

# Surface chemistry of synthetic carbon adsorbents and their application in the adsorption of amines

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## Introduction

Activated carbons are widely used for purification and separation applications, such as purification of permanent gases, removal of volatile organic compounds from streams of gases and liquids, hydrocarbon vapor recovery, purification of active pharmaceutical ingredients, and preparing electrode materials in energy storage devices.

Granular activated charcoal (GAC) is a popular form of activated carbon due to price and availability. It is produced from a wide range of carbon precursors, from coal to coconuts shells. The chemical variability of the GAC feedstocks reduces their purity and consistency. Naturally derived carbons are friable and can produce fines during their processing and handling. Whereas the defined composition and morphology of the synthetic carbons make them mechanically resistant and capable of withstanding high pressures when used in packed columns. Also, the surface chemistry of the synthetic carbons is highly customizable with dispersion pHs ranging from as low as 2.5 to as high as 11. Commodity GACs typically have basic dispersion pHs.

The objective of this work was to demonstrate the selectivity of an acidic synthetic activated carbon for the removal of molecules with dangling amines groups. A common and naturally derived GAC was tested for comparison.

## Methods and Materials

### Material Characterization

The commercially available activated synthetic carbon Carboxen<sup>®</sup> 1032 was obtained from MilliporeSigma. For the adsorption experiments, a customized 30-70  $\mu\text{m}$  fraction of Carboxen<sup>®</sup> 1032 (labeled M1032) was used along with a wood-based activated charcoal (WAC) that was ground and sieved to get the 30-70  $\mu\text{m}$  fraction. Pore volumes and surface areas were determined using N<sub>2</sub> porosimetry at 77 K. The pHs values for the carbons were measured by weighing one gram of sample and placing it in 20 mL deionized water. The carbon was magnetically stirred for 1 hour before measuring its pHs. N<sub>2</sub> adsorption isotherm measurements were carried out in a porosimeter from Micromeritics<sup>®</sup> (ASAP2020). Pore sizes, surface areas, and dispersion pHs are provided in **Table-1**.

**Table 1. Textural properties and dispersion pHs**

Carbon	BET Surface Area (m <sup>2</sup> /g)	BET Total Pore Volume (cm <sup>3</sup> /g)	Micropore Volume (cm <sup>3</sup> /g)	Mesopore Volume (cm <sup>3</sup> /g)	Macropore Volume (cm <sup>3</sup> /g)	Dispersion pHs
WAC	994	1.19	0.47	0.64	0.08	10.0
M1032	911	1.25	0.35	0.67	0.23	3.3

An acidic carbon (M1032) and a basic charcoal control (WAC) were used to analyze the effect of carbon dispersion pHs in amine adsorption as both the carbons had similar particle size and textural properties.

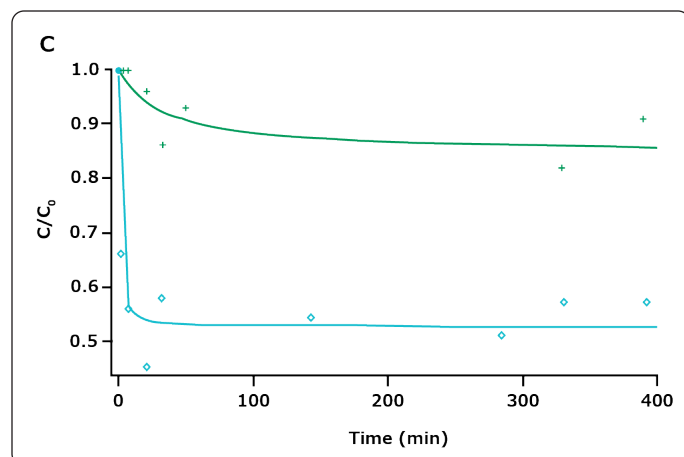
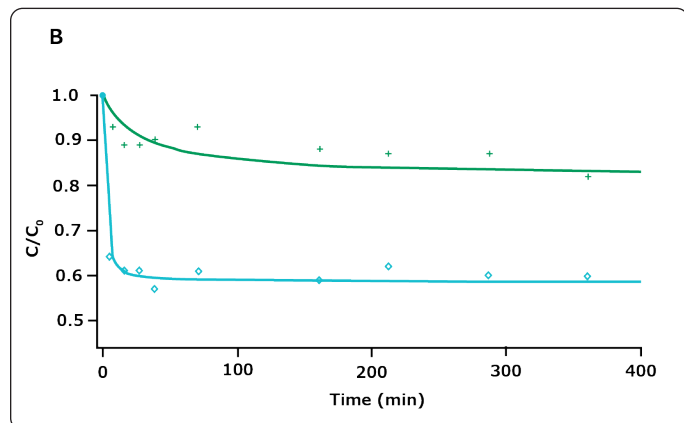
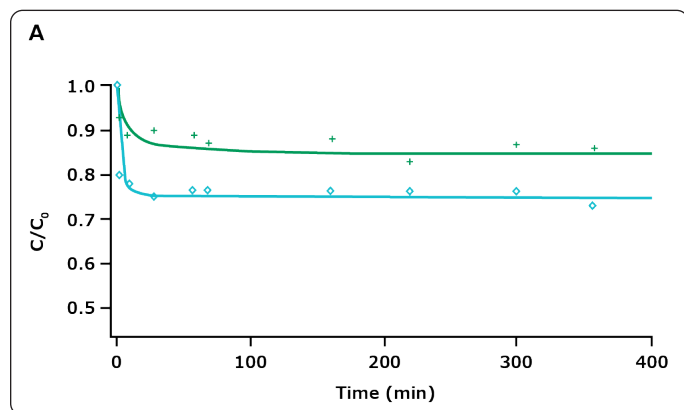
It is the surface chemistry that dictates the dispersion pHs of the carbons. Functionalization of the carbon surfaces with oxygen functional groups alters the materials' pHs and hydrophobic/hydrophilic properties. Careful control of the activation or activations allows for controlled and tailored surface oxygen functionalization. The pHs of Carboxen® Synthetic Carbons can be tailored from 2.5 to 10.5. Commodity-activated charcoals typically have basic dispersion pHs like the WAC given in Table-1. For purification involving the removal of basic compounds like amines, an acidic carbon works best. The synthetic carbon M1032 has an acidic pH of 3.3. Carboxen® Synthetic Carbons are activated through physical means. Therefore, there is no chemical residue left on the carbon that could create a chemical leaching concern in-use.

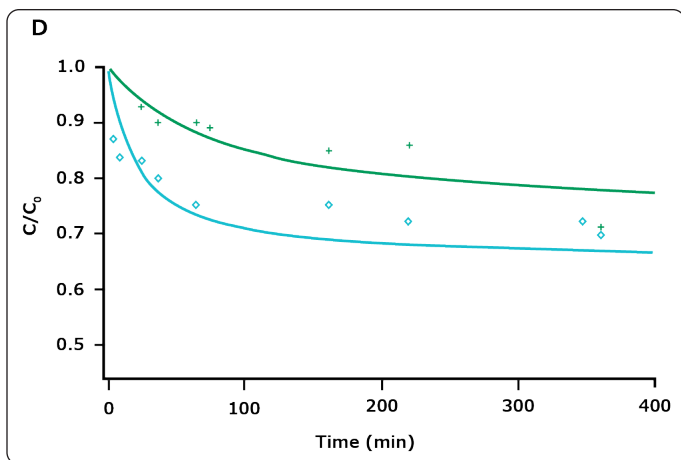
### Amine Adsorption Experiments

Four water soluble molecules with amine functionality were studied, benzylamine, tyramine, 4-nitro-o-phenylenediamine, and 2-phenethylamine. Amine solutions were prepared using 100 mg amine and 100 mL HPLC grade water. One hundred microliters of amine solution were diluted 10 times before the HPLC analysis. The amine solutions with a concentration of 1 mg/mL were kept in contact with 100 mg of the carbon adsorbent. Kinetic adsorption experiments were carried out in 100 mL flasks and stirred at 150-300 rpm. Experiments were conducted without temperature control (i.e. laboratory temperature (~ 20 °C)) for the four amine compounds. The kinetic studies were repeated for benzylamine and 2-phenethylamine with temperature control at 15 °C. Eleven 100- $\mu$ L samples were drawn and diluted to 1-mL each in a 24-hour period. The aliquots were filtered with 1 mL luer slip tip syringes and Millex®-LH Durapore® PTFE membranes. The concentration of amine in the solution was determined by HPLC coupled to a UV detector at 238 nm. The analysis was done using an Ascentis® Express C18 HPLC column. Mobile phases 5mM ammonium acetate, pHs 4.8 (unadjusted) and 5mM ammonium acetate 0.1% acetic acid in 5:95 water:acetonitrile; gradient: 95% to 40% in 8 minutes, held at 40% for 2 min.

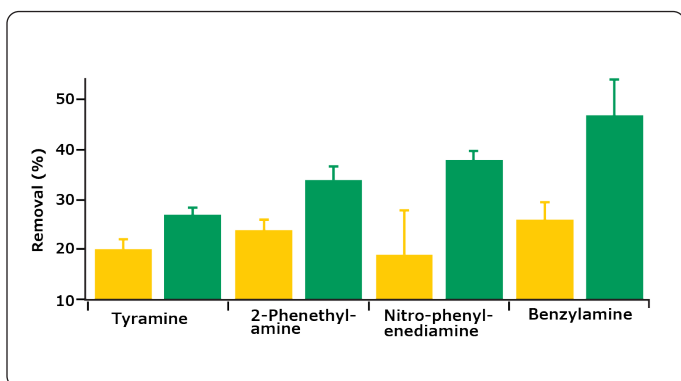
### Results

At a ratio of 1:1 carbon to adsorbate, amine adsorption kinetics of the acidic carbon was faster than the adsorption kinetics for the charcoal at room temperature (~ 20 °C) (**Figure-1**). The amine removal (%) was significantly higher for M1032 than that for the activated charcoal at room temperature (~ 20 °C) (**Figure-2**). The acidic surface groups on the synthetic carbon enabled an increased adsorption capacity to retain the basic compounds.





**Figure-1.** Pseudo-first order kinetics at room temperature ( $\sim 20\text{ }^{\circ}\text{C}$ ) for WAC ( $\diamond$ ) and M1032 (+) for the removal of A) tyramine B) 2-phenethylamine, C) 4-nitro-phenylenediamine and D) benzylamine.



**Figure 2.** Amine removal (%) using activated charcoal (solid yellow bars) and M1032 (green bars) measured at temperature ( $\sim 20\text{ }^{\circ}\text{C}$ )

The kinetic studies were repeated for benzylamine and 2-phenethylamine with temperature control at  $15\text{ }^{\circ}\text{C}$ . The equilibrium capacity of the acidic carbon towards benzylamine was significantly greater at  $625 \pm 1\text{ mg/g}$  as compared to that of the activated charcoal at  $488 \pm 24\text{ mg/g}$ . Activated charcoal retained less 2-phenethylamine at equilibrium  $351 \pm 6\text{ mg/g}$  compared to  $401 \pm 24\text{ mg/g}$  for the acidic carbon. Both the initial rate and rate constant were higher for the acidic carbon when adsorbing 2-phenethylamine. The initial rate was almost 4 times faster for the acidic synthetic carbon and the rate constant was twice that of the charcoal. The half-time for 2-phenethylamine was faster for the acidic carbon. But for benzylamine the half-time was not significantly different between the acidic carbon and activated charcoal. The 2-phenethylamine half-life using acidic carbon was 17 min while that of the charcoal was 55 min. The half-life, initial rate, and rate constant were not significantly different for both carbons when adsorbing benzylamine.

## Conclusions

Comparing the adsorption capacity of the two carbons having similar surface area, pore-volume, pore and particle size distribution permitted the evaluation of the effect of surface chemistry on adsorption performance. The synthetic carbon M1032 has a low dispersion pH and showed an improved adsorption of basic amine compounds. Using a carbon adsorbent of high oxygen content and low dispersion pHs increased the adsorption of basic adsorbates.

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