

# Carboxen® Synthetic Carbon Adsorbents for Industrial Water Purification

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## Abstract

This paper summarizes a selection of field studies that utilized Carboxen® 563 Synthetic Carbon for the purification of chemical wastewater and contaminated groundwater. A comparison was made between traditional granular activated charcoal and Carboxen® 563 for the removal of target molecules, and the *in situ* regeneration potential of Carboxen® 563 after regeneration was investigated. In addition, a cost analysis for a full scale system was made to demonstrate the lower in-use cost of Carboxen® 563 Synthetic Carbon.

## Introduction

The purification of water is of critical importance to the sustainability of the world's aquatic ecosystems. The demand for clean water is steadily rising, while the availability of water free of organic chemical contamination is on the decline<sup>[1,2]</sup>. Wastewater streams in industrial processes are highly regulated and are required to undergo purification prior to their discharge.

Granular activated charcoal (GAC) has been utilized to purify water since at least the 1700s<sup>[3]</sup>. GAC is produced from a wide range of carbon precursors, from coal to coconuts shells. Due to chemical variability of GAC feedstocks, their consistency and purity are limited. MilliporeSigma's line of Carboxen® Synthetic Carbon adsorbents are engineered from synthetic carbon precursors that enable the production of high purity materials with superior performance and reusability. Carboxen® Synthetic Carbon adsorbents have demonstrated to efficiently remove many common water pollutants including small chlorinated molecules, aromatics, pesticides, herbicides, phenolics, and other volatile organic compounds (VOCs), in both the laboratory and field studies.

Comparison of Granular Activated Charcoal and Synthetic Carbon Adsorbents.

## Mechanical Properties and Particle Shape

Carboxen® Synthetic Carbons are spherical particles that pack better than GAC, thus providing an optimal packed bed efficiency (i.e. reduced backpressure and increased throughput). Optical micrographs of GAC and Carboxen® Synthetic Carbon are provided in **Figure 1**. Carboxen® Synthetic Carbons have excellent attrition resistance and thus can withstand repeated handling without cracking and generating fines, often observed with GAC. They have been developed to withstand pressure up to 16,000 psi in industrial applications.

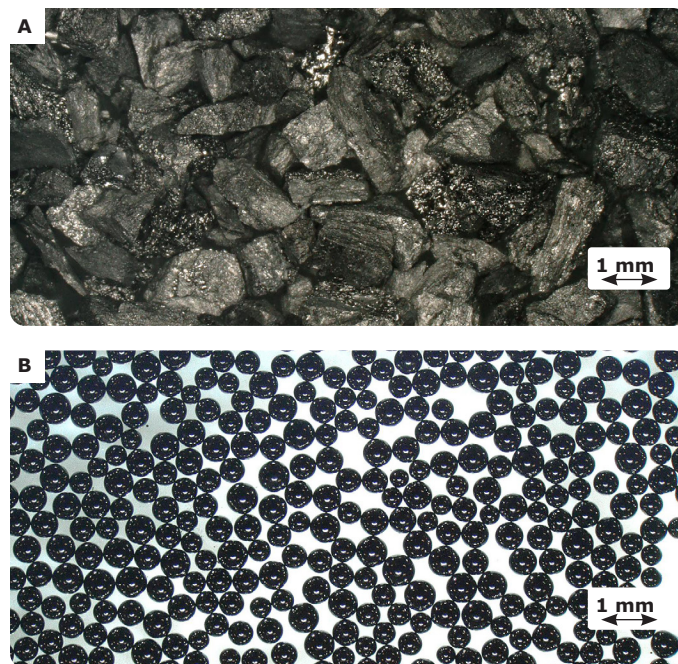
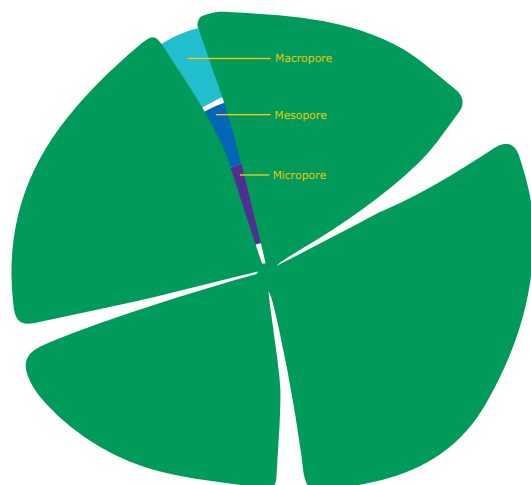


Figure 1. Optical micrographs of A) Granular Activated Charcoal and B) Carboxen® Synthetic Carbon.

## Pore Structure

The GACs primarily have a microporous pore structure, whereas Carboxen® Synthetic Carbons have tapered pores, from macro- to meso- to microporous nature. The tapered pores improve the adsorbent's kinetic and thermodynamic efficiency, enabling greater capacity while operating at increased throughputs. An illustration of the tapered pore structure that can be built into Synthetic Carbons is provided in **Figure 2**.



**Figure 2.** Illustration of tapered pore structure from macro- to meso – to micro porous.

## Surface Chemistry

Functionalization of carbon surfaces with oxygen functional groups alters the materials' pH and hydrophobic/hydrophilic properties. Careful control of the activation or activations allows the controlled and tailored surface oxygen functionalization. The pH of Carboxen® Synthetic Carbons can be tailored from 2.5 to 10.5. The pH can also be selected to meet the application needs. For instance, if the purification involves the removal of a basic compound, an acidic carbon will work best and similarly acidic compounds will require basic carbon adsorbents. The surface chemistries dictates the hydrophobic/hydrophilic properties and with proper oxygen functionalization the Synthetic Carbon adsorbent can be made anywhere from hydrophilic to extremely hydrophobic. The Carboxen® Synthetic Carbons are activated through physical means. Therefore, there are no concerns of chemical leaching during their use due to the residual chemical left on the carbon.

## Methods

This paper summarizes a selection of field studies that utilized Carboxen® 563 Synthetic Carbon for the purification of chemical wastewater and contaminated groundwater. For these applications Carboxen® 563 was selected because of the material's hydrophobic nature. The hydrophobicity of Carboxen® 563 gives the material its high adsorption capacity for VOCs in water. Since water has low affinity for the hydrophobic carbon adsorbent, it does not compete with the adsorbate molecules (i.e. chemical contaminants) for active adsorbent sites.

The findings from 3 field studies are provided in the Results Section. The first field study was conducted at Pease Air Force Base in Newington, NH. This site was selected as the ground water source is contaminated with vinyl chloride, dichloroethene, and trichloroethene. In the second field study, industrial groundwater contaminated with benzene, toluene, xylenes, ketones, and chlorinated solvents was remediated. The third field study was conducted at a chemical manufacturing facility for removal of 1,2-dichloroethane from a chemical waste stream that contained 30-45 % sulfuric acid. These field studies covered a wide range of water contaminants. A comparison was made between traditional GAC and Carboxen® 563 Synthetic Carbon for the removal of target molecules and the *in situ* regeneration potential of Carboxen® 563' Synthetic Carbon was investigated. In addition a cost analysis for a full scale system was made to demonstrate the lower in-use cost of Carboxen® 563 Synthetic Carbon.

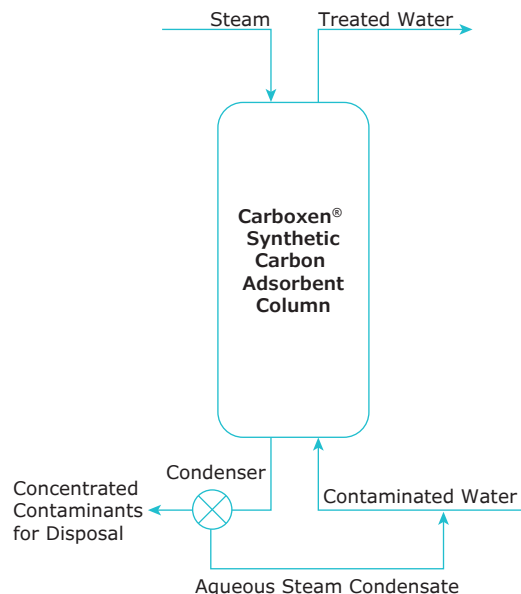
## Results

### Field Study 1 – Groundwater Remediation

The US EPA Superfund Innovative Technology Program conducted a field study demonstrating the technical feasibility and cost-effectiveness of Carboxen® 563 Synthetic Carbon as compared to GAC for remediation of groundwater<sup>[4]</sup>. The pilot scale field study was conducted at Pease Air Force Base in Newington, NH. This site was selected as the ground water source is contaminated with vinyl chloride, dichloroethene, and trichloroethene. These compounds are regulated by the National Primary Drinking Water Regulations and are associated with an increased risk of liver problems and cancer. The pilot scale system used 2 adsorbent columns with a feed rate of 1 gpm. A steam regeneration system was used to regenerate the adsorbent bed. The first test was a head-to-head comparison of Carboxen® 563 and a common GAC used in water purification. The field study found that Carboxen® 563 Synthetic Carbon had 3-10 times the capacity at 5 times the flow rate as compared to GAC.

Following the first test, both adsorbent columns were loaded with Carboxen® 563 . After 13,700 bed volumes (BVs), the breakthrough occurred. The adsorbent bed was then regenerated with steam at 130 °C. The steam regeneration recovered upwards of 90% of the adsorbed contaminants. Most of the VOCs were

recovered after 3 BVs of steam condensate. The steam condensate contained an easily separable organic layer. The organic layer comprised between 85 to 90% of the total VOCs loaded on the adsorbent. The aqueous steam condensate can be passed through the regenerated column and safely discharged as treated water. The adsorption column is then restarted. A process flow diagram is given in **Figure 3**.



**Figure 3.** Carboxen® Synthetic Carbon closed loop adsorption/regeneration system for water purification

The study was conducted over a 3-month period with 4 total cycles completed. The Carboxen® Synthetic Carbon adsorbent showed a negligible capacity reduction after the multiple regenerations. The information obtained from the pilot study was used to develop a conceptual design and cost estimate for a full-scale treatment process (100 gpm). The design used 2 columns with 300 kg of Carboxen® Synthetic Carbon per column, each having a 1.5-minute empty bed contact time (EBCT) at 100 gpm. The cost analysis assumed regeneration every 8,000 BVs or every 8 days. Although based on the cost modeling, the installation cost of the Carboxen® Synthetic Carbon system was found to be significantly greater than the installation cost of a GAC treatment system. But, the annual operation cost of the Carboxen® Synthetic Carbon system is much lower than a GAC system. This is mainly due to the need for GAC to be shipped off site and reactivated (i.e. partially burned) and blended back with fresh GAC and/or landfilled. It should be noted for clarity that GAC cannot be regenerated *in situ*. The cost analysis indicated that after 2 years the total present worth of the Carboxen® Synthetic Carbon adsorbent treatment system is less than the GAC treatment system.

The actual cost of the Synthetic Carbon adsorbent system is influenced by how effective the regeneration is over long periods of time. The true lifetime of the adsorbent can only be determined with certainty by conducting many load/regeneration cycles under true

application conditions over a period of multiple years. Extrapolating the life expectancy from experimental and pilot studies operated for short durations is challenging. Nonetheless, a proof of concept regarding regeneration efficiency is needed. Pilot plant studies were conducted to assess the regeneration effectiveness. Philadelphia tap water was spiked with chloroform and treated in a Carboxen® Synthetic Carbon adsorbent/regeneration column. The test ran for 24 weeks, and it was found that steam at 130 °C regenerated the column for up to 9 cycles. The tenth steam regeneration used an increased amount of steam but did not fully restore the capacity. After 9 cycles a stronger regeneration was required. A methanol regeneration returned the capacity back to its virgin state. The experiment was terminated at this point, but it is anticipated that this process can be run for several cycles and can achieve an operational lifetime of multiple years<sup>[1]</sup>.

Field studies 2 and 3 use a similar process to that shown in **Figure 3**.

### Field Study 2 – Industrial Groundwater Remediation

Industrial groundwater contaminated with benzene, toluene, xylenes, ketones, and chlorinated solvents in the Western US was purified with Carboxen® 563 Synthetic Carbon<sup>[5]</sup>. A column with a 1 ft diameter and 3 ft height was operated at an EBCT of 2.5 min in an up flow fixed bed mode (3gpm/ft<sup>3</sup>). The adsorbent treated greater than 9,000 BVs while maintaining a leakage below 1 ppb. Influent concentrations ranged from 1 to 4 ppm. The adsorbent was regenerated with methanol and capacity was restored.

### Field Study 3 – Chemical Waste Stream Toxic Chemical Removal

A chemical manufacturing facility in the Eastern US utilized Carboxen for removal of 300-600 ppm of 1,2-dichloroethane (EDC) from a chemical waste stream that contained 30-45 % sulfuric acid<sup>[5]</sup>. Both Carboxen® 563 and Carboxen® 572 Synthetic Carbons had 10 times the capacity of GAC and treated the effluent to less than 1 ppm of EDC. The adsorbents were regenerated with 4 BVs of methanol. The regeneration recovered 95% of the EDC loaded on the adsorbent and restored the adsorbent capacity.

## Conclusions

In the removal of volatile organic compounds from water, Carboxen® Synthetic Carbon operates at much faster flow rates than granular activated charcoal while treating between 5-10 times more bed volumes to the water quality criteria of the remediation site. Due to the ability to regenerate Carboxen® Synthetic Carbons *in situ*, industrial and/or residential water purification processes can be operated in a closed loop adsorption-regeneration system. Such a system has a much lower operating costs and also eliminates the need for adsorbents to be shipped off site for reactivation and or disposal.

## References

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