Sorption of cationic organic substances onto synthetic oxides: Evaluation of sorbent parameters as possible predictors

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HIGHLIGHTS

- Principal research on sorption behavior of organic cations in aquatic systems.
- Column tests with 3 probe molecules on 5 sorbents at 4 electrolyte concentrations.
- Study on the relation between sorption strength and sorbent characteristics.
- Sorption coefficients predictable by concentration of OH groups on sorbent surface.

GRAPHICAL ABSTRACT
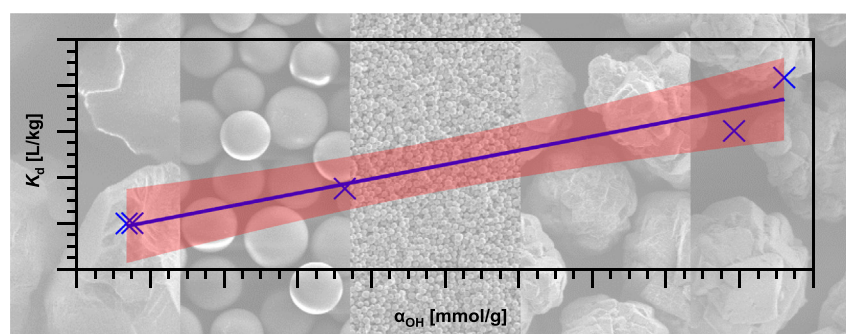
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ABSTRACT

Knowledge on the sorption behavior of cationic organic substances in aquatic systems is vital for their risk assessment due to the increasing detection of such chemicals in the hydrosphere. Their sorption behavior is strongly influenced by sorption processes onto mineral surfaces (e.g., oxides, clays). To contribute to the development of prediction tools, the impact of sorbent characteristics on the sorption strength was studied in a highly-idealized model system. In addition to the properties of the solid phase, the concentration of other ions in direct competition for sorption sites and the molecular structure of the sorbate were changed to separate ion exchange and non-ion exchange processes. The study includes in total 120 systematic column experiments using five extensively characterized synthetic oxides (three silica gels, two aluminum oxides), three probe molecules (two structurally related cationic substances, one neutral compound), and four distinctively different NaCl concentrations. The results show that the concentration of OH groups on the sorbent surface is a meaningful descriptor for the observed variations in sorption capacity onto different oxides. Compound-specific linear correlations were obtained, enabling the prediction of sorption coefficients. In addition, a more complex sorption behavior of organic cations compared to uncharged molecules were observed as demonstrated by the sorption results at different electrolyte concentrations. Thus, the study provides an important step towards a better principal mechanistic understanding of organic cation sorption. However, further work using other sorbents including natural ones and other probe molecules is needed to verify the identified relationships within the scope of developing reliable prediction models for cation sorption.

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1. Introduction

In the last years, numerous studies on the prediction of (linear) sorption coefficients (K_d values) for organic cations on geosorbents have

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been published (e.g., Kah and Brown, 2007; Bronner and Goss, 2011; MacKay and Vasudevan, 2012; Droge and Goss, 2013a, 2013b; Sathyamoorthy and Ramsburg, 2013; Samaraweera et al., 2014). However, no generally accepted and universally applicable model is available until now. Recent comprehensive reviews (Endo and Goss, 2014; Webster, 2014; Schaffer and Licha, 2015) give an overview on proposed models and their limitations. The demand for developing improved sorption models for ionizable organic compounds was enforced in various studies that documented a significant number of chemicals being present in the aquatic environment (e.g., pharmaceuticals, personal care products, pesticides) which are either partially or completely ionized (Manallack, 2009; Franco et al., 2010).

The commonly applied standard method for predicting sorption coefficients of organic chemicals (e.g., log K_{OC} – log K_{OW} correlations) (e.g., Chiou et al., 1979; Karickhoff, 1981; Sabljic et al., 1995) is generally based on the assumption of interactions between neutral organic compounds and solid organic carbon, but does not consider the electrostatic interactions of a charged molecule with the charged solid surface nor any relationships between polar compounds and polar surfaces (Tolls, 2001; Cunningham et al., 2004; Kah and Brown, 2007; Schaffer et al., 2012a; ECETOC, 2013). Since a large proportion of soils and sediments have a negative net surface charge, these model concepts fail for organic cations (Tolls, 2001; Kah and Brown, 2007). Here, the sorption is dominated by cation exchange processes and is, thus, clearly underestimated (Brownawell et al., 1990; Bi et al., 2006; Bäuerlein et al., 2012; Droge and Goss, 2012, 2013a, 2013b; Schaffer et al., 2012b; Niedbala et al., 2013; Kutzner et al., 2014, 2016).

In recent years, it became apparent that sorption processes of organic cations onto environmental surfaces are more complex than a simple partitioning between the aqueous phase and the organic matter of a solid. Depending on the sorbate properties and the boundary conditions of the aqueous solution, other sorbent constituents such as oxides or clay minerals are of increasing relevance (Brownawell et al., 1990; Tolls, 2001; Figueroa et al., 2004; Gao and Pedersen, 2005; Martínez-Hernández et al., 2014). Consequently, knowledge of the relationships between sorption strength and characteristic properties of inorganic sorbents (e.g., oxides) is vital to generate improved predictions.

Currently, the most robust and accurate method for predicting sorption coefficients is the concept of poly-parameter linear free energy relationships (pp-LFERs) (Endo and Goss, 2014). The sorption coefficients are determined herein by multiple linear regression of selected sorbate parameters, which are representative of different interaction types. All remaining influencing factors (properties of sorbent and water phase) are described by the regression parameters adapted to experimental data. Consequently, the obtained predictors are valid only for the considered system (similar sorbents and solution conditions) and the transfer to other (heterogeneous) systems and conditions is limited (Schaffer and Licha, 2015). However, the additional consideration of sorbent-related key parameters is of importance in particular to predict cation exchange processes. Therefore, this study focuses on the possibility to relate evaluated sorption coefficients to sorbent properties for identifying system parameters that are meaningful for predictions. For this purpose, a highly-idealized model system was used to evaluate the parameters of the solid that correlate with experimentally determined K_d. Accordingly, largely monophasic synthetic solids of high purity were used in the sorption studies. In contrast to natural surfaces (e.g., soils, sediments, organic matter) these do not contain a complex mixture of heterogeneous phases with a number of overlapping interactions and thus allow a more simplified inspection of the individual processes. The sorption of three probe compounds (two structurally related cationic substances with and without oxygen containing moieties, one neutral compound) on five synthetic oxides (3 silica gels, 2 aluminum oxides) were evaluated under comparable experimental conditions. As reported in earlier studies of the authors (Kutzner et al., 2014, 2016; Schaffer et al., 2017), cation exchange is the most relevant but not the sole mechanism for the sorption of organic cations in aquatic systems.

To separate ion exchange from the remaining other processes, the sorption of probe molecules was investigated over a wide concentration range of a background electrolyte (NaCl) and onto sorbents with different properties. The selected oxides have either a predominately negatively (silica) or positively charged (alumina) surface at the selected pH and thus cation exchange should play either a significant or minor role. Silica and alumina were selected as sorbents as they represent best natural mineral surfaces and belong to the most abundant minerals in the earth's crust. Furthermore, they can be purchased with high purity from chromatography material suppliers. However, the initially aim of this study was not to directly transfer the results to real field scenarios, but rather focuses on principal research as a contribution to a better understanding of the mechanisms and being an element for the development of more sophisticated models for complex systems.

2. Material and methods

2.1. Chemicals

Two cationic and one neutral compound were selected as model sorbates in the presented study. The experiments were carried out at a constant pH of 5.6. This pH is the pH of pure water in equilibrium with the atmospheric CO_2. It was selected because it lies between the pH_{PZC} values of the different sorbent types and no additional buffer is required in the experiments (a buffer would add undesired competing cations). At this pH, the silica gels are negatively charged whereas the aluminum oxides are positively charged. Comparing the results for both sorbents allows to differentiate between the different types of interaction. All probe molecules along with their physico-chemical properties are given in Table 1. Metoprolol (MET) and isopropyl (4 methylbenzyl) amine (iP4MBA) have already been used in own previous research (Schaffer et al., 2012b; Niedbala et al., 2013; Kutzner et al., 2014, 2016). MET as tartrate salt with a minimum content of 98% was purchased from Sigma-Aldrich (Steinheim, Germany) and iP4MBA with a minimum content of 95% was obtained from Evo Blocks (Budapest, Hungary). Benzyl alcohol (BA) with a minimum content of 99% was purchased by Alfa Aesar (Karlsruhe, Germany). MET is a typical example for organic cationic pollutants occurring in surface and waste waters (e.g., Ternes, 1998; Heberer, 2002; Huggett et al., 2003; Vieno et al., 2006). MET and iP4MBA are structurally related (secondary amine, para-substituted benzene ring) and due to their high pK_a values positively charged in all experiments. However, in comparison to iP4MBA, the molecular structure of MET is larger and more complex due to the additional oxygen-containing ether and hydroxyl group. Consequently, these substructures provide considerably more H-acceptor/donor functionalities for MET (4/2) than for iP4MBA (1/1) and thus enable further interactions additional to cation exchange. In contrast, BA is uncharged at pH = 5.6 but hydrophilic due to the hydroxyl group contained in the molecule, so that the contribution of non-ionic interactions to the total sorption (e.g., hydrogen bonds, hydrophobic sorption) can be examined. All other used inorganic chemicals were of high purity (>99%, analytical grade). Ultrapure water for the preparation of all solutions was obtained from the water purification system GenPure from TKA (Niederelbert, Germany).

2.2. Sorbents and sorbent characterization

Silica gel-1 (Silica gel 60, 200–500 μm, amorphous) was purchased from Merck (Darmstadt, Germany). Silica gel-2 (Nucleodur 100–50, 50 μm, spherical), silica gel-3 (Nucleodur 300–5, 5 μm, spherical) and aluminum oxide-1 (Aluminum oxide 90, neutral, 50–200 μm) were obtained from Macherey-Nagel (Düren, Germany). Aluminum oxide-2 (Aluminum oxide 150, basic, 63–200 μm) was received from Merck (Darmstadt, Germany). Silica gel-1 and silica gel-2 have also already been used in other studies of Kutzner et al. (2014, 2016). The net surface charge of silica gels is negative at a consistent experimental pH of 5.6, based on the literature value of the point of zero charge of the