Research article

# Removal of dissolved organic carbon by aquifer material: Correlations between column parameters, sorption isotherms and octanol-water partition coefficient

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## ARTICLE INFO

## ABSTRACT

The correlation between octanol-water partition coefficient ($K_{OW}$) and the transport of aqueous samples containing single organic compound is well documented. The concept of the $K_{OW}$ of river water containing the mixture of organics was evolved by Pradhan et al. (2015). The present study aims at determining the $K_{OW}$ and sorption parameters of synthetic aqueous samples and river water to finding out the correlation, if any. The laboratory scale columns packed with aquifer materials were fed with synthetic and river water samples. Under the operating conditions, the compounds in the samples did not separate, and all the samples that contain more than one organic compound yielded a single breakthrough curve. Breakthrough curves simulated from sorption isotherms were compared with those from the column runs. The sorption parameters such as retardation factor ($R_f$), height of mass transfer zone ($H_{MTZ}$), rate of mass transfer zone ($R_{MTZ}$), breakpoint column capacity ($q_b$) and maximum column capacity ($q_x$) estimated from column runs, sorption isotherms and models developed by Yoon-Nelson, Bohart-Adam and Thomas were in agreement. The empirical correlations were found between the $K_{OW}$ and sorption parameters. The transport of the organics measured as dissolved organic carbon (DOC) through the aquifer can be predicted from the $K_{OW}$ of the river water and other water samples. The novelty of the study is to measure $K_{OW}$ and to envisage the fate of the DOC of the river water, particularly during riverbank filtration. Statistical analysis of the results revealed a fair agreement between the observed and computed values.

## 1. Introduction

The concentration of organic compounds, measured as dissolved organic carbon (DOC), in water sources, is rising due to the ever-increasing discharges from cities and industrial units (Luo et al., 2014; Cheng et al., 2005; Dave and Dikshit, 2011). The attenuation of these organics by riverbank filtration (RBF), a natural purification process, is precedent in the literature (Kuhn and Muller, 2000). Mark et al. (2012) studied RBF system in Ohio, USA and observed around 90% removal of a large group of pharmaceuticals, endocrine disruptors (EDs) and pesticides by sorption. To further understand the removal, columns packed with the aquifer material were operated. Results from this indicated 20—80%

removal of diazepam, meprobamate, phenytoin and tris (2-chloroethyl) phosphate (TCEP) and less than 20% removal of atrazine, carbamazepine, and sulfamethoxazole. Weiss et al. (2003) investigated three RBF sites along the Ohio, Wabash, and Missouri Rivers in the Midwestern United States and reported the reduction of 30—70% DOC. The removal of disinfection by-products (DBPs) at RBF sites was 50—100% whereas in column runs removal was 40%—80%. The higher reduction of DOC in RBF systems has been attributed to the mixing of ground water.

A comparison between sorption and biodegradation of 14 organic micro-pollutants was made by Bertelkamp et al. (2014) in soil columns. The retardation factor ($R_f$) for most compounds was estimated to be close to 1. Scheytt et al. (2004) and Burke et al. (2013) detected several pharmaceuticals, psychoactive drugs, β-blockers, plasticizers, etc. in 20 wastewaters and found their $R_f$ in column runs to vary between 1.0 and 5.0. Lorphensri et al. (2007) found the sorption of the pharmaceuticals from the synthetic

solutions to be correlated well with the $K_{OW}$ and suggested hydrophobically motivated sorption as the dominant mechanism. However, it is cumbersome to carry out sorption experiments to study the fate and transport of aqueous organics. The solution to such a problem can be arrived through models or devise a water quality parameter that can be correlated to retardation factor ($R_f$) and other sorption parameters. With this in view, octanol-water partition coefficient ($K_{OW}$) has been chosen as one of the water quality parameters to correlate it with sorption parameters. Pradhan et al. (2016) exhibited the relationship between $K_{OW}$ of the samples having more than one organic compound and sorption capacity of the aquifer material. Also, Weber (1972) developed a mass transfer model to simulate breakthrough curves using the experimental data from batch studies. The height of mass transfer zone ($H_{MTZ}$) of a few single organic and inorganic compounds has been measured from the batch test data by Geankoplis (1993), Medvidoviæ et al. (2013), Gupta et al. (2004), and Al-Degs et al. (2009). Considering the work of Pradhan et al. (2016) along with the simulation of column sorption parameters from the batch sorption data, it was logical to find answers to the following:

- Can the breakthrough curves for the samples containing more than one organic compound be simulated from the batch sorption data?
- Can $K_{OW}$ be used to predict the sorption parameters or breakthrough curves of the natural water samples or the aqueous samples that have several organic compounds?

Considering RBF, column and batch sorption experiments with the aquifer material were planned and executed. This work presents the (i) measurement of $K_{OW}$ of the eight synthetic aqueous samples and two river water samples (ii) generation of the breakthrough curves and sorption isotherms from the samples (iii) subsequent analysis of the data to obtain sorption parameters (iii) and the correlation between $K_{OW}$ and sorption parameters.

Sorption parameters include sorption capacity, breakthrough capacity ($q_b$), the exhaustion capacity ($q_x$), retardation factor ($R_f$), saturation concentration ($C_x$), time required for saturation uptake ($t_x$), breakthrough time ($t_b$), height of the mass transfer zone ($H_{MTZ}$) and, the rate of the mass transfer zone ($R_{MTZ}$). Breakthrough capacity ($q_b$) is the mass of adsorbate removed by the adsorbent at breakpoint concentration or the maximum acceptable concentration of the adsorbate. The exhaustion capacity ($q_x$) is the mass of the adsorbate removed by unit weight of the adsorbent at saturation concentration ($C_x$). $R_f$ is the ratio of the velocity of water to that of the contaminant through the sorbent. Yahaya et al. (2011) and Sekhula et al. (2012) computed time required for 50% breakthrough for computing $R_f$, $C_x$ and $q_x$ using Yoon-Nelson, Bohart-Adam, and Thomas models respectively. The value of $C_x$, $R_f$, $q_x$, $t_b$, $t_x$, $H_{MTZ}$, and $R_{MTZ}$, depends upon hydrophobic and hydrophilic nature of the samples, diffusion, dispersion, the height of the column, the characteristics of the sorbent, and operational condition (Medvidoviæ et al., 2013).

## 2. Materials and methods

### 2.1. Sorbent

Aquifer materials used as sorbents were collected from two RBF sites. The first sample was collected at a depth of 30 cm near the Srinagar RBF site (30°13′12.29″N and 78°46′47.02″E) on the bank of the river Alaknanda in Uttarakhand, India. The second sample was collected at a depth of 3 m from the Torgau RBF site (51°52′08.32″ N and 13°09′43.41″E) on the bank of the river Elbe in Saxony, Germany. Aquifer materials were characterized for (i)

grain size distribution (BIS:1970) (ii) BET surface area and (iii) fraction of organic carbon content ($f_{oc}$). BET surface area was determined by the Micrometrics ASAP 2010 BET Surface Area Analyzer and $f_{oc}$ was measured by the Shimadzu-SSM-5000A-TOC-V$_{CSN}$ analyzer.

### 2.2. Aqueous samples

Eight synthetic aqueous samples containing organic compounds and two river water samples were fed to the columns packed with aquifer materials. Organic compounds were dissolved in the water collected from the Upper Ganga Canal (UGC), at Roorkee (Uttarakhand, India) to simulate natural matrix of the synthetic samples. Six synthetic samples that had single organic compound were prepared by dissolving toluene, nitrobenzene, phenol, propanoic acid, 2-propanol or glucose. The other two samples were the mixture of (i) toluene and 2-propanol and (ii) toluene and phenol. Natural samples used for the column runs were taken from the Hindon River at Barnawa (29°06′49.72″N and 77°26′28.20″E), India and Elbe River, Terassenufer (51°3′13.91″N and 13°44′44.03″E), Germany. The organic compounds in the river water samples analysed by Gas Chromatography-Mass Spectroscopy (GC-MS) and their range of log $K_{OW}$ have been reported by Pradhan et al. (2016).

Aqueous samples were characterized for DOC and ultraviolet absorbance (UVA) (APHA, 2005). Pradhan et al. (2013) have mentioned procedural details for measuring $K_{OW}$ and specific UV absorbance (SUVA). DOC was measured by Shimadzu-TOC-V$_{CSN}$ analyzer. For each sample, UV absorbance (UVA) was measured at maximum wave length ($\lambda_{max}$) by the Hach-DR-5000-UV-VIS Spectrophotometer. All the chemicals were procured from SD Fine Chemicals Limited, India.

### 2.3. Sorption isotherms

The OECD-106 (1997) guidelines used by Tancredi et al. (2004), Hameed et al. (2008) and Nguyen and Ball (2006) were followed to obtain sorption isotherms. Batch reactors charged with the samples and the aquifer materials in varying amount were stirred until DOC was stabilized. Solid phase DOC that adsorbed onto aquifer material was plotted against equilibrium solution phase DOC to get sorption isotherms. The slope of the isotherms represents soil-water partition coefficient ($K_d$) in L/kg.

### 2.4. Breakthrough curves

Two stainless steel columns of 100 cm length and 11 cm diameter were operated in the Environmental Engineering Laboratory, Indian Institute of Technology Roorkee, India to generate breakthrough curves. Another column of 25 cm length and 3.5 cm diameter was run at the Institute of Water Chemistry, Dresden University of Technology, Dresden, Germany. Columns were packed with the slurry of the aquifer material in water. Peristaltic pumps were used to maintain the flow rate. The bulk density of the aquifer material was measured in two steps; (i) the material was taken out from the packed columns (ii) it was dried and weighed. Non-reactive NaCl tracer test was carried out to determine the effective porosity ($\eta_e$) of the aquifer material in the columns. The details about columns and their operation are given in Table 1.

## 3. Results and discussion

### 3.1. Characteristics of aquifer material

Results from the sieve analysis of the aquifer material are