of the carbon sample. Basicity of carbon samples was determined by similar procedure where carbon samples were placed in contact with 0.1 N HCl solution and titrated against standard NaOH solution.

Zero point charge pH (pH_{ZPC})

The point of zero charge of as received and oxidized ACs were determined by the solid addition method (11). 20 ml of 0.1 M KNO₃ solution was taken in series of test tubes and pH₀ values of the solution were roughly adjusted from 2 to 12 by adding either 0.1N HNO₃ or KOH. Then the total volume of each solution was made exactly to 30 ml by adding the KNO₃ solution of the same strength. The pH₀ of the solutions were then accurately noted and then One gram of carbon sample was added to test tube. The suspensions were allowed to equilibrate for 24 h with intermittent manual shaking. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_i) values ($\Delta pH = pH_0 - pH_i$) was plotted against the pH₀. The point of intersection of the resulting curve at which $\Delta pH = 0$ gave the value of pH_{ZPC} of carbon.

Adsorption study

The adsorption capacity of as-received and modified activated carbons was compared. 0.1 g of adsorbent and a 20.0 mL of tartrazine dye solution (100–1000 mg L⁻¹) were placed in various 50.0 mL test tubes. The mixtures were agitated

intermittently for 270 min at room temperature. UV/visible spectrophotometer was used to quantify the residual of dye in solution after adsorption at a maximum wavelength of 426.8 nm.

The amount of dye adsorbed at equilibrium q_e (mg/g) was calculated from the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

Where C_o and C_e (mg/L) are the liquid phase concentrations of dye at initial and equilibrium, respectively, V (L) the volume of the solution, and W (g) is the mass of adsorbent used.

III. RESULTS AND DISCUSSION

Effect of oxidation on the Pore Structure of ACs

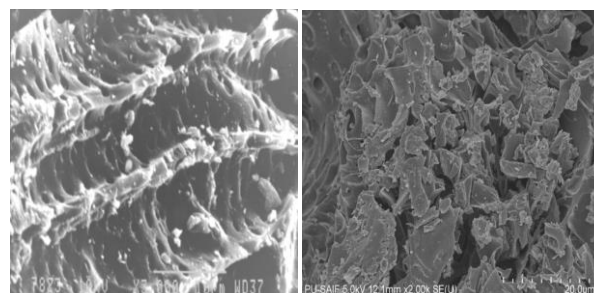
Our work shows a correlation between the oxidation, degassing, pore volume, and surface area. BET surface area data is shown for the treated and untreated ACs in Table 1. Aqueous phase oxidation lowered ACs surface area while degassing caused an increase in surface area. In addition, we observe that the average micropore size changed very little from the original value while the pore volume decreases with increasing oxidation. Similar results have been reported by Stavropoulos et al.(12).

Table.1. Pore size, surface area and pore volume of as-received and modified activated carbons

Samples	BET surface area (m ² /g)	Average pore radius (Å)	Micropore volume (cm ³ /g)
As-received AC	1607.43	10.7	0.850
Oxidized with HNO ₃	712.71	10.8	0.381
Oxidized with HNO ₃ + degassed at 950°C	883.68	10.6	0.470

SEM observations of AC Fig. 1a revealed its porous texture. Fig. 1b shows the scanning electron micrograph of AC oxidized with nitric acid. The figure shows evidence that AC structure changed after oxidation.

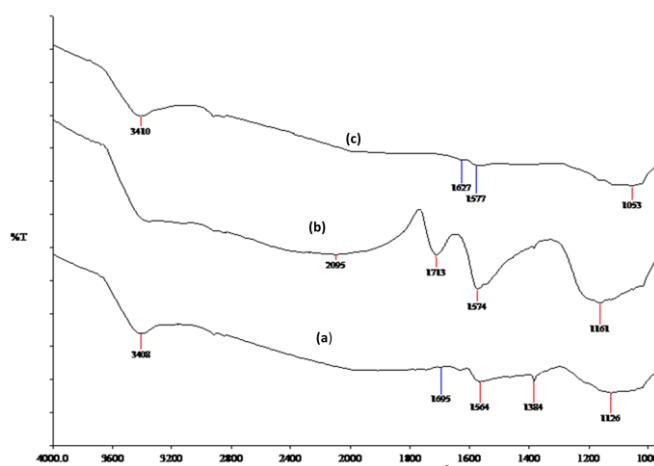
Fig.1. Scanning electron micrographs of AC before (a) and after (b) Oxidation with nitric acid



Effect of Oxidation on Surface Chemistry

FTIR was used for qualitative analysis of the chemical functionality of untreated and treated ACs. Spectra are shown in Fig.2. Spectra show the differences in infrared absorption of as-received AC, oxidized with concentrated nitric acid and degassed at 950°C. The FT-IR spectra of as-received AC shows peak at 1564 cm⁻¹ that represents the C=C bond conjugated with another C=C or a C=O bond. Low intensity of bands for as-received carbon indicates the presence of fewer groups. However new and intense peaks appeared in the spectrum of oxidized sample. The band at 1713 cm⁻¹ represents C=O stretching vibration of carboxylic acids, 1574 cm⁻¹ represent the stretching of aromatic rings. Peak at 1384 cm⁻¹ correspond to C-O stretching. On degassed sample intensity of these bands decreases due to removal of carbon-oxygen groups.

Fig.2. FTIR spectra of (a) As-received AC (b) oxidized with nitric acid and (c) 950°-degassed samples of carbon



Composition and acidity/basicity of different as-received and modified activated carbon samples are presented in Table.2. The proportion of each element, specially the oxygen content

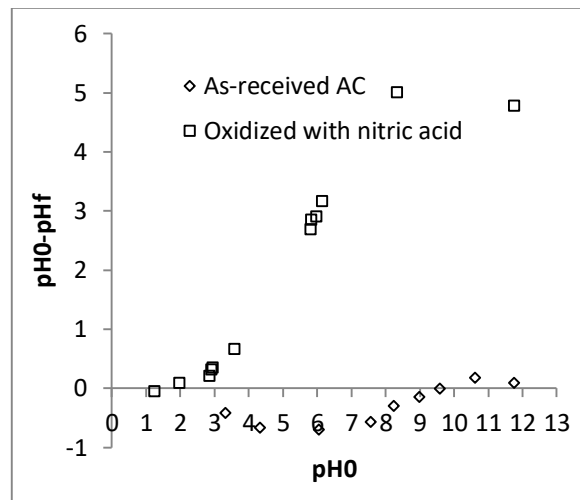
gives more precise idea about the surface functional groups of AC. Oxidation results the product with low carbon and hydrogen content and increase in oxygen content. There is large increase in percentage of oxygen content in carbon oxidized with nitric acid as compare to carbon oxidized with hydrogen peroxide. Nitrogen and sulfur contents were not reported in Table 2 since the amount of these elements was not significant (<1%). Acidity and basicity values confirmed the amphoteric behavior of these samples, in general more basic samples are the less acidic ones. It is seen from the table, acidity of carbon sample increases on oxidation and ACG-100 oxidized with nitric acid have the highest acidity and lowest basicity implies the presence of large amount of oxygen containing surface groups on oxidized samples. These results also agree with composition of samples.

TABLE.2. CHEMICAL COMPOSITION AND SURFACE ACIDITY/BASICITY OF AS RECEIVED AND OXIDIZED CARBON SAMPLES

Carbon Sample	Surface acidity, meq/100 g	Surface basicity, meq/100 g	%C	%H	%O
As-received AC	40	167	57.73	3.73	18.03
Oxidized with H ₂ O ₂	250	23	57.21	1.82	21.24
Oxidized with HNO ₃	837	20	54.92	2.63	28.84

Fig.3 shows the plot between ΔpH and pH_0 for as-received and oxidized ACG-100. The point of intersection of curves with abscissa gave the pH_{ZPC} . The point of zero charge for ACG-100 is found to be 9.7 and for oxidized ACG-100 to be 1.7. This wide variation in pH_{ZPC} of as-received and oxidized activated carbons shows the difference in the surface functional groups. Shift in the value of pH_{ZPC} from 9.7 for ACG-100 to around 1.7 for oxidized ACG-100 confirm the increase in degree of acidity

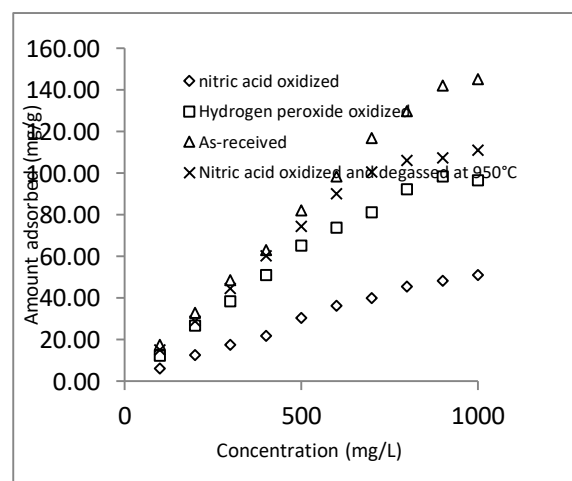
Fig.3. Point of zero charge of as-received AC and AC oxidized with nitric acid



Effect of ACFs Oxidation on Adsorption

We studied adsorption of tartrazine dye onto as-received, oxidized and degassed ACs. Fig.4. shows the tartrazine adsorption isotherms for different oxidation treatment and degassed samples. The decrease in uptake of tartrazine is more in case of nitric acid oxidized carbon as compare to hydrogen peroxide treated sample and increase in uptake on degassing implied that acidic groups played a negative role in the adsorption of dye. The total available pore volume and surface area also lower for oxidized sample as compare to as-received sample. But for degassed sample there is again increase in pore volume.

Fig.4. Adsorption isotherms of tartrazine for as-received, oxidized and degassed ACs





IV. CONCLUSION

The effects of oxidation and degassing on pore structure and surface chemistry have been identified and can be used to tailor ACs for removal of specific contaminants. The decrease in adsorption performance upon oxidation can be attributed to an increase in acidic oxygen containing functional groups and decrease in micropore volume. These results may help in optimization of adsorbent and designing an adsorption equipment for the removal of tartrazine from aqueous solution.

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