

## Ion adsorption components in liquid/solid systems

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**Abstract:** Experiments on  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  adsorptions on vermiculite in aqueous solutions were conducted to investigate the widely observed adsorbent concentration effect on the traditionally defined adsorption isotherm in the adsorbate range 25—500 mg/L and adsorbent range 10—150 g/L. The results showed that the equilibrium ion adsorption density did not correspond to a unique equilibrium ion concentration in liquid phase. Three adsorbate/adsorbent ratios, the equilibrium adsorption density, the ratio of equilibrium adsorbate concentration in liquid phase to adsorbent concentration, and the ratio of initial adsorbate concentration to adsorbent concentration, were found to be related with unique values in the tested range. Based on the assumption that the equilibrium state of a liquid/solid adsorption system is determined by four mutually related components: adsorbate in liquid phase, adsorbate in solid phase, uncovered adsorption site and covered adsorption site, and that the equilibrium chemical potentials of these components should be equalized, a new model was presented for describing ion adsorption isotherm in liquid/solid systems. The proposed model fit well the experimental data obtained from the examined samples.

**Keywords:** adsorbent effect; adsorbate/adsorbent ratio; adsorption component; chemical potential;  $\text{Zn}^{2+}$ ;  $\text{Cd}^{2+}$ ; vermiculite

### Introduction

The Langmuir isotherm refers to a mathematical relationship describing a plot of the volume of gas adsorbed on a solid as a function of the pressure at constant temperature (Langmuir, 1918). When adopted to describe adsorption phenomena in liquid-solid systems the Langmuir-type isotherm is given in the form with the equilibrium adsorption density ( $q_e$ , ratio of adsorbate quantity to adsorbent quantity) as a single function of the equilibrium adsorbate concentration in liquid phase ( $C_e$ ) (Singh and Mohan, 2004; Cordeiro *et al.*, 2005; Özacar and Sengil, 2004; Sahu *et al.*, 2000). The essential requirement for  $q_e$  being a single function of  $C_e$  is that  $q_e$  should correspond to a unique  $C_e$ , independent of initial adsorbate and adsorbent concentrations. This did not appear to be true as  $q_e$  was not found to have a unique value at a given  $C_e$  in many studies including the work done by Langmuir himself (1918). Similar to what was found by Langmuir (1918) for gas molecule adsorption on solid phases, inconstancy of the equilibrium coefficients defined by the Langmuir equation was widely observed in liquid-solid adsorption systems. The general trend was that the equilibrium constant ( $K_L$ ) and the adsorption capacity parameter ( $q_m$ ) were not constant over the entire adsorption domain and that their values not only varied with adsorbent concentration but also differed with different initial adsorbate concentration intervals (Cseh and Benz, 1998; Al-Asheh *et al.*, 2003; Mura-Galelli *et al.*, 1991).

Associated with the inconstancy of equilibrium constants, a decline of the adsorption isotherm with increasing adsorbent concentration, interpreted as particle concentration effect or adsorbent effect (Voice

and Weber, 1985; Pan *et al.*, 1999), was reported in a number of laboratory studies on different types of adsorbates and adsorbents (O'Connor and Connolly, 1980; Voice *et al.*, 1983; Cox *et al.*, 1997; Sanudo Wilhelmy *et al.*, 1996; Qin *et al.*, 2004). As the sample pH and ionic strength were controlled in most of those studies, the particle concentration effect could not be explained by changes in pH and ionic strength factors.

Pan and Liss (1998a, b) suggested that at the equilibrium state the chemical potential of the adsorbate in liquid phase ( $\mu_L$ ) should be equal to that in solid phase ( $\mu_S$ ). Thus, based on the observation that the equilibrium adsorbate concentration in liquid phase  $C_e$  did not correspond to a unique value of the adsorption density  $q_e$ , they concluded that  $q_e$  is not a state variable, since  $C_e$  is a single function of  $\mu_L$  while  $q_e$  is not. According to the metastable-equilibrium adsorption (MEA) theory (Pan and Liss, 1998a, b), the experimentally determined  $q_e$  is a variable at an MEA state and its chemical potential depends on the MEA state of the adsorbed molecules and therefore on the history of adsorption processes. By affecting the MEA state or the adsorption reversibility, changes in the adsorbent concentration  $W_0$  lead to fundamental influences on adsorption isotherms. By including an adsorbent factor, Pan and Liss (1998a) further developed a Langmuir-type isotherm and a Freundlich-type isotherm. The key question relating to the MEA theory is whether or not the ideal equilibrium  $q_e$  in principle should correspond to a unique  $C_e$  at different adsorbent concentration levels.

Depending on how samples were obtained, inconstancy of the coefficients might be accounted for by many factors, e.g., presence of the third phase (Voice and Weber, 1985; Benoit, 1995); pre-adsorbed

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substances (Grolimund *et al.*, 1995); particle-particle interactions (Benoit, 1995; Nyffeler *et al.*, 1984); implicit adsorbate competition (Curl and Keioleian, 1984; Higgo and Reos, 1986); impact on reversibility due to presence of other reactions (Mura-Galelli *et al.*, 1991; Nagayasu *et al.*, 2005), and so on. The most fundamental factor, however, may be whether or not the corresponding coefficients are rationally defined by the applied mathematical equations.

In contrast to the equilibrium adsorbate concentration in liquid phase ( $C_e$ ), the equilibrium adsorption density  $q_e$  is a ratio of adsorption quantity to adsorbent quantity. In addition to the chemical potentials of the adsorbate in liquid phase ( $\mu_L$ ) and solid phase ( $\mu_s$ ), the adsorption potential of the adsorbent is also an essential component of the adsorption system. The present study was thus conducted to investigate: (1) if  $q_e$  will correspond to a unique ratio of  $C_e$  to the adsorbent concentration; (2) if the inconstancy of the traditionally defined equilibrium coefficient can be fully explained by the adsorbent effect; and (3) if the equilibrium adsorption condition can be simply determined by the relationship between the chemical potentials of the adsorbate  $\mu_L$  and  $\mu_s$ , or if not, what other factors need to be taken into account.

## 1 Materials and methods

### 1.1 Materials

The vermiculite mineral used as the adsorbent was a product of the Second Mineral Plant of Lingshou County, Hebei Province, China, with a chemical formula of  $Mg_3(H_2O)(Mg_{3-x}(AlSiO_3O_{10})(OH)_2)$  and a surface area of  $400 \times 10^3$ – $800 \times 10^3$  m<sup>2</sup>/kg. In order to obtain homogeneous samples the vermiculite minerals were sieved to the size of 0.2–0.4 mm, washed several times with distilled water and dried for about 5 d at room temperature.

Analytical grade zinc sulphate ( $ZnSO_4 \cdot 7H_2O$ ) and cadmium sulphate ( $3CdSO_4 \cdot 8H_2O$ ) were used to prepare the standard adsorbate solutions by dissolving the chemicals in distilled water.

### 1.2 Equilibrium tests

A series of equilibrium adsorption tests were carried out over relatively wide concentration ranges, 25–500 mg/L for the adsorbates (zinc and cadmium) and 10–150 g/L for the adsorbent (vermiculite). The adsorbate and adsorbent concentrations used varied to some extent to accommodate the experimental designs.

The samples were prepared by transferring an accurately weighed amount of the adsorbent and 100.00 ml of standard adsorbate solution of different concentrations into a 250-ml ground-glass stopper flask. Equilibrium experiments were conducted in a shaker bath shaken at a speed of 200 r/min for 24 h at a constant temperature of 30°C. After that the samples

were filtrated and the adsorbate concentration in the aqueous phase was determined by flame atomic absorption spectrometry (AAS).

Results from pre-tests indicated that adsorptions approached equilibrium after 10 h, and a period of 24 h was thus considered sufficient to ensure that the equilibrium was reached. Control and parallel tests were performed, and each experiment was repeated at least three times. The standard deviation analysis indicated good agreement between parallel and repeated measurements and average measurement values were thus used as basic data. The adsorption capacity of the adsorbent ( $q_m$ ) was estimated by linear correlation analysis of experimental data.

In experimental testing the basic relationship between adsorption components, sample pH and the ionic strength were not controlled. The idea was to obtain adsorption systems consisting of only the concerned adsorbate and adsorbent in pure water solution. In other experiments conducted with the objective of investigating the influence of pH on  $Zn^{2+}$  and  $Cd^{2+}$  adsorption sulfuric acid ( $H_2SO_4$ ) was used to adjust the sample pH.

## 2 Results and discussion

### 2.1 Adsorbent effect

The data from the equilibrium sample series are presented in four types of plots for  $Zn^{2+}$  in Fig.1 and  $Cd^{2+}$  in Fig.2. When plotted against the equilibrium adsorbate concentration in liquid phase ( $C_e$ ), the equilibrium adsorption density  $q_e$  decreases while the equilibrium adsorption quantity  $Q_e$  increases with increasing adsorbent concentration  $W_0$  (Figs. 1a and 1b, Figs. 2a and 2b), showing clearly the influence of  $W_0$  on  $Q_e$ – $C_e$  and  $q_e$ – $C_e$  relations. The plots in Figs. 1a and 2a indicate that unless  $W_0$  or  $C_0$  is given, the traditionally defined adsorption isotherm (the  $q_e$ – $C_e$  plot) cannot be determined. In contrast, the curves corresponding to different  $W_0$  levels are more or less overlapping where  $q_e$  is expressed as a function of  $C_e/W_0$  and where  $Q_e/C_0$  is expressed as a function of  $C_e/C_0$  (Figs. 1c and 1d, Figs. 2c and 2d). Although there are deviations among the measured values (shown by the deviation of the measured points from the trend curves), there is a clear trend that the adsorbate/adsorbate and adsorbate/adsorbent ratios are uniquely related with each other in the tested area regardless of the  $C_0$  and  $W_0$  levels. Measurements of different  $W_0$  sample series gave similar results when conducted at different times in a number of separated experiments, thus suggesting good reproducibility. The observed adsorbent effect is in agreement with the reports from Pan *et al.* (2002) and Qin *et al.* (2004).

### 2.2 Adsorbate/adsorbent ratios

The dimensions of  $C_e$  and  $q_e$  are different. Unlike  $C_e$  which is a ratio of the total adsorbate quantity in

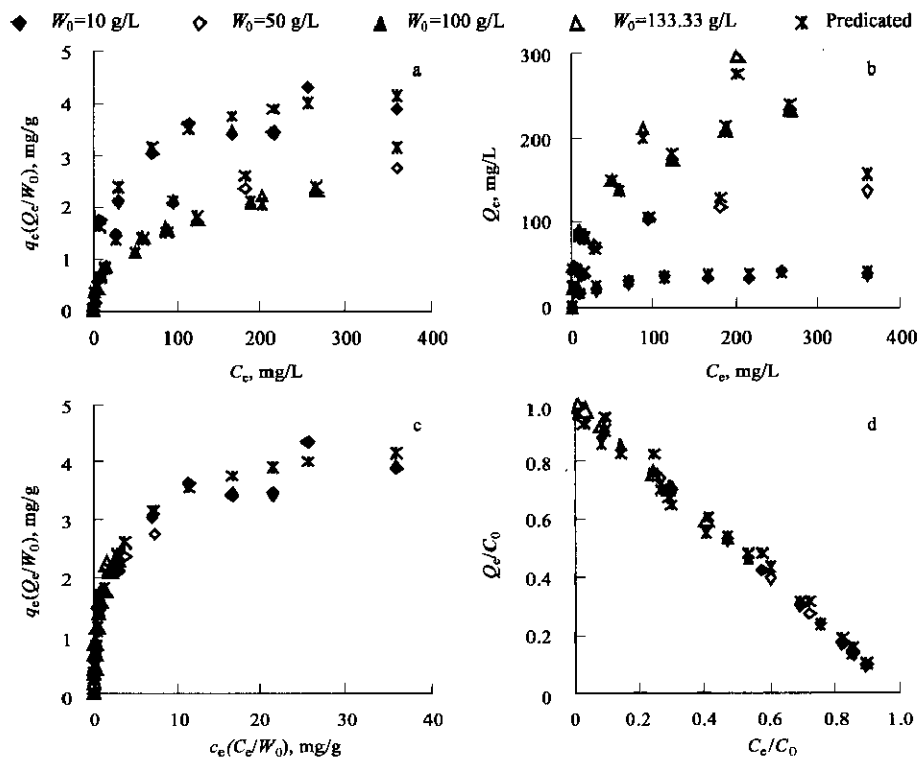


Fig.1 Adsorption of Zn<sup>2+</sup> on vermiculite at different adsorbent concentration ( $W_0$ ) levels  
a.  $q_e$ - $C_e$  plot; b.  $Q_e$ - $C_e$  plot; c.  $q_e$ - $c_e$  plot; d.  $Q_e/C_0$ - $C_e/C_0$  plot; predicted values are given by Eq. (8) with  $k=1.07$  and  $q_w=4.65$  mg/g (for symbols definitions see Appendix)

bulk solution to the system volume given in mg/L,  $q_e$  is a ratio of the total quantity of adsorbate adsorbed on solid surface ( $Q_e$ , mg/L) to the adsorbent quantity ( $W_0$ , g/L) given in mg/g. The adsorption density is calculated as  $q_e = Q_e/W_0 = (C_0 - C_e)/W_0$  using  $C_e$  values measured in experiments. Thus for a given  $C_0$ , the relationship between  $q_e$  and  $C_e$  will further depend on  $W_0$  while that between  $q_e$  and  $C_e/W_0$  is in principle determined. There is no doubt that  $q_e$  is a function of  $C_e$ . The point is that  $q_e$  is not a single function of  $C_e$  but rather a single function of the ratio  $C_e/W_0$ . If this argument holds in general, the phenomena of  $q_e$  corresponding to a unique  $C_e/W_0$  should be observed in designed experiments. The plots in Figs.1c and 2c give support for this argument. Carefully designed trials were further conducted to test the relationship between the adsorbate/adsorbent ratios by fixing the  $C_e/W_0$  ratio at different  $C_0$  and  $W_0$  levels. Since  $q_e = C_e/W_0 - C_e/W_0 = c_0 - c_e$ , then for a given  $c_0$ ,  $q_e$  will correspond to a unique  $c_e$ , and for a given  $c_e$ ,  $q_e$  should therefore correspond to a unique  $c_0$ . This means that the verification of  $q_e$  corresponding to a unique  $c_0$  is equivalent to the verification of  $q_e$  corresponding to a unique  $c_e$ . Testing the relationship between  $q_e$  and  $c_0$  is much easier than testing the relationship between  $q_e$  and  $c_e$  as there are practical difficulties in obtaining fixed values for  $c_e$ .

Tables 1 and 2 give the experimental data (values of parallel tests) for Zn<sup>2+</sup> and Cd<sup>2+</sup> adsorption on

vermiculite at three given  $c_0$  levels. The general trend noticed in the tables is that for a given  $c_0$ ,  $c_e$  and particularly  $q_e$  remain nearly unchanged. Differences in the  $q_e$  values at given  $c_0$  levels were found to be statistically insignificant and their relative deviation (RD) values (see definition of RD below Table 1) were surprisingly low. In comparison, deviations between the measured  $c_e$  values at given  $c_0$  levels are larger. The measured values of  $c_e$  are much lower than the corresponding  $q_e$  values, so that a small measurement error will have a greater effect on RD values for  $c_e$  than for  $q_e$ . The differences in absolute values of the measured  $c_e$  for a given  $c_0$  were found to be within the allowed range of measurement accuracy.

The observed  $q_e$ - $c_e$  relationship in the tested range confirms that unless  $W_0$  is given,  $q_e$  corresponds to a unique  $C_e/W_0$  rather than to a unique  $C_e$ , and that the decline of the  $q_e$ - $C_e$  isotherm with increasing  $W_0$  is an expected result in the tested  $W_0$  range.

The physical meaning of the observed  $q_e$ - $c_e$  relation (Figs.1c and 2c, Tables 1 and 2) is that given the system volume as well as other conditions, the adsorption density is uniquely determined by the ratio of initial adsorbate concentration  $C_0$  to adsorbent concentration  $W_0$ . Therefore, as long as  $c_0$  is kept constant,  $q_e$  will be constant, irrespective of variations in  $C_0$ ,  $W_0$  or  $C_e$ . Reports concerning the relationship between the adsorbate/adsorbent ratios observed in the present study have not been found elsewhere in the

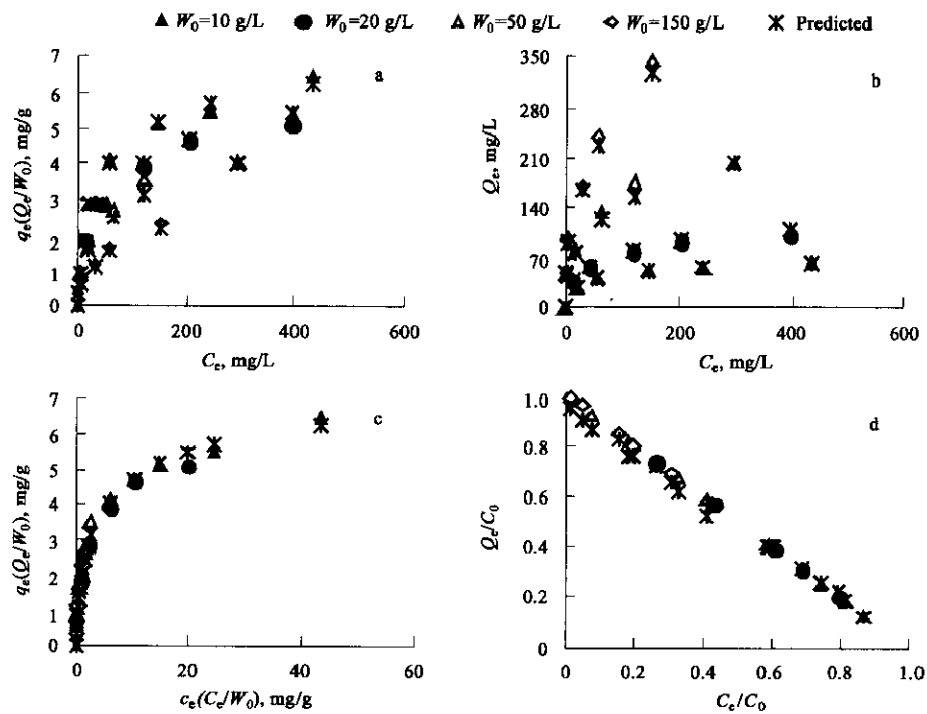


Fig.2 Adsorption of Cd<sup>2+</sup> on vermiculite at different adsorbent concentration ( $W_0$ ) levels  
a.  $q_e$ - $C_e$  plot; b.  $Q_e$ - $C_e$  plot; c.  $q_e$ - $c_e$  plot; d.  $Q_e/C_0$ - $C_e/C_0$  plot; predicted are values given by Eq. (8) with  $k=1.104$  and  $q_m=7.35$  mg/g (for symbols definitions see Appendix)

Table 1 Measured adsorbate/adsorbent ratios (Zn<sup>2+</sup>/vermiculite, temperature: 30°C)

$C_0$ , mg/L	$W_0$ , g/L	$C_e$ , mg/L	Mean $C_e$ , mg/L	$c_0(C_0/W_0)$ , mg/g	$c_e(C_e/W_0)$ , mg/g	Mean $c_e$ , mg/g	$RD(c_e)$	$q_e(Q_e/W_0)$ , mg/g	Mean $q_e$ , mg/g	$RD(q_e)$
25	50	1.48	1.46	0.5	0.030		-0.150	0.470		0.011
25	50	1.44		0.5	0.029		-0.173	0.471		0.013
40	80	2.42	2.50	0.5	0.030		-0.132	0.470		0.010
40	80	2.57		0.5	0.032		-0.078	0.468		0.006
50	100	4	3.98	0.5	0.040		0.148	0.460		-0.011
50	100	3.96		0.5	0.040		0.137	0.460		-0.010
75	150	5.89	5.88	0.5	0.039		0.127	0.461		-0.010
75	150	5.86		0.5	0.039	0.035	0.121	0.461	0.465	-0.009
50	50	8.26	8.48	1	0.165		-0.112	0.835		0.025
50	50	8.7		1	0.174		-0.064	0.826		0.015
80	80	13.89	14.18	1	0.174		-0.066	0.826		0.015
80	80	14.46		1	0.181		-0.028	0.819		0.006
100	100	17.87	19.05	1	0.179		-0.039	0.821		0.009
100	100	20.22		1	0.202		0.087	0.798		-0.020
150	150	31.02	30.98	1	0.207		0.112	0.793		-0.026
150	150	30.94		1	0.206	0.186	0.109	0.794	0.814	-0.025
100	50	28.19	28.56	2	0.564		-0.164	1.436		0.083
100	50	28.92		2	0.578		-0.142	1.422		0.072
160	80	51.15	52.62	2	0.639		-0.051	1.361		0.026
160	80	54.09		2	0.676		0.003	1.324		-0.002
200	100	74.25	73.30	2	0.743		0.101	1.258		-0.052
200	100	72.35		2	0.724		0.073	1.277		-0.037
300	150	112.06	110.18	2	0.747		0.108	1.253		-0.055
300	150	108.29		2	0.722	0.674	0.071	1.278	1.326	-0.036

Notes: For symbols definitions see Appendix;  $RD$ , relative deviation;  $RD(c_e)=(c_e-\text{mean } c_e)/(\text{mean } c_e)$ ,  $RD(q_e)=(q_e-\text{mean } q_e)/(\text{mean } q_e)$

Table 2 Measured adsorbate/adsorbent ratios (Cd<sup>2+</sup>/vermiculite, temperature: 30°C)

C <sub>0</sub> , mg/L	W <sub>0</sub> , g/L	C <sub>e</sub> , mg/L	Mean C <sub>e</sub> , mg/L	c <sub>0</sub> (C <sub>0</sub> /W <sub>0</sub> ), mg/g	c <sub>e</sub> (C <sub>e</sub> /W <sub>0</sub> ), mg/g	Mean c <sub>e</sub> , mg/g	RD(c <sub>e</sub> )	q <sub>e</sub> (Q <sub>s</sub> /W <sub>0</sub> ), mg/g	Mean q <sub>e</sub> , mg/g	RD (q <sub>e</sub> )
30	60	0.63	0.625	0.5	0.011		-0.256	0.490		0.007
30	60	0.62		0.5	0.010		-0.267	0.490		0.008
40	80	0.95	0.91	0.5	0.012		-0.158	0.488		0.005
40	80	0.87		0.5	0.011		-0.229	0.489		0.007
50	100	1.73	1.71	0.5	0.017		0.226	0.483		-0.007
50	100	1.69		0.5	0.017		0.198	0.483		-0.006
75	150	2.34	2.63	0.5	0.016		0.106	0.484		-0.003
75	150	2.92		0.5	0.019	0.014	0.380	0.481	0.486	-0.011
50	50	3.91	4.115	1	0.078		-0.082	0.922		0.008
50	50	4.32		1	0.086		0.014	0.914		-0.001
80	80	6.51	6.59	1	0.081		-0.045	0.919		0.004
80	80	6.67		1	0.083		-0.021	0.917		0.002
100	100	9	8.93	1	0.090		0.056	0.910		-0.005
100	100	8.86		1	0.089		0.040	0.911		-0.004
150	150	12.73	13.02	1	0.085		-0.004	0.915		0.000
150	150	13.31		1	0.089	0.085	0.042	0.911	0.915	-0.004
100	50	15.9	16.675	2	0.318		-0.134	1.682		0.030
100	50	17.45		2	0.349		-0.049	1.651		0.011
160	80	29.24	28.705	2	0.366		-0.004	1.635		0.001
160	80	28.17		2	0.352		-0.041	1.648		0.009
200	100	38.17	39.14	2	0.382		0.040	1.618		-0.009
200	100	40.11		2	0.401		0.093	1.599		-0.021
300	150	56.37	57.645	2	0.376		0.024	1.624		-0.005
300	150	58.92		2	0.393	0.367	0.070	1.607	1.633	-0.016

Notes: For symbols definitions see Appendix; relative deviation:  $RD(c_e)=(c_e-\text{mean } c_e)/(\text{mean } c_e)$ ,  $RD(q_e)=(q_e-\text{mean } q_e)/(\text{mean } q_e)$

literature.

2.3 Coefficient inconstancy

For describing adsorption in liquid/solid systems, the Langmuir equation is given as,

q<sub>e</sub>= q<sub>m</sub>C<sub>e</sub>/(K<sub>L</sub> + C<sub>e</sub>) (1)

where K<sub>L</sub> is the equilibrium coefficient (commonly referred to as the Langmuir constant) and q<sub>m</sub> is the adsorption capacity. When q<sub>e</sub> and q<sub>m</sub> are given in mg/g, K<sub>L</sub> has the same dimension as C<sub>e</sub> in mg/L. Establishment of the Langmuir equation was based on an assumption that at equilibrium the adsorption rate k<sub>1</sub>p(1-θ) is equal to the desorption rate k<sub>2</sub>θ,

k<sub>1</sub>p(1-θ) = k<sub>2</sub>θ (2)

where p stands for the partial pressure of gas molecules at equilibrium (which is equivalent to C<sub>e</sub> for liquid/solid systems), θ is the fraction of the adsorption sites on solid surface occupied by gas molecules at equilibrium (equivalent to q<sub>e</sub>/q<sub>m</sub> or Q<sub>e</sub>/Q<sub>m</sub>), and k<sub>1</sub> and k<sub>2</sub> are the proportionality factors for the adsorption and desorption rates, respectively

(Langmuir, 1918). Substitution of p, θ, k<sub>1</sub> and k<sub>2</sub>, respectively, by C<sub>e</sub>, q<sub>e</sub>/q<sub>m</sub> and K<sub>L</sub> (the ratio of k<sub>2</sub> to k<sub>1</sub>) into Eq. (2) will yield Eq.(1). Rewriting Eq.(1) as

C<sub>e</sub>= q<sub>m</sub>(C<sub>e</sub>/q<sub>e</sub>) - K<sub>L</sub> (3)

shows that for K<sub>L</sub> and q<sub>m</sub> being constant, C<sub>e</sub>/q<sub>e</sub> should be linearly related to C<sub>e</sub>.

The equilibrium coefficients of Eq.(3) obtained by linear correlation analysis of Zn<sup>2+</sup> and Cd<sup>2+</sup> adsorption on vermiculite are given in Table 3. The values of the squared correlation coefficient (R<sup>2</sup>) are higher than 0.938 at all adsorbent concentration levels tested. The equation parameters (K<sub>L</sub> and q<sub>m</sub>), however, are not constant and they decrease with increasing adsorbent concentration, except for K<sub>L</sub>=20.362 at W<sub>0</sub>= 10 g/L for Zn<sup>2+</sup> adsorption (Table 3). The results in Table 3 confirm that the adsorbent concentration effect is the key factor responsible for the variation of equilibrium parameters. The high R<sup>2</sup> values in Table 3 suggest that the Langmuir equation can be applied to describe the q<sub>e</sub>-C<sub>e</sub> relationship at a given adsorbent

concentration level. It will not, however, be possible to use a single Langmuir equation to fit the combined data obtained from all tested adsorbent concentration levels.

Table 3 Estimated equilibrium coefficients of Langmuir equation for zinc and cadmium adsorption on vermiculite at different adsorbent concentration levels ( temperature: 30℃)

Adsorbent concentration, g/L	Zn <sup>2+</sup>			Adsorbent concentration, g/L	Cd <sup>2+</sup>		
	<i>q<sub>m</sub></i> , mg/g	<i>K<sub>L</sub></i>	<i>R</i> <sup>2</sup>		<i>q<sub>m</sub></i> , mg/g	<i>K<sub>L</sub></i>	<i>R</i> <sup>2</sup>
10	4.260	20.362	0.998	10	6.785	59.805	0.982
50	3.387	43.087	0.996	20	5.514	37.410	0.997
100	2.391	28.498	0.993	50	4.350	27.253	0.993
133.33	2.175	16.955	0.938	150	2.358	16.372	0.951

Note: *R*<sup>2</sup>, squared linear correlation coefficient

2.4 Adsorption components

When developing his equation, Langmuir (1918) actually mentioned four interrelated components in the gas molecule adsorption system. These components in the liquid/solid system are the adsorbate in liquid phase *c*, the adsorbate on solid surface *q*, the uncovered adsorption site *w<sub>u</sub>* (or the fraction of uncovered adsorption sites 1- $\theta$ ), and the covered adsorption site *w<sub>c</sub>* (or  $\theta$ ). Considering that the adsorption is a process in which *c*, *q*, *w<sub>u</sub>* and *w<sub>c</sub>* all undergo changes with time, an ion adsorption reaction model is presented in Fig.3 for an adsorption system with unit system (*V*= 1 L) and adsorbent concentration (*W<sub>0</sub>*=1 g/L). Thus in the system, the total number of the available adsorption sites in equivalent quantity is *w<sub>0</sub>*=*W<sub>0</sub>**q<sub>m</sub>*=*q<sub>m</sub>*, and the ratio of the initial ion concentration *C<sub>0</sub>* to *W<sub>0</sub>* is *c<sub>0</sub>*=*C<sub>0</sub>*/*W<sub>0</sub>*=*C<sub>0</sub>*. Since the number of ions adsorbed onto the solid surface corresponds to the number of the covered adsorption sites, namely *w<sub>c</sub>*=*q* and thus *w<sub>u</sub>*=*q<sub>m</sub>*-*q*.

Based on the model described in Fig.3, the adsorption reaction will be

$$c + w_u = q + w_c \tag{R(1)}$$

which implies that an adsorbate in the liquid phase *c* plus an uncovered adsorption site *w<sub>u</sub>* yields an adsorbate on the solid surface *q* plus a covered adsorption site *w<sub>c</sub>*.



Fig.3 Ion adsorption reaction model proposed for a system with system volume *V*=1 L and adsorbent concentration *W<sub>0</sub>*=1 g/L (the ratio of initial ion concentration *C<sub>0</sub>* to *W<sub>0</sub>*:*c<sub>0</sub>*= *C<sub>0</sub>*/*W<sub>0</sub>*=*C<sub>0</sub>*, the total available adsorption sites: *w<sub>0</sub>*=*W<sub>0</sub>**q<sub>m</sub>*=*q<sub>m</sub>*, the model assumes that the ions in the solvent (*c*) move to the solid phase (*q*) balanced by the uncovered adsorption sites (*w<sub>u</sub>*) and covered adsorption sites (*w<sub>c</sub>*), and the adsorption equilibrium arrives at *c<sub>e</sub>**w<sub>u</sub>*=*kq<sub>e</sub>**w<sub>c</sub>*)

If there are no other substances in the system than the adsorbate, adsorbent and water, and the temperature and the volume of the aqueous system is

kept unchanged, the change in Gibbs free energy of the system at any state of the adsorption process will be,

$$\begin{aligned} dG &= dG_c + dG_{w_u} + dG_q + dG_{w_c} \\ &= d(c\mu_c + w_u\mu_{w_u} + q\mu_q + w_c\mu_{w_c}) \end{aligned} \tag{4}$$

The term  $\mu_i$  in Eq. (4) denotes the chemical potential of component *i*, which is related to the component activity *a<sub>i</sub>*, activity coefficient  $\gamma_i$  and concentration *c<sub>i</sub>* by

$$\mu_i = \mu_i^\theta + RT\ln(a_i) = \mu_i^\theta + RT\ln(\gamma_i c_i) \tag{5}$$

where  $\mu_i^\theta$  denotes the chemical potential of pure substance *i* at standard temperature and pressure, and *R* is the universal gas constant. Substituting  $\mu_i$  from Eq.(5) into Eq.(4), replacing *c*, *w<sub>u</sub>* and *w<sub>c</sub>* by *c<sub>0</sub>*-*q*, *q<sub>m</sub>*-*q* and *q*, respectively, to denote the activity of relevant components:

$$\begin{aligned} dG &= (\mu_{w_c}^\theta - \mu_{q_e}^\theta - \mu_{c_e}^\theta + \mu_{w_u}^\theta) dq + \\ &\quad RT[2\ln(q_e) - \ln(c_0 - q_e) - \ln(q_m - q_e)] dq \end{aligned} \tag{6}$$

At equilibrium changes in *G* with respect to *q* will be zero,

$$\begin{aligned} dG/dq &= \mu_{w_c}^\theta + \mu_{q_e}^\theta - \mu_{c_e}^\theta - \mu_{w_u}^\theta + \\ &\quad RT\ln(q_e^2/(c_0(q_m - q_e))) = 0 \end{aligned} \tag{7}$$

where the subscript “e” denotes the equilibrium state. For given adsorbate and adsorbent, the standard chemical potential terms are constants. Thus

$$\begin{aligned} k &= \exp((\mu_{w_c}^\theta + \mu_{q_e}^\theta - \mu_{c_e}^\theta - \mu_{w_u}^\theta)/(RT)) \\ &= c_0(q_m - q_e)/q_e^2 = (c_e w_u)/(q_e w_c) = c_e(1 - \theta)/(q_e \theta) \end{aligned} \tag{8}$$

which shows the importance of the adsorbent ratios  $\theta$  and 1- $\theta$  in maintaining the balance between *q<sub>e</sub>* and *c<sub>e</sub>*. Since the ratio  $\theta$  is dimensionless, Eq.(8) based on R (1) provides theoretical support for the observed results that *q<sub>e</sub>* corresponds to a unique *c<sub>e</sub>*.

Eq.(7) can be expressed as

$$dG/dq = \mu_{w_c} + \mu_{q_e} - \mu_{c_e} - \mu_{w_u} = \sum \mu_i = 0 \quad \text{or}$$

$$\mu_{c_e} + \mu_{w_u} = \mu_{q_e} + \mu_{w_c} \tag{9}$$

Eq.(9) states that the equilibrium condition for ion adsorption reaction is “the sum of  $\mu_{c_e}$  and  $\mu_{w_u}$  equal to that of  $\mu_{q_e}$  and  $\mu_{w_c}$ ”, which means that unless  $\mu_{w_u}$  equals  $\mu_{w_c}$ , the chemical potential of the adsorbate in liquid phase  $\mu_{c_e}$  is not equal to that in solid phase  $\mu_{q_e}$ . This explains both the observed adsorbent effect and the inconstancy of the traditionally defined equilibrium coefficient. It is known that  $\mu_i^A$  equal to  $\mu_i^B$  is the equilibrium condition for diffusion of component  $i$  from point  $A$  to point  $B$  in the same solvent. For ion adsorption, the equilibrium condition should be different since there is one more element involved in the adsorption reaction, namely, the charged surface of the adsorbent, which determines the adsorption potential. It is logical that since the adsorption is a reaction between the adsorbate and the adsorbent, the chemical potential of both the adsorbate and the adsorbent of the system should be equalized at equilibrium.

The basic idea of R(1) is the presence of four essential components in the adsorption system,  $c_e$ ,  $q_e$ ,  $w_u$  and  $w_c$ . The core part of R(1) is the assumption that these four components are of equal importance in maintaining the equilibrium state. The concentrations (or activities) of the four components are all state variables that determine the equilibrium state of the system, and a change in any of them will lead to changes in the other three, bringing the system to a new equilibrium state.

There is no essential difference between Eq. (8) and the Langmuir equation except for that in the

Langmuir equation, the desorption rate is assumed to be  $J_d = k_2\theta$ , while in Eq. (8) it is

$$J_d = k_2 q_e \theta$$

It can be argued that if the adsorption rate is related to both the adsorbate concentration in liquid phase and the fraction of the uncovered adsorption sites, the desorption rate should also be related to the adsorbate concentration in solid phase rather than uniquely depending on the amount of the covered adsorption sites. Thus at equilibrium,

$$\begin{aligned} k_1 c_e (1-\theta) &= k_2 q_e \theta \\ k &= k_2/k_1 = c_e (1-\theta)/(q_e \theta) \end{aligned} \tag{10}$$

Eq.(10) can be rewritten as

$$y = (c_e(q_m - q_e))^{1/2} = k^{1/2} q_e \tag{11}$$

which shows that  $y$  is linearly related to  $q_e$ .

The linear correlation plot of Eq. (3) for the Langmuir-type model and that of Eq.(11) for the new model are compared in Fig.4, using the combined data sets obtained at five adsorbate and four adsorbent concentration levels. It is seen from the figures that for both zinc and cadmium ions the new model fits the combined data much better than the Langmuir-type model. Values of  $q_m$  and  $k$  in Eq.(8) were estimated, respectively, as 4.65 and 1.07 for  $Zn^{2+}$  and 7.35 and 1.22 for  $Cd^{2+}$ . As already shown in Figs.1 and 2, most predicted values by Eq. (8) are very close to the measured values for both  $Zn^{2+}$  and  $Cd^{2+}$ , with relative deviations around 5%.

2.5 pH effect

Ion adsorptions in the aqueous solution can be affected by many factors. The sample pH and the ionic strength, for example, are essential as ion adsorption is

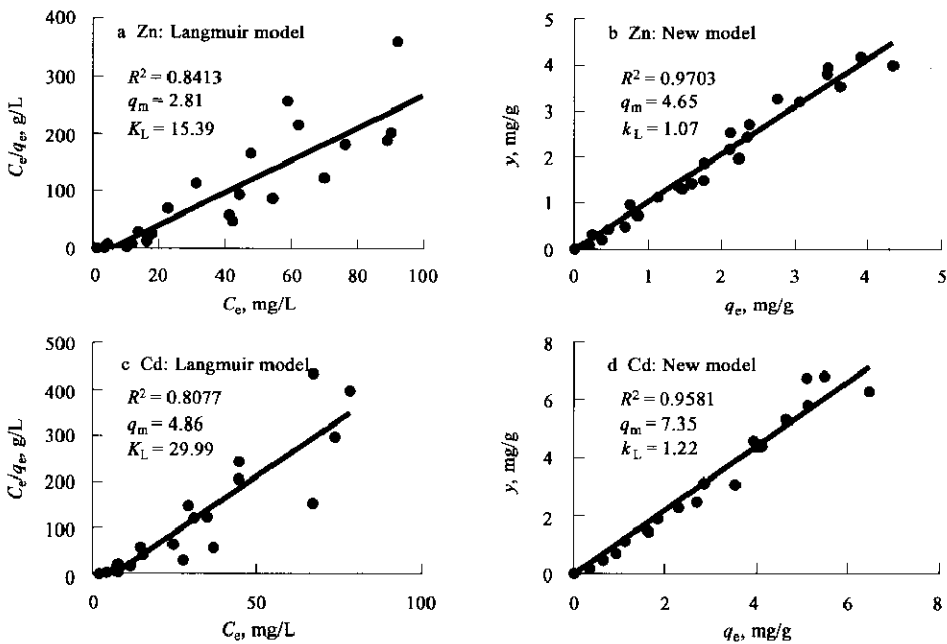


Fig.4 Linear correlation curves for the Langmuir-type model Eq.(3) and the new model Eq.(11)  
For symbols definitions see Appendix,  $y = ((C_e/W_0)(q_m - q_e))^{1/2}$  defined by Eq.(11)

governed by electrostatic factors (Greathouse and Cygan, 2005; Hao *et al.*, 2003). The common way to control sample pH and ionic strength is to introduce a buffer system by adding acids, bases and salts. In order to test the basic relationship between the adsorption components, however, the experiment was designed to exclude other substances (particularly other types of ions) from the system, as their presence might change the composition and thus the energy state of the system, causing unexpected ion interactions as well as adsorption site competition.

Data in Table 4 show that, when the sample pH was not controlled, the adsorption of  $Zn^{2+}$  and  $Cd^{2+}$  on vermiculite caused small changes in equilibrium pH with a trend towards decreasing pH with increasing initial adsorbate concentration. The slight change in pH, however, did not result in significant influence on the adsorption of both ion types and the relative deviations between the measured and predicted  $q_e$  values were low at all  $C_0$  levels (Table 4).

A series of tests of the pH effect on  $Zn^{2+}$  and  $Cd^{2+}$

adsorption were conducted by adding different amounts of sulfuric acid ( $H_2SO_4$ ) to the adsorption system, and some results are presented as examples in Table 5. It is seen from the table that the adsorption density of  $Zn^{2+}$  and  $Cd^{2+}$  remains nearly unchanged when the adjusted initial solution pH is higher than 4, but decreases quickly as the pH drops down from 4 to 2.2. The observed negative effect of the acid addition indicates that the cation adsorption can be significantly affected if high amounts of  $H^+$  ions are present in the sample solution. It is also noticed that in the sample without addition of the acid the equilibrium pH is slightly lower than its initial pH while in the sample with addition of the acid the equilibrium pH value is higher than its initial value (Table 5). This infers that the effect of pH on  $Zn^{2+}$  and  $Cd^{2+}$  adsorption is very likely a result of competition between the cations ( $Zn^{2+}$ ,  $Cd^{2+}$ ,  $H^+$ ) for available adsorption sites. Mechanisms and influences of the change in pH and ionic strength within different ranges will be topics of further studies.

Table 4 Equilibrium solution pH in samples without adjustment of pH

Initial ion concentration, mg/L		50	100	200	300	400	500
$Zn^{2+}$	pH	6.58	6.5	6.42	6.31	6.21	6.22
	Measured $q_e$ , mg/g	0.46	0.86	1.42	1.76	2.12	2.34
	Predicted $q_e$ , mg/g	0.45	0.82	1.40	1.82	2.15	2.41
	Relative deviation	-0.009	-0.042	-0.012	0.034	0.017	0.029
$Cd^{2+}$	pH	6.69	6.57	6.48	6.35	6.24	6.13
	Measured $q_e$ , mg/g	0.33	0.64	1.13	1.61	2.05	2.30
	Predicted $q_e$ , mg/g	0.32	0.62	1.14	1.59	1.98	2.33
	Relative deviation	-0.030	-0.034	0.008	-0.011	-0.034	0.010

Notes: Adsorbent conc. was 100 g/L for  $Zn^{2+}$ ; 150 g/L for  $Cd^{2+}$

Table 5 Adsorption of  $Zn^{2+}$  and  $Cd^{2+}$  on vermiculite at different pH levels

$Zn^{2+}$			$Cd^{2+}$		
Initial pH	Equilibrium pH	Adsorption, mg/g	Initial pH	Equilibrium pH	Adsorption, mg/g
6.66*	6.54	0.470	6.83*	6.70	0.481
5.21	6.51	0.465	5.70	6.58	0.477
3.56	6.41	0.436	4.50	6.60	0.474
3.20	6.12	0.413	3.84	6.40	0.470
2.87	5.71	0.316	2.73	5.87	0.402
2.24	3.73	0.070	2.22	3.50	0.108

Notes: The initial pH of the solution was adjusted by addition of sulfuric acid, initial adsorbate concentration  $C_0=50$  mg/L, adsorbent concentration  $W_0=100$  g/L, temperature: 30°C; \* values in the first row are obtained from the samples without addition of acid

3 Conclusions

The results obtained from the present study suggest that:

(1) The equilibrium adsorption density  $q_e$  will not correspond to a unique equilibrium concentration of the adsorbate in liquid phase  $C_e$  unless the adsorbent concentration  $W_0$  of the system is given. The observed phenomenon that for a given adsorption system, the adsorbate/adsorbent ratios,  $q_e$ ,  $c_e$  and  $c_0$  are related with unique values is in agreement with the theory of thermodynamics.

(2) The equilibrium state of a liquid/solid adsorption system with an even distribution of adsorbate and adsorbent should be in principle determined by four mutually related concentration components,  $c_e$ ,  $q_e$ ,  $w_0$ , and  $w_e$ . The equilibrium condition defined by the chemical potentials of the components is " $\sum \mu_i = 0$ ".

(3) The model proposed in this paper can be used for describing ion adsorption in aqueous solutions for the selected adsorbates and adsorbent in the tested range.

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Appendix

The following symbols are frequently used in the text:

- $C_0$ : the initial adsorbate concentration in liquid phase (mg/L);
- $C$ : the adsorbate concentration in liquid phase (mg/L);
- $C_e$ : the equilibrium adsorbate concentration in liquid phase (mg/L);
- $Q$ : the adsorbate quantity in solid phase per unit system volume (mg/L);
- $Q_e$ : the equilibrium adsorbate quantity in solid phase per unit system volume (mg/L),  $Q_e = C_0 - C_e$ ;
- $W_0$ : the adsorbent concentration of the system (g/L);
- $q_m$ : the adsorption capacity (ratio of maximum adsorption quantity to adsorbent quantity) (mg/g);
- $Q_m$ : the ratio of maximum adsorption quantity to system volume (mg/L),  $Q_m = W_0 q_m$ ;
- $q$ : the adsorption density (ratio of adsorption quantity to adsorbent quantity) (mg/g);
- $q_e$ : the equilibrium adsorption density (ratio of equilibrium adsorption quantity to adsorbent quantity) (mg/g),  $q_e = Q_e/W_0 = (C_0 - C_e)/W_0$ ;
- $c$ : the ratio of  $C$  to  $W_0$  (mg/g);
- $c_e$ : the ratio of  $C_e$  to  $W_0$  (mg/g);
- $c_0$ : the ratio of  $C_0$  to  $W_0$ , (mg/g),  $c_0 = (C_e + Q_e)/W_0 = c_e + q_e$ ;  $w_0$ : the ratio of the total number of the available adsorption sites to  $W_0$  (mg/g), defined as  $w_0 = W_0 q_m/W_0 = q_m$ ;
- $w_e$ : the ratio of the number of the covered adsorption sites to  $W_0$  (mg/g), defined at equilibrium as  $w_e = q_e$ ;
- $w_u$ : the ratio of the number of the uncovered adsorption sites to  $W_0$  (mg/g), defined at equilibrium as  $w_u = q_m - q_e$ ;
- $\theta$ : the ratio of adsorption density to adsorption capacity,  $\theta = q/q_m = Q/Q_m$ ;
- $\delta$ : the ratio of adsorption quantity to initial adsorbate concentration,  $\delta = q/c_0 = Q/c_0$ .

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