

## PlumeStop® Technical Bulletin 2.1

# Sorption of Contaminants from Solution: Terms & Principles

### Quick Reference:

- Principles of PlumeStop sorption
- PlumeStop sorption isotherms
- Significance as a remediation tool

### Background

PlumeStop® Liquid Activated Carbon™ is composed of very fine particles of activated carbon (1-2  $\mu\text{m}$ ) suspended in water through the use of unique organic polymer dispersion chemistry. Once in the subsurface, the material behaves as a colloidal biomatrix, sorbing to the aquifer matrix, rapidly removing contaminants from groundwater, and expediting permanent contaminant biodegradation.

### Wide-Area Dispersive Distribution

Unlike any other sorbent technology, PlumeStop can be installed in the subsurface through dispersive flow from low-pressure injection (without fracturing the formation), providing a wide-area, thin-film coating of the aquifer matrix. It does not create preferential flow pathways, plug the formation, or compromise monitoring wells through extreme carbon loading, as is often the case with pressure-emplaced powdered activated carbon.

More information on low-pressure ease of distribution and dispersive emplacement of PlumeStop can be found in [PlumeStop Technical Bulletin 1.1: Distribution through a Permeable Medium](#).

### Rapid Removal of Contaminants from Groundwater

PlumeStop rapidly sorbs organic contaminants from aqueous solution within the timescale of hours. Pollutants partition directly into the PlumeStop particles that are sorbed to the soil formation, thereby removing the pollutants from groundwater. Contaminant advection in the aqueous phase is therefore eliminated, and partitioning into the vapor phase is also reduced (Henry's Law). Results can be dramatic, with groundwater cleanup objectives often met within days of PlumeStop application.

Sorption of contaminants by PlumeStop is the subject of the present technical bulletin.

## **Acceleration of Contaminant Biodegradation**

Once sorbed to the soil and with contaminants partitioned onto its surface, PlumeStop is colonized by contaminant-degrading bacteria. These bacteria may be naturally present or applied as an inoculum. The concentration of the contaminants and the degradative microflora on the PlumeStop surface reduces mass-transfer kinetic constraints and supports greater speed and efficiency of degradation compared to solution-phase bioremediation.

The net result is a substantial increase in the instantaneous rate and extent of contaminant destruction. Information on post-sorption biodegradation and rate acceleration by PlumeStop can be found in [PlumeStop Technical Bulletin 3.1: Post-Sorption Contaminant Biodegradation](#).

## **PlumeStop Contaminant Sorption**

### ***Activated Carbon***

The sorptive capacity of PlumeStop arises from its activated carbon content. The use of activated carbon for removal of organic contaminants from vapor and water streams is widespread in the environmental industry. Additionally, activated carbons are often the final polishing step in potable water clean up owing to their non-toxic nature and ability to remove very low levels of organic (and some inorganic) contaminants.

Activated carbon materials can be formed from a range of organic and mineral carbonaceous feedstocks through heat and/or chemical treatment to provide a high-purity material with a microporous structure that yields a very high adsorptive surface area of 500 – 1,500 m<sup>2</sup>/g (1). As a result of this high surface area, the sorptive capacity of the carbon is increased significantly over that of the natural carbon. In the case of PlumeStop, this increase is 50 – 100 x greater than an equivalent mass of natural soil organic carbon (foc) (dry mass basis).

### ***Forms of Activated Carbon***

Traditionally, activated carbon has been available in two principle forms – Powdered Activated Carbon (PAC) and Granular Activated Carbon (GAC), both finding use

primarily in *ex situ* applications. The development of PlumeStop introduces a third class of composition – that of a *Liquid Activated Carbon* (LAC).

This new carbon composition extends the range of possible uses to include *in situ* applications, most notably subsurface applications, owing to the ability of the material to disperse freely through and coat permeable granular media (PlumeStop Technical Bulletin 1.1: Distribution through a Permeable Medium).

### **Contaminant Removal by Activated Carbon**

Contaminant removal by activated carbon occurs principally through adsorption. This is driven by the hydrophobic / lipophilic character of the sorbing species but also by electrostatic Van der Waals interactions between the sorbent and sorbate (1).

By nature, there is no fixed ‘capacity’ of sorption by activated carbon in the sense of filling a container, but rather an equilibrium between sorbed-phase and desorbed-phase concentrations that is itself dependent on:

- The nature of the activated carbon (sorbent);
- The mass of the activated carbon;
- The concentration and hydrophobic / lipophilic nature of the contaminant (sorbate)
- The concentration of the contaminant (sorbate);
- The presence of, and interactions with, other contaminants and naturally occurring species.

### **Isotherms**

The influence of the above factors on the sorption equilibrium of contaminants on PlumeStop may be conveniently described using sorption isotherms—plots of sorbate mass adsorbed per mass of sorbent as a function of equilibrium concentration of sorbate in solution. These are commonly summarized from empirical data using the Freundlich equation<sup>1</sup> (2). Example sorption isotherms for benzene and TCE are presented in Figures 1 and 2. Freundlich parameters of common groundwater contaminants on PlumeStop are presented in Table 1.

<sup>1</sup>Freundlich Equation is  $q_e = K_f C_e^{1/n}$

and can be linearized as:  $\log q_e = \log K_f + 1/n * \log C_e$

$q_e$  = equilibrium loading on the sorbent (mg chemical/g sorbent)

$C_e$  = equilibrium concentration in the water (mg chemical/L)

$K_f$  = adsorption capacity at unit concentration (mg/g)/(mg/L)<sup>1/n</sup>

1/n = strength of adsorption (dimensionless)

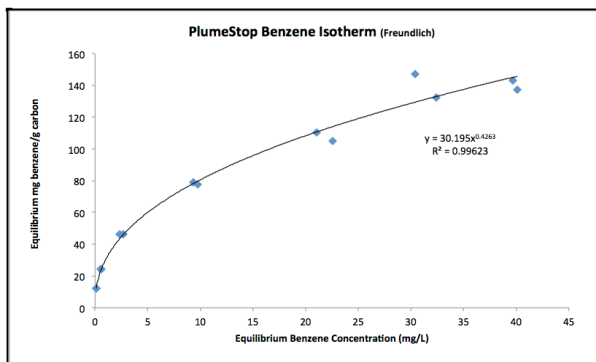


Figure 1. Sorption isotherm of benzene on PlumeStop

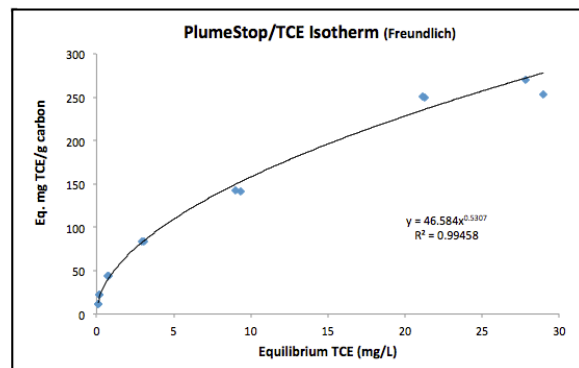


Figure 2. Sorption isotherm of TCE on PlumeStop

Note that while each contaminant will have a slightly different sorption isotherm with PlumeStop, the Freundlich nature of these isotherms means that sorption efficiency always increases as the solution concentration drops – the sorbed: solution ratio increases as the curve steepens at the lower end. In practical engineering terms, this translates as greater capture efficiency at lower concentrations, and as such may present a welcome contrast to the majority of remediation technologies that typically exhibit decreasing performance at lower contaminant concentrations.

Table 1. Selected PlumeStop® Freundlich Adsorption Isotherm Constants

Non-chlorinated Species			Chlorinated Species		
Compound	K <sub>f</sub>	1/n	Compound	K <sub>f</sub>	1/n
Benzene	30.2	0.427	PCE	105	0.422
Toluene*	97.0	0.429	TCE	46.6	0.531
Ethylbenzene*	163	0.415	cis-1,2-DCE	11.7	0.548
o-xylene	217	0.428	VC*	4.16	0.339
p-xylene*	226	0.418	1,1,1-TCA	19.2	0.634
MtBE	6.54	0.397	1,2-DCA	11.3	0.454
Naphthalene*	132	0.420	Chlorobenzene	135	0.315
Phenanthrene*	215	0.440	1,2-Dichlorobenzene	326	0.209
Benzo(a)pyrene*	34.0	0.440	2-Chlorotoluene	173	0.202
Styrene*	327	0.480	Pentachlorophenol*	443	0.340

K<sub>f</sub>=(mg/g)/(mg/L)<sup>1/n</sup>; n = dimensionless. Data derived empirically, unless \* Data estimated from literature.

### ***Sorption and Bioavailability***

Importantly, the capture of organic species by the activated carbon results from a partitioning equilibrium between sorbed-phase and aqueous phase concentrations rather than a 'fixed binding' as is the case in immobilization technologies. As a result, the binding remains dynamic, with contaminants continually sorbing and desorbing on the PlumeStop surface. However, the sorbed-phase concentration always dominates the equilibrium when sufficient activated carbon is present.

On the macro scale, the partitioning equilibrium of organic species on the carbon surface resembles 'fixed binding' as the contaminants are removed from the aqueous phase by the sorbent. However, on the micro scale, the repeated local desorption and re-sorption allows the contaminants to move about the sorbent surface. This process is strongly beneficial to post-sorption contaminant biodegradation because it overcomes local depletion of substrate around the immobile contaminant-degrading microorganism and thus ensures continued contaminant bioavailability.

Contaminant degradation is further enhanced through the concentration of the contaminants and degrading microflora together on the carbon surface, increasing the instantaneous rate of reaction through first-order kinetic principles (3) and overcoming limitations of degradation threshold ( $S_{min}$ ) concentrations (4, 5).

### **Significance as a Remediation Tool**

#### ***PlumeStop is not a Binding / Immobilization Technology***

Although a key property for the success of PlumeStop in groundwater remediation is the ability to rapidly remove contaminants from the aqueous phase, sorption of contaminants by PlumeStop is secondary to the reagent's primary function. The ultimate purpose of PlumeStop is to expedite contaminant degradation at low concentrations for the management of back-diffusion, diffuse plume elimination, and reduction of flux across property boundaries. Contaminant sorption supports this degradative process and in so doing conveniently provides a rapid reduction in risk rather than long-term immobilization and storage.

#### ***PlumeStop as a Means of Engineering Plume Dynamics***

Within the context of Contaminant Fate & Transport, the sorptive capacity of PlumeStop provides a means of controlling contaminant migration rate and/or residence time within a treatment zone. This control can be used to reduce attenuation

distance and therefore restrict plume expansion on monitored natural attenuation (MNA) projects, as well as for risk-based corrective action strategies. It can similarly provide a means of increasing contaminant residence time within a focused treatment zone to increase efficiency and reduce the spatial footprint of compatible reagent injections.

### ***PlumeStop as a Means of Reducing Risk***

Rapid removal of contaminants from the aqueous phase provides a correspondingly fast reduction in risk within the timescale of days. Contaminants are rapidly removed from the aqueous phase, thereby reducing migration and exposure via groundwater pathways. Partitioning from groundwater to the vapor-phase is also reduced as a consequence (Henry's Law).

### ***PlumeStop as a Means of Enhancing Contaminant Biodegradation***

Contaminant biodegradation is accelerated on PlumeStop (Technical Bulletin 3.1: Post Sorption Contaminant Biodegradation). This is attributed to the reduction of mass-transfer kinetic constraints on contaminant bioavailability as a result of bringing the contaminants and the degrading microflora together on the PlumeStop surface (3). Additionally, PlumeStop can accumulate very low-level contaminants on its surface until threshold concentrations for microbial activity ( $S_{min}$ ) are secured. As a result, bioremediation can be made effective for clean-up of trace plumes and back-diffusion management that otherwise respond poorly to biostimulation or augmentation.

### ***PlumeStop as a Means of Back-Diffusion Management***

The combined features of PlumeStop – wide-area dispersion, contaminant capture, contaminant biodegradation enhancement, and bio-regeneration of sorptive capacity – create a novel tool for back-diffusion management (Technical Bulletins 1.1: Distribution through a Permeable Medium; 3.1: Post Sorption Contaminant Biodegradation; and 4.1: Regeneration of Sorptive Capacity). The material may be dispersed freely through the primary porosity, where it will sorb to the soil, capture and degrade contaminants, and maintain a diffusion gradient out of the secondary porosity, thereby providing sustained capture and destruction of back-diffusing mass.

### **Literature Cited**

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