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Ion exchange and adsorption equilibrium studies on clinoptilolite, bentonite and vermiculite

V.J. Inglezakis *, M. Stylianou, M. Loizidou

National Technical University of Athens, School of Chemical Engineering, Unit of Environmental Science and Technology (UEST), Heroon Polytechniou 9 Str., Zografou, 15773 Athens, Greece

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ABSTRACT

In the present paper three natural minerals used in many industrial and environmental applications namely zeolite clinoptilolite and the clays bentonite and vermiculite are studied by utilising ion exchange and adsorption. In particular, the Dubinin–Astakhov adsorption isotherm is used modified by introducing a solubility-normalized adsorption potential for studying the ion exchange process. The equation, is applied in experimental isotherms in order to determine adsorption energy and heterogeneity parameter for the ion exchange of Pb^{2+} in the natural minerals. The results indicate that the modified Dubinin–Astakhov adsorption isotherm represents the experimental data well and at the same time provides the heterogeneity parameter of the materials, which is an important adsorbent physical parameter as well as the adsorption energy. In order to deepen the study and link the results to the pore structure BET analysis is presented as well.

1. Introduction

Ion exchange equilibrium has been studied for many decades and numerous theories have been proposed. Published reports of isotherms for zeolites usually fall into three groups: extension of gaseous adsorption isotherm equations, the Dubinin–Polyani potential theory and thermodynamic methods [1–5]. The simple gaseous model isotherms, for example the Langmuir and Freundlich isotherms, have been found to be accurate for some zeolite systems, but they are often not applicable [6]. The Polanyi potential theory has been applied to carbon adsorption of organic mixtures from aqueous mixtures and has been found to apply to zeolites in many instances [7,8]. Historically, thermodynamic approaches have been found to be of limited utility when applied to ion exchange in zeolite [9–12].

Starting from the latter case, most of the rigorous approaches require knowledge of the true mechanism involved in the ion exchange process. The rigorous modeling of ion exchange equilibrium involves the activity coefficients in liquid and solid phase of all the exchanging species. Even if the thermodynamic parameters are known the most rigorous approaches are incapable to incorporate several interfering phenomena encountered in an ion exchange system. In the study of Lehto and Harjula [13] several chemical and physical phenomena interfering with ion exchange equilibria are discussed, like the hydrolysis and dissolution of ion exchangers, the sorption of electrolytes and the hydrolysis of cations. As a result, applying equilibrium models, the resulted parameters, as for example ion exchange selectivity coefficients, would merely be measures of the net effect of exchanger hydrolysis, cation hydrolysis and ion exchange [13]. Clearly, all these interfering phenomena introduce a serious and maybe a unsolvable problem. Even if the model is describing the underlying process it could fail because of errors associated to several parameters or due to the unavailable parameters of an interfering phenomenon.

Under these circumstances, simpler equilibria models are used in the related literature of ion exchange on natural minerals. The most common for liquid phase adsorption and ion exchange systems are the Langmuir and Freundlich isotherms [14–22]. However, the parameters involved in the simple Langmuir and Freundlich isotherms give only a limited insight on the adsorption mechanism and nature. As an alternative, the Dubinin–Radushkevich adsorption isotherm is the most versatile, proven and useful model for predicting, as well as describing, equilibrium adsorption capacities of organic vapours on ordinary commercial activated carbons. For specialized carbons the more general Dubinin–Astakhov equation with an additional parameter can be used, namely, the heterogeneity parameter. These Dubinin equations have the advantages of including: carbon property parameters (heterogeneity parameter), vapour property parameters (adsorption energy) and temperature.

The theoretical analysis of this isotherm as well as its modification for use in liquid adsorption and ion exchange systems has been presented by Inglezakis [23] in a previous paper. The modified Dubinin–Astakhov equation has been successfully applied on a large number of experimental data

* Corresponding author. Tel.: +30 210 7723 108, +30 210 7723 285.
E-mail address: v_inglezakis@yahoo.com (V.J. Inglezakis).

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and the adsorption energy and heterogeneity parameter for the ion exchange of several cations in the zeolite clinoptilolite have been successfully evaluated. Based on this work, in the present paper three natural minerals utilised in ion exchange systems, namely zeolite clinoptilolite, bentonite and vermiculite are studied and the respective parameters are presented.

2. Theoretical background

The Dubinin–Radushkevich (DR) equation is based on earlier adsorption potential theory by Polanyi and Dubinin suggesting that the adsorption process is by micropore volume filling as opposed to layer-by-layer adsorption on pore walls. The Dubinin–Astakhov (DA) and its special case, Dubinin–Radushkevich adsorption isotherms have been extensively used for the adsorption of gases and vapours [24,25], in lesser extent for the adsorption of organic solutes from aqueous solutions [26–28] and in some cases for ion exchange/adsorption of metallic ions [23,29–32] on porous sorbents (Table 1).

The Dubinin–Astakhov adsorption isotherm has been extended to cover the case of adsorption from aqueous solutions [23,26,28,41,42]. By analogy to the vapours, the adsorption potential for solutes in aqueous solutions is defined as [23]

$$\varepsilon = R\,T \ln\left(\frac{C_s}{C}\right) \tag{1}$$

where R (J/mol K) is the ideal gas constant, T the temperature (K), C (mg/ml) is the equilibrium solute concentration and C_s (mg/ml) its solubility. Here note that in the case of ion exchange when salts are dissolved to produce ions, we are interested in the "solubility" of the ion. The Dubinin–Astakhov adsorption isotherm is

$$q = q_0 \exp\left[-\left(\frac{\varepsilon}{E}\right)^n\right] \tag{2}$$

where E (J/mol) is the adsorption energy, n the heterogeneity parameter and q_0 (mg/g) is the maximum mass of the adsorbed species per unit mass of sorbent [24,25,43]. For $n=2$ we have the well-known Dubinin–Radushkevich adsorption isotherm. In the present paper the solubility-normalized adsorption potential is applied (S-model) [23]:

$$q = q_0 \exp\left[-\left(\frac{RT\ln\left(\frac{C_s}{C}\right)}{\sqrt{2}E}\right)^n\right] \tag{3}$$

Its linear form is

$$\ln q = \ln q_0 - \left(\frac{1}{\sqrt{2}E}\right)^n \left[RT\ln\left(\frac{C_s}{C}\right)\right]^n \tag{4}$$

It is well known that the heterogeneity parameter n is related to the adsorbent structure; the more homogeneous the pores the greater its value [28,44–46]. For example, a number of experiments on several types of activated carbon verified that the heterogeneity parameter n varies, increasing as the microporous structure becomes more homogeneous, i.e. the breadth of the micropore distribution about some mean pore size decreases [47,48]. It should be noted that n values depend on both the adsorbate and the adsorbent and it is very difficult to have a universal exponent [49,50]. Thus, particularly in natural minerals systems the heterogeneity factor n should be an adjustable, experimentally derived parameter and thus, the more general Dubinin–Astakhov adsorption isotherm should be used [23].

In theory, E and q_0 calculated from the Dubinin–Radushkevich adsorption isotherm should be independent of the exchanging cation [23]. However, the ideal application of this theory requires that both the exchange material and cation be completely non-polar. The non-idealities found in practice in ion exchange systems could account for the variability of the coefficients [42]. Given the adsorption capacity q_0 this equation is forced to match the experimental data by changing the heterogeneity parameter n. Then the adsorption energy is calculated from the slope of the linearized equation. For the analysis using the Dubinin–Astakhov adsorption isotherm a critical parameter is the adsorption capacity q_0 of the material, or the maximum exchange level (M.E.L.) for the ion exchange case [23].

3. Experimental section

3.1. Samples and characterization

Three different natural minerals were used in this study and in particular, zeolite (clinoptilolite, 0–5 mm), vermiculite (0–5 mm) and bentonite (<90 μm). Zeolite and bentonite were supplied by

Table 1
The use of the Dubinin–Astakhov equation in ion exchange and aqueous phase adsorption.

Absorbent	Absorbate	Adsorption potential function	Adsorption isotherm[a]	n[a]	E (kJ/mol)	Reference
Clinoptilolite	NH_4^+, Zn^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Sr^{2+}, Ni^{2+}, Pb^{2+}, Cs^+	Normalized	DA	5.84 ± 2.09 (2.1–10.4)	16.7 ± 3.21 (9.47–21.74)	[23]
Clinoptilolite	Pb^{2+}	Normalized	DA	5.2	17.49–18.90	[23]
Clinoptilolite	Pb^{2+}	Normalized	DA	4.2	17.17	This study
Clinoptilolite	Cd^{2+}	Normalized	DA	3.52–7.14	18.44–24.27	[55]
Clinoptilolite	Phenol	Non-normalized	DA	4	11.18–12.40	[33]
Clinoptilolite	Cs^+	Non-normalized	DR	2	11.2–12.9	[34]
Clinoptilolite	Co^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}	Non-normalized	DR	2	8.81–11.95	[30]
Bentonite	Pb^{2+}	Normalized	DA	3	24.97	This study
Bentonite	Cu^{2+}, Zn^{2+}	Non-normalized	DR	2	0.52–1.25	[35]
Bentonite	Pb^{2+}	Non-normalized	DR	2	8.80	[36]
Bentonite	Boron	Non-normalized	DR	2	3.3–4.85	[37]
Bentonite	Pb^{2+}, Ni^{2+}	Non-normalized	DR	2	10.28–10.80	[38]
Bentonite	Cr^{3+}, Cr^{+6}, Ag^+	Non-normalized	DR	2	9.91–10.19	[39]
Vermiculite	Pb^{2+}	Normalized	DA	1.7 and 9.5[b]	11.56 and 12.95	This study
Vermiculite	Cr^{6+}	Non-Normalized	DR	2	5.9	[40]

[a] The direct use of the Dubinin–Radushkevich (DR) adsorption isotherm means that the heterogeneity parameter is taken equal to 2. On the other hand, when the Dubinin–Astakhov (DA) adsorption isotherm is used the heterogeneity parameter is experimentally evaluated.

[b] Two kinds of micropores (two linear regions of DA equation).