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Competitive effects and interactions during sorption of SMP fractions on activated carbon: Response surface approach for visualization of sorption profiles

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ABSTRACT

The objectives of this study were to investigate the significance of the effects and interactions for during competitive sorption of soluble microbial products (SMP). Batch experiments were conducted to assess the competitive sorption characteristics and individual affinity of glucose (carbohydrate) and bovine serum albumin (BSA) (protein) as two representative fractions of SMP. The influence of surface availability was investigated by using carbon particles with different particle sizes (5–75 μm, 75–850 μm, and 850–1000 μm) and different carbon amounts. Competitive effects and interactions were evaluated for each adsorbate and surface availability. Competitive sorption mechanisms were quantified in relation to surface affinity of the SMP fractions. Sorption capacity profiles of the SMP fractions at equilibrium were developed using second-degree polynomial models for the experimental data and compared with the estimates obtained from the modified Langmuir-like model which uses single parameter sorption data to estimate competitive sorption profiles of systems with two adsorbates. Adequacy limitations of the modified Langmuir-like model for each SMP fraction were evaluated based on the significance of the synergistic and antagonistic effects between the two SMP fractions and the carbon surface availability.

1. Introduction

Soluble microbial products (SMP), also referred as soluble extracellular polymeric substances (EPS), consist of soluble cellular components which are released during cell lysis prior to diffusing through the cell membrane (Reid et al., 2008). SMP consist of pool of organic compounds which contain primarily carbohydrate and protein that result from substrate metabolism (usually with biomass growth) and biomass decay. SMP represent a significant fraction of soluble chemical oxygen demand (COD) in effluents from biological treatment processes (Chalor and Gary, 2007; Janga et al., 2007; Rosenberger et al., 2006; Shon et al., 2004; Jarusutthirak et al., 2005). SMP could inhibit the nitrification process, affect biofilm structure, viscosity, hydrophobicity, flocculation, and other physical characters of the sludge (Tansel et al., 2008; Ni et al., 2008; Reid et al., 2006) and result in operational problems in membrane bioreactors and downstream treatment (Chuang et al., 2009; Kornboonraksa et al., 2009; Tansel et al., 2006, 2005). However, activated carbon is extensively used in wastewater treatment for removal of organic and inorganic pollutions (Uygur and Kargi, 2004; Sirianuntapiboon et al., 2007; Tansel and Nagarajan, 2004).

Langmuir adsorption model has been used extensively to represent the sorption phenomena based on the coverage of the surface by a solute layer. When multiple solutes are present in a solute-sorbent system, the sorption phenomena is complicated by solute–solute, solute-surface interactions both in the aqueous phase and in the solid phase as shown in Fig. 1. For multiple solute systems, based on the assumptions similar to the original Langmuir model, a competitive sorption model has been proposed by Markham and Benton (1931). However, the extension of the Langmuir-like theory to adsorption in binary adsorbate systems has been shown to be thermodynamically valid only when the sorption capacities of the two components are equal (Broughton, 1948). When the sorption capacities for the adsorbates are not equal; at some sites, adsorption occurs without competition. Based on this hypothesis, Jain and Snoeyink (1973) developed an improved competitive Langmuir-like model as follows (referred as modified Langmuir-like model):

$$q_{e1} = \frac{\left(q_{m,1} - q_{m,2}\right) + AC_{eq1}}{1 + AC_{eq1}} + \frac{q_{m,2}AC_{eq1}}{1 + AC_{eq1} + BC_{eq2}} \quad (1)$$

and

$$q_{e2} = \frac{q_{m,2}AC_{eq2}}{1 + AC_{eq1} + BC_{eq2}} \quad (2)$$

where,

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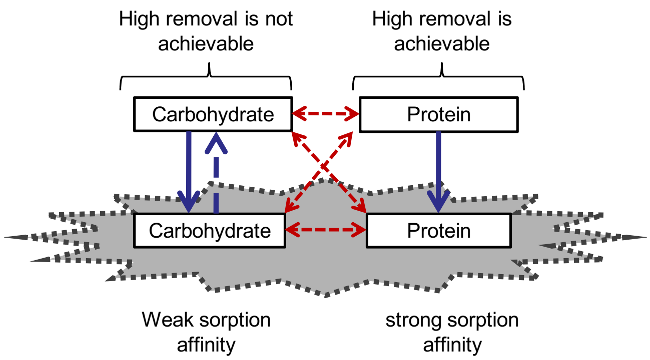

Fig. 1. Solute–sorbent and solute–solute interactions that affect competitive sorption mechanisms of SMP fractions (carbohydrate and protein) on sorbent (activated carbon).

q_{e1} and q_{e2}: amounts of solutes 1 and 2 adsorbed per unit weight of adsorbent at equilibrium concentrations Ceq1 and Ceq2 (mg/g), respectively

$q_{m,1}$ and $q_{m,2}$: maximum amounts of solutes 1 and 2, respectively, that can be adsorbed per unit weight of adsorbent (mg/g)

A and B: affinity constants of components 1 and 2, respectively, that are derived from single-solute systems (L/mg).

The first term on the right hand side of the equation (4) represents the Langmuir-like expression for the amount of species 1 adsorbed without competition and the second term represents the amount of species 1 adsorbed in competition with species 2. Wurster et al. (2000) observed that the modified competitive Langmuir-like model successfully predicted multi-component adsorption using single-solute parameters, even when the difference in the adsorbate capacities was relatively significant. However, the modified Langmuir-like model uses the parameters estimated from the single-solute systems to develop the sorption profile of the multi-solute system. In a multi-solute system, the competitive effects may include not only the solute-surface availability but also the interactions of the solutes with each other (i.e., synergistically and antagonistically). Hence, the adequacy of the modified Langmuir-like model may deteriorate as these interactions become more significant.

The response surface methodology (RSM) is a tool which is used to investigate the response of a system to the changes in a set of design variables (Box et al., 2005). A second-degree polynomial model is used to develop the response surface as the approximating function. The second-order model with two variables can be expressed as follows:

$$z = ß_0 + ß_1 x + ß_2 y + ß_{11} x^2 + ß_{22} y^2 + ß_{12} xy + \varepsilon \tag{3}$$

where,

x and y: independent variables

z: dependent variable (response variable)

$\beta_0, \beta_1, \beta_{11}, \beta_{22}, \beta_{12}$: parameters estimated by the 2nd order model

ε: error term

In equation (1), the terms which constitute the response surface model have the following significances:$\beta_1 x$ and $\beta_2 y \rightarrow$ main effects for variable x and variable y

$\beta_{11} x^2$ and $\beta_{22} y^2 \rightarrow$ curvatures of the response surface

$\beta_{12} xy \rightarrow$ interaction between variable x and variable y

The parameters in equation (1) are determined by regression analysis and insignificant terms are eliminated from the model. Hence, the response surface model allows a representative visualization of the response in relation to several parameters without reference to the theoretical phenomena. Although the RSM is often considered in context of design of experiments to conduct the minimum number of experiments to develop the response surface, it can also be used (i.e., using a second-degree polynomial model) for to visualize the response of a system to variables which can be independent controlled (Box et al., 2005).

The objectives of this study were to investigate the significance of the effects and interactions for during competitive sorption of SMP on activated carbon. Batch experiments were conducted to assess the competitive sorption characteristics and individual affinity of glucose (carbohydrate) and bovine serum albumin (BSA) (protein) as two representative fractions of SMP. The data obtained from competitive sorption studies were visualized for each SMP fraction in multiparametric formats. The data were also analyzed by the modified Langmuir-like model which uses single parameter sorption data to estimate competitive sorption profiles of systems with two adsorbates. The response surfaces for each SMP fraction were developed using a second-degree polynomial model for the experimental data collected and the modified Langmuir-like model. Competitive effects and interactions were evaluated for each adsorbate and surface availability. Adequacy limitations of the modified Langmuir-like model were evaluated for cases where significant synergistic and antagonistic effects between the two SMP fractions are observed.

2. Materials and methods

2.1. Materials

2.1.1. Activated carbon specifications

The coal based activated carbon (Calgon, Activated Carbon Technologies, USA) with a specific surface area of >1000 BET m^2/g, an iodine number of >800 mg/g was used during the experiments. The maximum ash and moisture contents of the carbon were 15% and 4%, respectively. Prior to use, the activated carbon was rinsed with distilled water to remove fines and dried at 105 °C in the oven.

2.1.2. Synthetic biologically treated sewage effluent

The composition of synthetic wastewater used in this study is presented in Table 1. The test solutions containing glucose as representative carbohydrate, BSA as representative protein, and mixtures of both carbohydrate and protein were prepared by diluting 1.0 g/L of stock solutions of glucose and protein to the desired concentrations. Stock solutions of glucose and protein were obtained by dissolving the exact quantities of 99.5% purity of glucose (Merck) and bovine serum albumin (Merck), in 1 L of double-distilled water, respectively. The ranges of concentrations of both

Table 1
Composition of test solutions used for sorption experiments.

Constituent	Concentration (mg/L)				
	Solution 1	Solution 2	Solution 3	Solution 4	Solution 5
Glucose	100	–	150	100	50
BSA	–	100	50	100	150
KH_2PO_4	8.5	8.5	8.5	8.5	8.5
$(NH_4)_2SO_4$	7.5	7.5	7.5	7.5	7.5
$NaHCO_3$	40	40	40	40	40
$MgSO_4.7H_2O$	7.5	7.5	7.5	7.5	7.5
$CaCl_2.2H_2O$	1.5	1.5	1.5	1.5	1.5
KCl	1.5	1.5	1.5	1.5	1.5
NaCl	7.5	7.5	7.5	7.5	7.5
$CuSO_4 \cdot 5H_2O$	0.015	0.015	0.015	0.015	0.015
$MnCl_2 \cdot 4H_2O$	1.0	1.0	1.0	1.0	1.0
$ZnSO_4 \cdot 7H_2O$	0.038	0.038	0.038	0.038	0.038
$FeCl_3 \cdot 6H_2O$	2.5	2.5	2.5	2.5	2.5