Supporting Information for

A Modified Polanyi-based Model for Mechanistic Understanding of Adsorption of Phenolic Compounds onto Polymeric Adsorbents

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Text S1.

Adsorbents

The nonionic crosslinked polymeric adsorbents, Amberlite XAD-4 and XAD-7, were provided by Rohm and Haas (USA). To remove possible residue organic impurities before employment, these adsorbents were washed by executing the following procedure: packed in a column (32-mm diameter), rinsed with 0.02 M NaOH, and washed by DI water until neutral pH. The adsorbent-loaded columns were then subjected to acidic flushing by introducing 0.05 M HCl and again DI water flushing to neutral pH. Finally, they were transferred to a Soxlet apparatus to extract with ethanol for 8 h and vacuum desiccated at 325 K for 8 h. These adsorbents were sieved with the sizes from 0.4 to 0.6 mm and stored in a closed container at room temperature.

Adsorbates Phenol (99+%), 4-methylphenol (99+%), 4-chlorophenol (99+%), 3-nitrophenol (+99%), and 4-nitrophenol (+99%) were purchased from Fisher Scientific Co. and prepared in DI water; 2-naphthol (+98%), bisphenol A (+99%) and nitrobenzene (+99%) were also purchased from Fisher Scientific Co. but prepared in methanol (HPLC grade). All these chemicals were used without further purification.

Text S2. Adsorption Experiments

All adsorption isotherms were carried out in amber glass bottles with Teflon-lined screw caps at 23±0.5 °C. Aqueous solute solutions were prepared by diluting stock solutions with deionized distilled water. The volume fraction of methanol in the adsorption solution was kept less than 0.1% to avoid co-solvent effects. Before introduced into the solution, XAD-4 was immersed in methanol to make the hydrophobic adsorbent compatible with water and then washed with DI water. More than 15 experimental data points for each test compound were employed with the equilibrium concentration ranging from 10^{-5}-10^{-3} of its solubility to greater than $10^{-1} \times$ solubility. The ratios of aqueous solution to solids were adjusted to achieve 25-75% adsorption of the target compounds, and an appropriate sized bottle was chosen for each sample to ensure minimal headspace to limit volatilization. 0.01M HCl and 0.1M NaOH solutions were used to adjust the solution pH if necessary. Notably, the final pH of 4-NP (pK_a =7.15) adsorption was kept at 4.0±0.05 to avoid dissociation since it has a lower pK_a (7.15). Then, the bottles containing a mixture of solute and resin were transferred to a shaker with a thermostat under 175 rpm. Preliminary sorption experiments indicated no substantial difference with the equilibrium time from 1 to 8 days (Figure S1). 48-h equilibrium time was thus chosen for single-ring aromatic compounds, while 4 days for multiple or condensed ring compounds (i.e., 2-NAPH, BPA).

After reaching apparent equilibrium, the experimental supernatants were withdrawn for analysis after quiescent settling of the adsorbents. High-performance liquid chromatography (HPLC) was employed to determine solute concentrations for all studied compounds. Less than 2% loss of the dissolved organic compounds in control bottles was

observed over the duration of the experiments. Thus, adsorption isotherms were developed

based on the differences between initial and equilibrium solute concentrations.
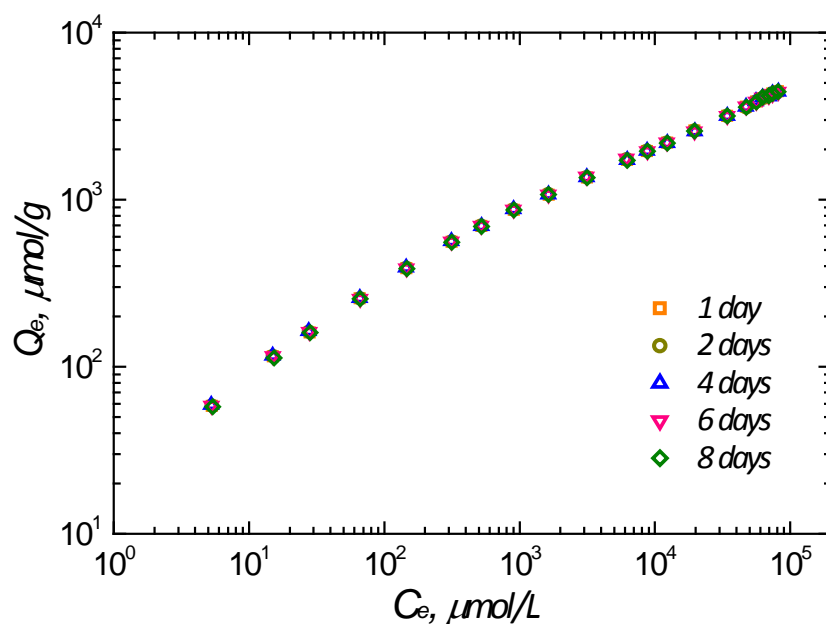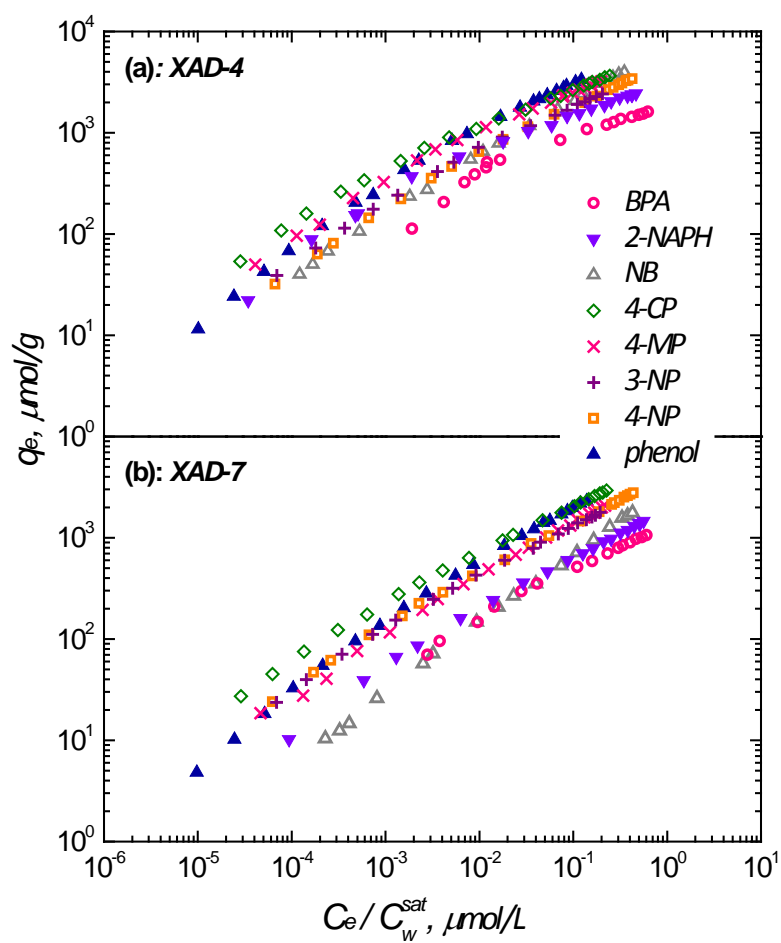

Figure S1. Effect of equilibrium time on the adsorption isotherms of 4-CP on XAD-4; equilibrium time was 1, 2, 4, 6 and 8 days, respectively.
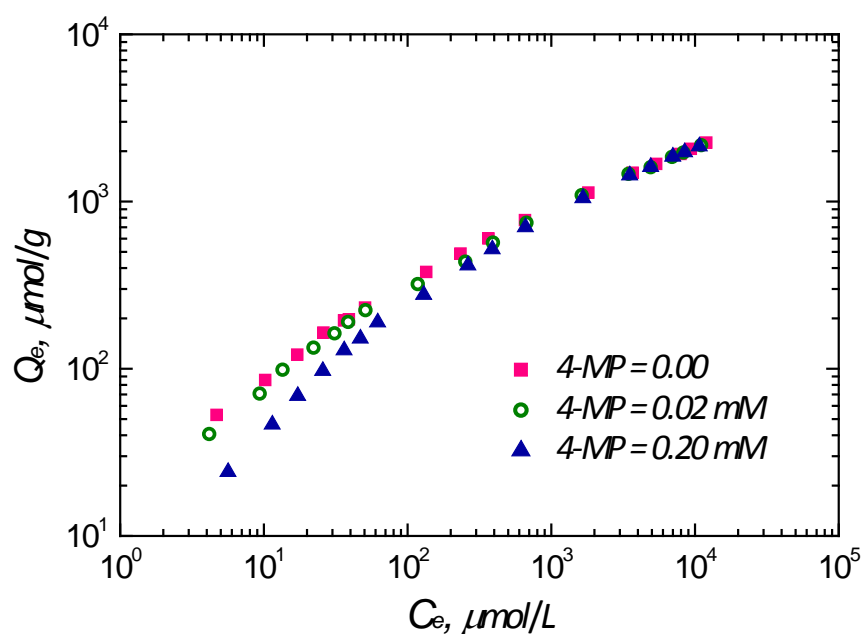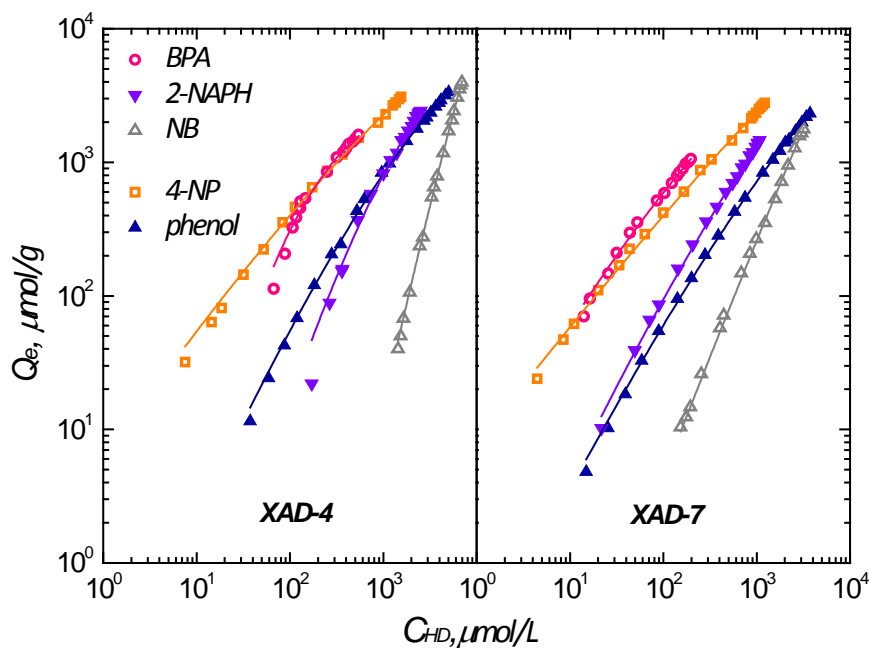

Figure S2. Effect of 4-MP as a competitor on the adsorption isotherms of 4-CP by XAD-4 at different 4-MP concentrations (0 – 0.20 mM).
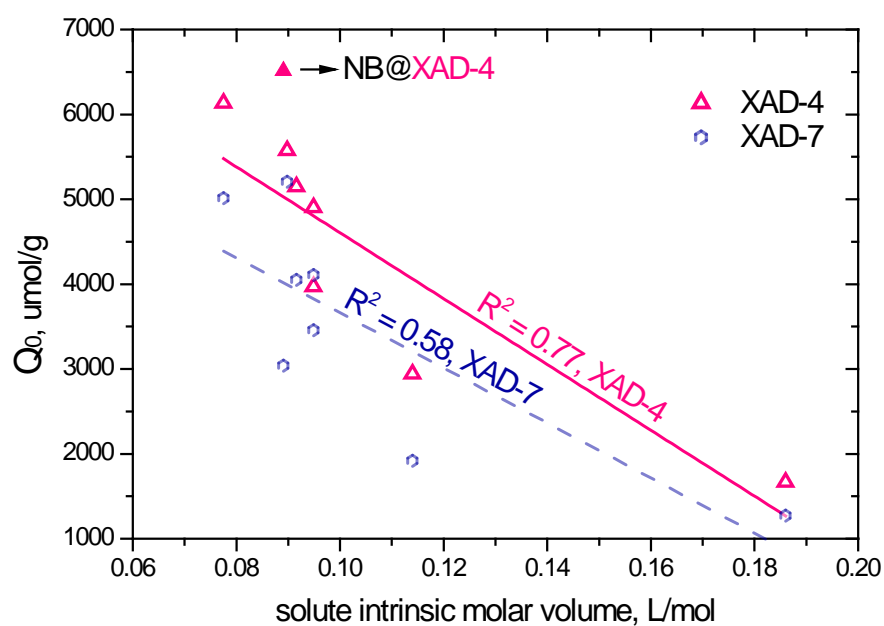
Figure S3. Correlations between Q^0, maximum adsorption capacity, and the molecular size of the solutes.

Figure S4. Adsorption isotherms of the target compounds on (a) XAD-4, (b) XAD-7 with the concentrations normalized by aqueous solubility.
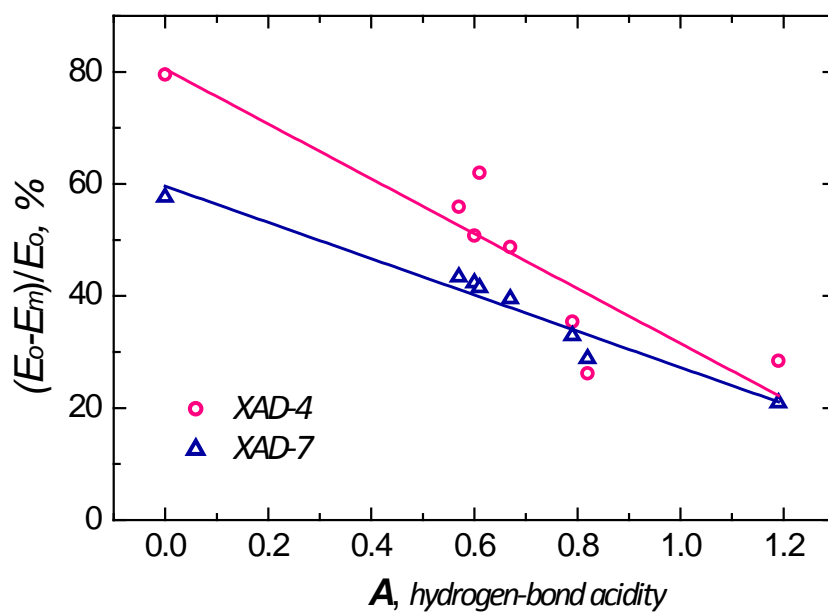

Figure S5. Hydrophobic interactions normalized isotherms of BPA, 2-NAPH, and NB on XAD-4 and XAD-7 (4-NP and phenol are included for comparison); solid lines are the model fittings by the modified D-A model.
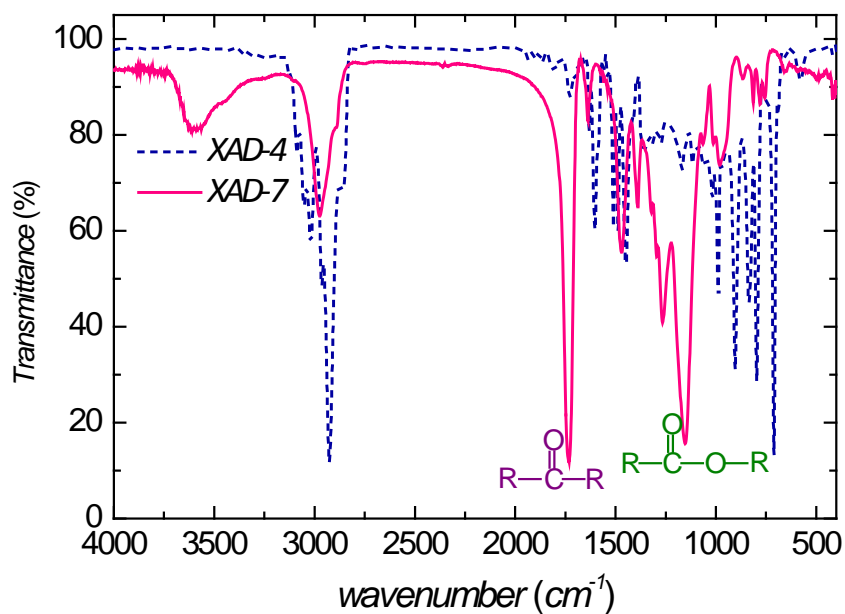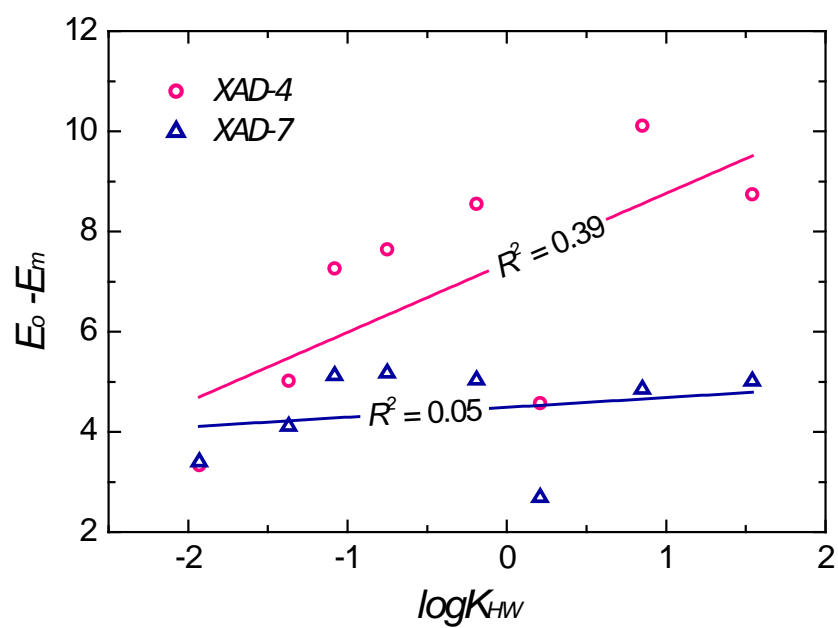

Figure S6. FT-IR spectra of the XAD-4 and XAD-7.
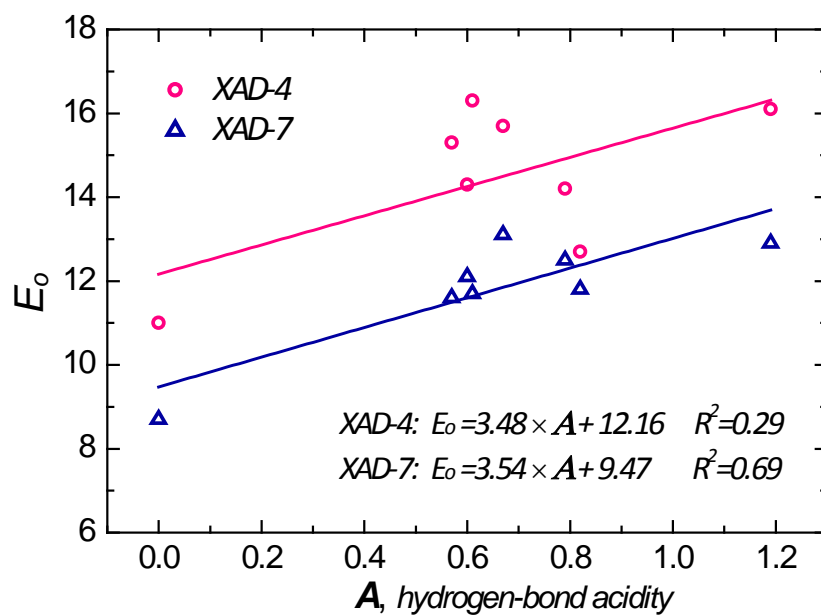
Figure S7. Relationships between "**A**" and the fitted "E_o" values of the original D-A model for the adsorption on XAD-4 and XAD-7.

Figure S8. Relationships between ($\dfrac{E_o - E_m}{E_o}$) and **A**, hydrogen-bond acidity.

Figure S9. Relationships between the values of $\log K_{HW}$ and $(E_o\text{-}E_m)$ i.e. the differences between the original D-A model fitted E_o and the modified D-A model fitted E_m.