Revisit sorption mechanisms of organic compounds on cation exchange resins

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INTRODUCTION

Many organic contaminants such as pesticides, dyestuffs, petrochemicals, chemical intermediates, pharmaceuticals, and personal care products are ionizable in water. Existing water and wastewater treatment techniques were not specifically designed to remove ionic organic compounds. Polymeric ion exchange resins can be an effective method in selective removal of ionic organic contaminants.

$$\overline{RSO_3^- H^+} + A^+ \rightleftharpoons \overline{RSO_3^- A^+} + H^+$$
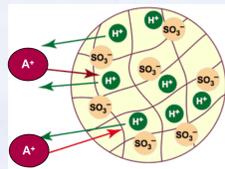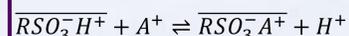
Sorption of ionic organic solutes is a combination of electrostatic interaction and non-electrostatic interactions between the nonpolar moiety of the solutes and the sorbents [1].

Cation Exchanger
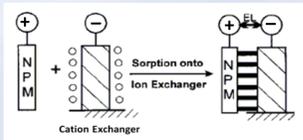
Poly-parameter linear free-energy relationships have been successfully used to predict individual interactions responsible for the transfer of contaminants between two solvents [2].

$$SP = c + eE + sS + aA + bB + vV + j^+J^+$$

E, S, A, B, V, J^+ are compound specific descriptors
e, s, a, b, v, j^+ are fitting parameters determined through multiple linear regressions.

OBJECTIVES

Sorption of organic cations on two strong cation exchange resins, Amberlite 200 (porous, polystyrenic) and MN500 (microporous, polystyrenic), was studied:

➤ To understand sorption behavior of organic compounds on two cation exchange resins in order to provide necessary information for synthesizing appropriate resin for efficient application in the removal of organic contaminants from water and waste water effluents.

➤ To develop quantitative models in order to estimate sorption capacity and the energy contributions of the dominant molecular interactions of a given cation towards an cation exchange resin.

MATERIALS AND METHODS

Resins and Chemicals

▪ Two strong cation exchange resins, Amberlite 200 and MN500

▪ Six aliphatic and three aromatic quaternary ammonia, four substituted phenols, five substituted anilines, nitrobenzene, and imidazol.

Adsorption Experiments

▪ Isotherms were created with 15-20 reactors containing increasing amounts of solute to resin ratio. Reactors were allowed to shake for 48 hours for equilibrium. Samples were collected and analyzed using HPLC, UV/Visible Spectroscopy, or TOC.

Model Development

Gibbs free energy changes for sorption of a training set of compounds on a resin ($\Delta G_{S-W,i}$) and selectivity can be related to the solute descriptors through pp-LFERs [3]:

$$\Delta G_{S-W,i}(\text{or } \alpha_{A/Na}) = eE + sS + aA + bB + vV + c + j^+J^+$$

Where

$$\Delta G_{S-W,i} = -RT \ln K_{S-W,i}$$

$$K_{S-W,i}(\text{or } \alpha_{A/Na}) = \frac{y_i x_{Na}}{y_{Na} x_i} = \frac{q_e}{Q_c - q_e} \cdot \frac{[Na^+]_0 + q_e \frac{m}{V}}{C_e}$$

After performing multiple linear regression

$$c = f_c(q_e), e = f_e(q_e), s = f_s(q_e), a = f_a(q_e)$$

$$b = f_b(q_e), v = f_v(q_e), j^+ = f_{j^+}(q_e)$$

After rearranging to solve for equilibrium sorption concentration (Ce) the model becomes:

$$C_e = \frac{Q_e}{Q_c - Q_e} \cdot ([Na^+]_0 + Q_e \frac{m}{V}) \cdot e^{\frac{f^{TOT}(Q_e)}{RT}}$$

Therefore, for the structurally similar solutes with known pp-LFERs descriptors, the C_e can be estimated at any arbitrary Q_e.
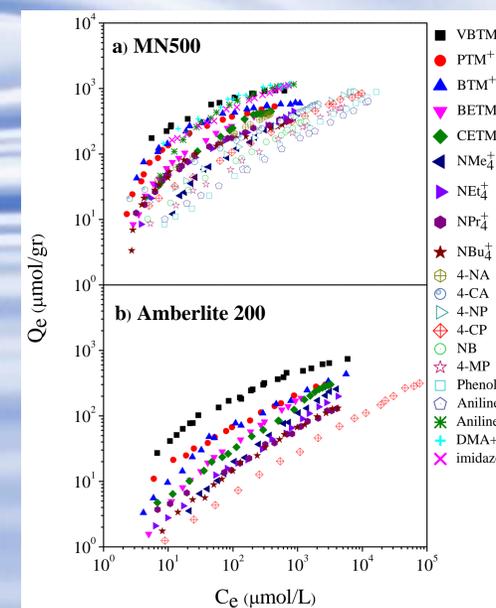
RESULTS AND DISCUSSION

A. pH Effect on Adsorption

To examine the relative contributions of non-electrostatic versus electrostatic interactions
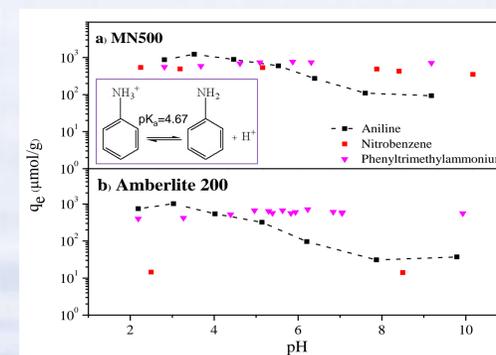
B. Adsorption Isotherms

To understand sorption behavior of various chemicals on the resins

MN500 (microporous) > Amberlite 200 (porous)

aromatic cations > aliphatic cations > neutral aromatic solutes

➤ synergistic combination of electrostatic and non-electrostatic interactions.

➤ Moisture content, hydration energy, aromaticity, Hydrophobicity [4].

C. Predictive Model

To estimate sorption capacity and quantify the relative contributions of various interaction forces to selectivity.

RMSE=0.97
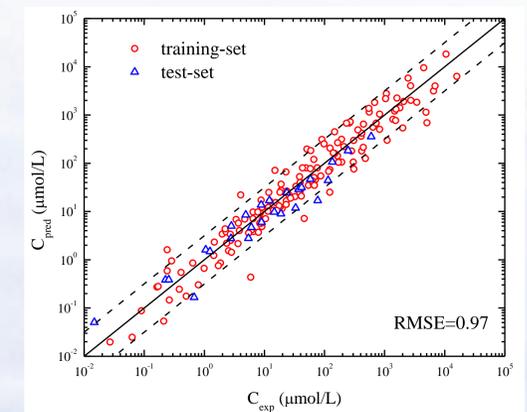
pp-LFERs results indicate:

➤ polarity/dipolarizity (S) effect was significant over entire range of sorbed concentration.

➤ dependency of free energy change on E, A and J+ increased with sorbed concentration.

➤ V and B descriptors had negligibly positive effect on sorption.

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