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A new statistical physics model to interpret the binary adsorption isotherms of lead and zinc on activated carbon

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ABSTRACT

New statistical physicochemical interpretations of an adsorption process at molecular level were developed to explain the binary adsorption isotherms of lead and zinc ions on activated carbon derived from *Styrax officinalis* seeds (Balikesir, Turkey) and a commercial activated carbon at different temperatures, 298, 308 and 318 K. The extended Hill model was developed to explain heterogeneous model in terms of the grand canonical ensemble in statistical physics. Steric and energetic parameters, like the numbers of ions per site n_1 and n_2, the densities of receptor sites N_{M1} and N_{M2} and the adsorption energies $(-\varepsilon_1)$ and $(-\varepsilon_2)$ were directly obtained from the fitting of the experimental adsorption isotherms by numerical simulation to describe the process. The simulation results suggested that two adsorbates per site were anchored on activated carbon surface. The magnitudes of the calculated adsorption energies indicated that Zn^{2+} and Pb^{2+} were physically adsorbed by the activated carbon. Thermodynamic potential functions, namely entropy, enthalpy and internal energy were calculated to explain the order and disorder of the adsorbate at the adsorbent surface during the binary adsorption process. The values of the free enthalpy and the internal energy indicated spontaneous adsorption process.

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1. Introduction

Heavy metals are discharged to environment from various industries such as electroplating, metal finishing, textile, storage batteries, mining, ceramic and glass. Lead and zinc are the most common heavy metals with toxic properties even if their concentration is very low in potable water with the maximum acceptable limit of 0.1–0.05 mg/L and 5.0 mg/L, respectively [1,2]. They cause serious environmental and health problems and are not biodegradable [3,4]. Therefore, lead and zinc ions need to be removed and eliminated from water and environment. Removal of these ions from wastewater is very difficult process and the methods such as ion exchange, chemical precipitation, membrane system, coagulation and adsorption have been used for their treatments [5]. During the past decades, precipitation and ion exchange are the most widely used methods for cleaning water contaminated with metal pollutants. Among the methods, adsorption is one of the most usable and universally physicochemical process to remove heavy metal ions from aqueous solution [6,7]. Activated carbon is a common adsorbent to be used heavy metals adsorption on activated carbon and adsorption mechanism is tried to explain using Langmuir and Freundlich isotherm models which are extensively used due to their simplicity and applicability [8–11].

In this work, a new statistical physics model was developed to interpret the binary adsorption of lead and zinc ions on activated carbon at molecular level at different temperatures using the grand canonical ensemble in statistical physics. A literature survey indicates that this model for the binary adsorption was established for the first time in the present research. In addition, three thermodynamic potential functions were also calculated to characterize the systems in macroscopic view.

2. Experimental

2.1. Preparation and properties of activated carbon

Styrax officinalis seeds (particle size less than 2 mm) were crushed and then mixed with KOH (weight ratio of 1:1) and distilled water and the mixture was dried at 105 °C. The impregnated sample was heated to the activation temperature of 800 °C for 1 h under N_2 flow (100 mL/min) at the rate of 10 °C·min^{-1}. The obtained activated carbon was filtered and washed with distilled water several times to remove residual chemicals [11]. In the present study, the commercial activated carbon (Calgon GRC 22), which is derived from coconut shell was also used in granular form (−7 + 12 mesh). The BET surface area of the *S. officinalis* seeds activated carbon and the commercial activated carbon

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were found to be 1212 m^2/g and 906 m^2/g, respectively [11,12]. The average pore diameters of the *S. officinalis* seeds activated carbon and the commercial activated carbon are 2.16 nm and 2.17 nm respectively. The ionic radius of Pb^{2+} and Zn^{2+} are 133 pm and 88 pm [13]. It means that lead and zinc ions can be gone into pores of the activated carbons easily. However, the adsorption capacities of activated carbon for Pb (II) ions have greater than Zn (II) ions due to the lower hydration enthalpy (1480 kJ/mol) of Pb (II) ions [12,14]. An analysis of the powder XRD data of the activated carbon (not provided in text) indicated that the main structures of activated carbon are amorphous and the broader reflections were observed in the range of 10–30°. The vibrational modes of functional groups of barren activated carbon and Pb^{2+} and Zn^{2+}-sorbed activated carbon were determined in the range of the 400–4000 cm^{-1} using Perkin Elmer spectrum one FT-IR. The FTIR bands are given in Fig. 1, showing that the band positions of the activated carbons before and after adsorption show great similarity with each other. It was observed that the main peaks belonging to Pb^{2+} and Zn^{2+}-sorbed activated carbon (3402, 2913, 1613, 1381, 1125 and 606 cm^{-1}) had shifted, explaining with carboxyl and hydroxyl groups are main contributors for metal adsorption [15,16]. After the metal adsorption on activated carbon, the bands at 1100 cm^{-1}, attributing stretching vibration of C–OH of alcoholic groups and carboxylic acids [17] and the band at 996 cm^{-1}, attributing to epoxy groups were disappear. These indicated that the metal ions reacted with these bands [18]. In addition, especially the band at 1605 cm^{-1} associated with C–O stretching in carboxylic groups [19] was shifted to 1640 cm^{-1}. Sánchez-Polo and Rivera-Utrilla [20] and Kyzas et al. [18] explain this situation as the dispersive interactions and ion-exchange reaction between the metal ion and the delocalized protonated π-electrons of the graphene layer.

Surface morphology of activated carbon and Pb^{2+} and Zn^{2+}-sorbed activated carbons was investigated with a scanning electron microscope (Leo EVO 40) and the scanning was done in situ on powder forms of the samples. The SEM images (Fig. 2) showed that the activated carbons had many pores with sharp edges and unsmooth surface (Fig. 2a). After the adsorption process, the metal ions are noticeable on the surface of activated carbons (Fig. 2b, c). In addition, Pb^{2+} and Zn^{2+} ion distribution maps (Fig. 2d, e) indicated that lead adsorption was higher than zinc at the same metal concentration ratio as expected [12].

2.2. Adsorption experiments

Adsorption studies were conducted by batch technique in a thermally controlled automatic shaker at 110 rpm at different temperatures for a prescribed time to attain equilibrium. 0.1 g of the activated carbons was introduced into test tubes (50 mL) containing various concentrations (20–100 mg/L) with 25 mL aqueous solutions of Pb (II) or Zn (II) at pH 4.5–5 at different temperatures (298–308 K). Appropriate concentrations of each heavy metal were prepared using the stock solutions (1000 mg/L, as their respective nitrate salts, Fischer and MERCK certified). Adsorption isotherm parameters were calculated by a non-linear method which was determined using the solver add-in with Microsoft's spreadsheet, Microsoft Excel. The exact concentration of all the prepared solutions and filtrate of Pb (II) and Zn (II) was measured by ICP-OES in University of Utah. At binary system, a molar ratio of 1:1 was used to determine the effect of each metal ion on the adsorption of Pb (II) and Zn (II) on the activated carbons. The amount of Pb (II) and Zn (II) adsorbed on the activated carbons, Q (mg/g.) was calculated by the mass balance Eq. (1).

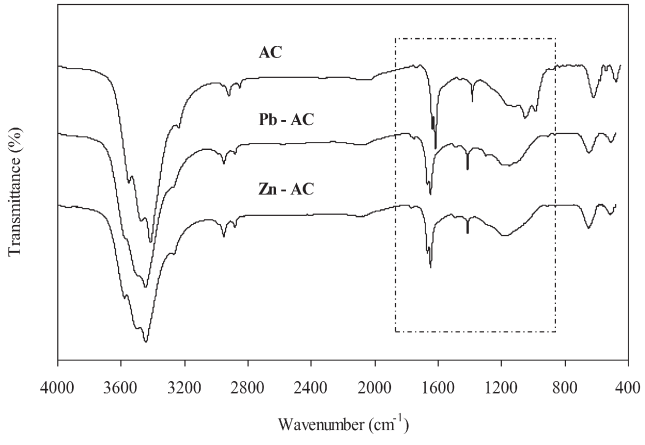

Fig. 1. FTIR spectra of the activated carbons before and after Pb (II) and Zn (II) adsorption.

$$Q = \frac{(C_0 - C) * V}{W} \tag{1}$$

where, C_0 (mg/L) is the initial metal ion concentrations and C (mg/L) is unadsorbed metal ion concentrations in solution at time t, V (L) and W (g) are the volume of the solution and the weight of the dry activated carbon respectively.

3. Theory

To establish a new statistical physics model, some approximations need to be considered and to simplify the process, the dissolved adsorbate ions which are diluted from the saturated solution adequately are treated as an ideal gas [21]. In addition, the mutual interaction between the adsorbate ions and solvent ones was neglected. The extended Hill model with two types of receptor sites was established in terms of the grand canonical ensemble in statistical physics. A variable number Na_1 of the first adsorbate on N_{M1} receptor sites and Na_2 of the second adsorbate on N_{M2} receptor sites are calculated and the binary adsorption mechanism of the metal ions was found characterized by the adsorption reaction, containing two stoichiometric coefficients, namely n_1 and n_2, using below equation.

$$n_i\, A^+ + R_i \rightleftarrows A^+_{ni} R_i \quad i = 1.2 \tag{2}$$

where, A^+ represents the adsorbate of lead or zinc ion.

The first step of the treatment was to express the grand canonical partition function of one receptor site describing the microscopic states of the adsorbing system using the following physical situation [22,23]:

$$z_{gc_i} = \sum_{N_i = 0,1\ldots} e^{-\beta(-\varepsilon_i - \mu_i)N_i} \tag{3}$$

where, $(-\varepsilon_i)$ is the receptor site adsorption energy of type, μ_i is the chemical potential of the adsorbed state, N_i is the receptor site occupation state, and β is defined as $1/(k_BT)$,where k_B is the Boltzmann constant and T the absolute temperature. The total grand canonical partition functions related to independent N_{M1} and N_{M2} receptor sites per surface unit can be written as:

$$Z_{gc} = (z_{gc1})^{N_{M1}} (z_{gc_2})^{N_{M2}} \tag{4}$$

The average site occupation numbers N_{o1} and N_{o2} of the two studied ions can be written as:

$$N_{o1} = k_B T \frac{\partial \ln Z_{gc}}{\partial \mu_1} \tag{5}$$

$$N_{o2} = k_B T \frac{\partial \ln Z_{gc}}{\partial \mu_2}. \tag{6}$$

When the thermodynamic equilibrium was reached, the equality between the chemical potentials can be written as:

$$\mu_{m1} = \mu_1/n_1 \text{ and } \mu_{m2} = \mu_2/n_2 \tag{7}$$

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