

## PlumeStop® Technical Bulletin 2.1

# Sorption of Contaminants from Solution: Terms & Principles

### Quick Reference:

- Basis 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 emplaced 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 through which it passes. It does not create preferential flow pathways, plug the formation, or compromise monitoring-wells through extreme carbon loading in contrasting respect to the majority of the surrounding porosity (i.e. the porosity external to the fractures or 'soil partings' themselves) as may be the case with pressure-emplaced powdered activated carbon products.

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](#) and [PlumeStop Technical Bulletin 1.2: PlumeStop Distribution in the Field](#).

### Rapid Removal of Contaminants from Groundwater

PlumeStop rapidly sorbs organic contaminants from aqueous solution (hours). Pollutants partition directly into the PlumeStop particles sorbed to the soil formation, removing the pollutants from groundwater. Contaminant advection in the aqueous

phase is therefore eliminated ('the plume is stopped') and partitioning into the vapor-phase is reduced also (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 in place and with contaminants partitioned onto its surface, PlumeStop is colonized by contaminant-degrading bacteria. These may be naturally present or applied as an inoculum. The bringing together of a degradative microflora and the target contaminant in local abundance (i.e. concentrated on the PlumeStop rather than dispersed in the groundwater and formation) reduces mass-transfer kinetic constraints and supports greater speed and efficiency of degradation.

The net result is a substantial increase in the instantaneous rate and extent of contaminant destruction. Information on post-sorption biodegradation and acceleration of biodegradation rate 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 lack of toxicity 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). In this manner, the sorptive capacity of the carbon is increased significantly over that of the natural carbon. In the case of PlumeStop, this increase is in the approximate range of 50 – 100 x that of 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 providing usage convenience in a range of (principally *ex situ*) applications.

The development of PlumeStop introduces a third class of composition – that of a *Liquid Activated Carbon* (LAC).

This in turn opens up usage convenience in further domains, most notably *in situ* subsurface applications owing to the ability of the material to be dispersed freely through and to coat permeable granular media (PlumeStop Technical Bulletin 1.1: Distribution through a Permeable Medium and PlumeStop Technical Bulletin 1.2: PlumeStop Distribution in the Field.)

### **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).

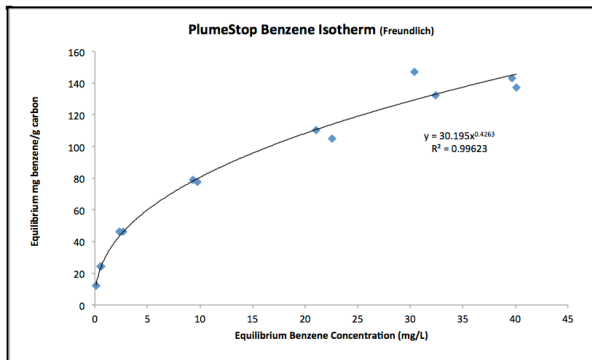
By nature, there is no fixed ‘capacity’ of sorption by activated carbon in the sense of filling a container, but rather an equilibrium of sorbed vs. desorbed-phase concentrations that is itself dependent on:

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

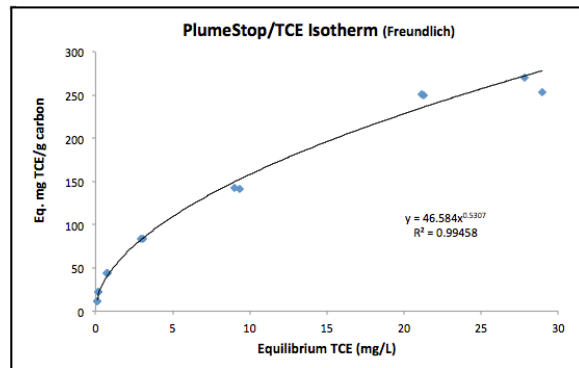
### **Isotherms**

The interaction of the above factors may be conveniently described using isotherms – plots of amount adsorbed (sorbate mass 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 equilibrium sorption isotherms for benzene and TCE are presented in Figure 1 and Figure 2. Freundlich parameters of common groundwater contaminants on PlumeStop are presented in Table 1.



**Figure 1. Sorption isotherm of benzene on PlumeStop**



**Figure 2. Sorption isotherm of TCE on PlumeStop**

It can be helpful to note that while the actual equation of each curve will vary, each share the consistent principle of sorption efficiency increasing as 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, which typically exhibit the contrary.

<sup>1</sup> Freundlich Equation is  $q_e = KC_e^{1/n}$  and can be linearized as:  $\log q_e = \log K + 1/n * \log C_e$

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

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

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

1/n = strength of adsorption (dimensionless)

**Table 1. Selected PlumeStop® Freundlich Adsorption Isotherm Constants**

Non-chlorinated Species			Chlorinated Species		
Compound	Kf	1/n	Compound	Kf	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

Kf = (mg/g).(L/mg); n = dimensionless. Data derived empirically, unless \* Data estimated from literature.

### **Sorption and Bioavailability**

Importantly, the capture of organic species by the activated carbon is achieved through a shift in partitioning equilibrium rather than a ‘fixed binding’ such as in immobilization technologies, and as such remains dynamic – contaminants sorb and desorb continually albeit with the sorbed-phase dominating at any given moment where sufficient activated carbon is present. On the macro scale, this resembles a binding phenomenon as the contaminants are ‘removed’ from the aqueous-phase by the sorbent; however on the micro scale, contaminants 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; it overcomes local depletion of substrate around the (sessile) contaminant-degrading microorganism and thus ensures continued contaminant bioavailability despite the removal of contaminants from the dissolved-phase on the macro scale.

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***

It is important to keep in mind that sorption of contaminants by PlumeStop is secondary to the reagent's primary function as a means of expediting 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 process and in so doing conveniently provides a rapid reduction in risk, but PlumeStop is not a binding / immobilization technology – its use is to promote contaminant capture from the aqueous-phase and *destruction* rather than immobilization and 'storage'.

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

Within a Contaminant Fate & Transport framework, the sorptive capacity of PlumeStop provides a means of engineering contaminant migration rate, and/or residence time within a treatment zone ("Plume" and "Stop").

This can be used in itself to reduce attenuation distance and therefore restrict plume expansion on monitored natural attenuation (MNA) projects, or to balance with risk modeling in the establishment of source-reduction targets. 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 (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 reduction in mass-transfer kinetic constraints to contaminant bio-availability through bringing together the contaminants and the degrading microflora in local abundance 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 (ibid.).

In this manner, 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 Bulletin 1.1: Distribution through a Permeable Medium; Technical Bulletin 3.1: Post Sorption Contaminant Biodegradation; and, Technical Bulletin 4.1: Regeneration of Sorptive Capacity). The material may be dispersed freely through the primary porosity, where it will lock in place, capture and degrade contaminants, and maintain a diffusion gradient out of the secondary porosity providing sustained capture and destruction of back-diffusing mass.

#### **Literature Cited**

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