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Surface active site model for Ni^{2+} adsorption of the surface imprinted adsorbent

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Abstract

In this work, a new surface active site (SAS) adsorption equilibrium model was presented, which explicitly accounted for the H^+ competitive adsorption with Ni^{2+} in adsorption equilibrium. Static adsorption experiments with Ni^{2+} as a model metal ion were carried out to determine the model parameters, those were, equilibrium constant for Ni^{2+} (K_a), for H^+ (K_s), characteristic number of binding sites for Ni^{2+} (n), for H^+ (a), and the non-imprinted factor (σ). It was found that those model parameters n and a were all constant, and that they all expressed that one active site bound two Ni^{2+} or two H^+, while the non-imprinted factor, σ, was effected by Ni^{2+} concentration, H^+ concentration in solution and imprinted Ni^{2+} concentration in the preparation. Simulated result was compared with experimental data of the adsorption for Ni^{2+}. It was showed that this model could be well used to predict the adsorption equilibrium for Ni^{2+} on the surface imprinted adsorbent. And it was demonstrated that the efficacy of the active sites formalism could be used in describing adsorption behavior for Ni^{2+} on the surface imprinted adsorbent.

Keywords: Adsorption model; Bioadsorption; Heavy metal ions; Ni^{2+} surface active site model; Surface imprinted adsorbent

1. Introduction

Recent years, the using of chitosan and waste biomass to remove heavy metal ions in wastewaters has received considerable attention due to high adsorption capacity, selectivity, and low cost. To increase stability of the adsorbent, the cross-linked or modified chitosan was also studied. Peng and Wang synthesized of carboxyl-containing grafted chitosan polymer, which had a high adsorption capacity for Pb^{2+} and Cd^{2+} [1]. Kawamura et al. reported that the porous cross-linked chitosan beads could be used to remove heavy metal ions [2]. This cross-linked chitosan adsorbent had high mechanical intensity, but the adsorption capacity for heavy metal ions was lower compared with that of the untreated chitosan because of the functional groups ($-NH_2$) reducing.

The molecular imprinting method introduced by Ekberg and Mosbach [3] can overcome this problem [4,5]. In fact, the adsorption process mainly happens on the adsorbent surface, and the pores of the adsorbent surface only have a little of the adsorption capacity for heavy metal ions because of the inner-diffusion resistance. So a new molecular imprinted adsorbent, based on the surface molecular imprinting technique of *Penicliium chrysogenum* mycelium from waste biomass (the surface imprinted adsorbent), has been prepared [6]. The surface imprinted adsorbent combines the advantages of the mycelium adsorbent with that of the imprinted chitosan adsorbent giving low cost and good adsorption capacity and high stability that allows the reuse of the adsorbent for up to 15 cycles. The adsorption capacity of the surface imprinted adsorbent for Ni^{2+} was almost twice that of the mycelium adsorbent, and an increase of 30–50% over that of the surface non-imprinted adsorbent.

Although the adsorption behavior of chitosan adsorbent removing heavy metal ions in aqueous systems has been studied over the last two decades, little adsorption model was reported. Fourest et al. reported that the adsorption process for heavy metal ion by Fungal mycelial by-products was chemical adsorption equilibrium [7,8]. Ishii et al. studied that the functional group ($-NH_2$) had an important effect upon heavy metal bioadsorption by chitosan adsorbent [9]. Huang and Jin

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presented that the bioadsorption for heavy metal ions was not simple physics adsorption but complexing interaction. Assumption $-NH_2$ as ligand and heavy metal ions as central-ion, the same adsorbent has different ligand number to different metal ions, consequently the saturation adsorption capacity was different [10].

Several researchers have employed the Langmuir and Freundlich isotherms to describe adsorption equilibrium of the heavy metal ions, but these two isotherms only evaluate the effect of heavy metal ion concentration in solution. However, the pH is an important parameter in most cases because the adsorption ability for most metal ions decreases with increasing H^+ concentration. Based on the ion-exchange model and using assumption of two-site adsorption by *Sargaaum* biomass, at different pH value, Schiewer put forward an adsorption model that successfully explained biosorption for Cd^{2+} and Cu^{2+} on *Sargaaum* biomass [11]. Tan et al. had also put forward an adsorption model of the imprinted chitosan resins for the imprinted ions, but in this model, the non-active adsorption of the functional groups was not considered [12]. The non-active adsorption includes all the adsorption process in addition to the active site adsorption, such as physical adsorption and randomly distributed groups (including the bands of cross-linked –OH or $-NH_2$ breaking, or the functional groups on the cross-linking agent) which can adsorb metal ions and H^+ in a non-active manner. At lower heavy metal ions concentration in solution, the heavy metal ions were prior adsorbed by the active site on the adsorbent surface, but the contribution of the non-active sites increased with increasing heavy metal ions concentration in solution.

In the 1990s, Brooks and Cramer presented a new protein adsorption equilibrium model, the steric mass-action (SMA) equilibrium formalism, to describe the ion-exchange equilibrium for protein [13]. The model was primarily used for ion-exchange chromatography involves three parameters which are the characteristic charge, equilibrium binding constant and the steric factor, respectively. To date, the SMA model accurately predicting the affinity adsorption for protein has been proven [14,15]. Although the adsorption process of the surface imprinted adsorbent removing the heavy metal ions is similar to that of the affinity adsorption for protein. Ion size, characteristic charge, and chemical behavior of heavy metal ion are all different from those of protein. In this paper, a new theoretical description of the adsorption equilibrium for heavy metal ion on the surface imprinted adsorbents was presented based on the SMA model and the affinity adsorption for protein. The model parameters were determined by static adsorption equilibrium experiments. The effect of H^+ concentration in solution and imprinted Ni^{2+} concentration in the preparation has been quantitatively estimated and discussed.

2. Theoretical development

For further study of the adsorption process of the surface imprinted adsorbent removing the heavy metal ions, the following assumption was brought forward, and a new surface adsorption equilibrium model for the heavy metal ions was advanced. Consider the surface imprinted adsorbent with a total capacity, L_t, equilibrated with a carrier solution containing H^+ counter-ions. The model formalism employs the following assumptions:

1. The solution and adsorbent phases approximate thermodynamically ideal allowing the use of concentration instead of activity.
2. At the adsorption equilibrium, the surface imprinted site, that is active sites, interacts with N heavy metal ions, every interaction process is presented by an equilibrium constant, K_{ai}.
3. Upon binding, the metal ions interact with a number of *binding sites,* $n_i, i = 1, \ldots, n$.
4. To consider an imprinted chitosan surface with a total active site concentration of L_n (mmol g^{-1} (*adsorbent*)), that is imprinted site concentration in preparation, and the imprinted Ni^{2+} are total removed, then the active adsorption sites are left.
5. At the higher H^+ concentration, H^+ interacting with adsorption sites decreases the adsorption capacity. Upon binding the H^+ interacts with the adsorption sites on the adsorbent surface given by characteristic number of binding sites for H^+, *a*.
6. There are randomly distributed groups, such as the bands of cross-linked –OH or $-NH_2$ breaking, or the functional groups on the cross linking agent, which can adsorb metal ions and H^+ in a non-active manner. At the same time, some crack on the adsorbent surface and mycelium core may have some physical adsorption for metal ions and H^+. Therefore these influence was given by its *non-imprinted factor,* σ_i. It is inversely related to the number of imprinted sites.

In this work, single-component equilibrium with Ni^{2+} as a model metal ion was studied to examine the usefulness of the model, for this system, $i = 1$.

For a system of Ni^{2+}, equilibrium expression with the available adsorption sites can be written as

$$c_p + n\hat{L}_a = Q \qquad (1)$$

where c_p and Q are the Ni^{2+} equilibrium concentrations in solution and the Ni^{2+} adsorption site-complex on adsorbent phase, respectively. $\hat{L}_a$ represents vacant available adsorption sites on adsorbent surface, including vacant imprinted and non-imprinted active sites for Ni^{2+}. L_a represents vacant imprinted active sites on adsorbent surface that is accessible for the adsorption of Ni^{2+}.

The equilibrium constant K_a for Ni^{2+} is given by

$$K_a = \frac{Q}{c_p \cdot [\hat{L}_a]^n} \qquad (2)$$

$$\hat{L}_a = (1 + \sigma)L_a \qquad (3)$$

According to assumption 4 and 6, the total non-imprinted active site concentration $\bar{L}_n$ is given by

$$\bar{L}_n = \sigma L_n \qquad (4)$$