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Sorption of Contaminants from Solution: Terms and Principles

PlumeStop® Technical Bulletin 2.1

Quick Reference:

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

1. Background

PlumeStop Liquid Activated Carbon™ is composed of very fine particles of activated carbon (1-2μm) suspended in water through the use of a 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, while still permitting their biodegradation.

2. Wide-Area Dispersive Distribution

Unlike any other sorbent technology, PlumeStop can be installed in the subsurface through dispersive flow via low-pressure injection (without fracturing the formation), providing a thin-film coating over a wide area 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.

3. Rapid Removal of Contaminants from Groundwater

PlumeStop rapidly sorbs organic contaminants from aqueous solution within hours of application. Pollutants partition directly into the PlumeStop particles that are

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sorbed to the soil formation, thereby removing the pollutants from groundwater. Pollutants are removed from groundwater through sorption to PlumeStop particles which have partitioned to the soil formation. Contaminant advection in the aqueous phase is thereby eliminated and contaminant 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. This technical bulletin delves more thoroughly into sorption of contaminants by PlumeStop.

4. Contaminant Biodegradation

In the soil matrix with contaminant partitioned onto its surface, PlumeStop is colonized by contaminant-degrading bacteria which may be naturally present or applied as an inoculum. PlumeStop essentially halts the flow of contaminants while still allowing them to be degraded by bacteria, preventing further movement of contaminants in the subsurface.

Information on post-sorption biodegradation of contaminants can be found in PlumeStop Technical Bulletin 3.1: Post-Sorption Contaminant Biodegradation.

5. PlumeStop Contaminant Sorption

Activated Carbon

The sorptive capacity of PlumeStop is due to 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 since they are non toxic and are able to remove even 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 m² /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 used primarily in *ex situ* applications. The development of PlumeStop introduces a third class of composition – *Liquid Activated Carbon* (LAC).

This new carbon composition extends the range of possible uses to include *in situ* applications, most notably subsurface applications, due to its ability 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 characteristics of the sorbing species and by electrostatic Van der Waals interactions between the sorbent and sorbate (1).

By nature, there is no fixed 'capacity' of sorption by activated carbon (i.e. filling a container), rather an equilibrium between sorbed-phase and desorbedphase concentrations which is dependent on:

- The nature of the activated carbon (sorbent);
- The mass of the activated carbon;
- The 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[1] (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.

[1] 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 $(mg/g)/(mg/L)^{1/n}$
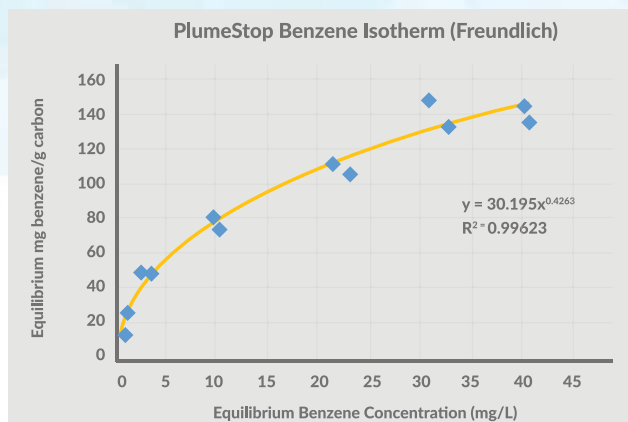**1/n** = strength of adsorption (dimensionless)

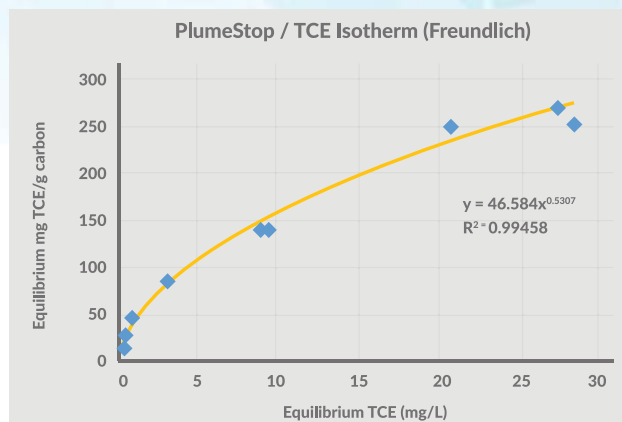**Figure 1.** *Sorption isotherm of Benzene on PlumeStop*

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_f**	**1/n**	**Compound**	**K_f**	**1/n**
Benzene	30.2	0.427	PCE	105	0.422
o-xylene	217	0.428	TCE	46.6	0.531
MtBE	6.54	0.397	cis-1,2-DCE	11.7	0.548
			1,1,1-TCA	19.2	0.634
			1,2-DCA	11.3	0.454
			Chlorobenzene	135	0.315
			1,2-Dichlorobenzene	326	0.209
			2-Chlorotoluene	173	0.202

$K_f = (mg/g)/(mg/L)^{1/n}$; n = dimensionless. Data derived empirically.

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.

6. Significance as a Remediation Tool

PlumeStop is not a Binding / Immobilization Technology

A key property of the success of PlumeStop in groundwater remediation is its ability to rapidly remove contaminants from the aqueous phase; in doing so, PlumeStop immediately decreases contaminant concentration and halts the progress of contaminant plumes thereby reducing flux across property boundaries. Ultimately, contaminant sorption allows contaminant-degrading bacteria more time to interact with and degrade, rather than simply immobilizing and storing long-term, the contaminants of concern.

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.

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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 Back-Diffusion Management

The combined features of PlumeStop – wide-area dispersion, contaminant capture, contaminant biodegradation, 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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