

Dual metal solution mapping study of competitive adsorption between cadmium and zinc in soil

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Abstract

Coherent common heavy metal Cd(II) and Zn(II) adsorption between two virgin Australian soils with different pH are studied using solution mapping in the metal concentration range up to 2×10^{-4} mol. Zn exhibited a greater affinity in single metal soil sorption system with alkaline soil PB than Cd but only marginal better in distribution behaviour in acidic soil AT. While in the competitive dual metal sorption system, the sorption preference for both metals in alkaline soil is Zn slightly over Cd, but Cd slightly over Zn in acidic soil. Furthermore, in dual metal sorption system, variations in sorption behaviour strongly in acidic soil but weakly in alkaline soil were observed suggesting competition of two metals on surfaces being dependent upon the nature of the soil.

Key Words

Adsorption, competition, soil, solution mapping, cadmium, zinc.

Introduction

Cadmium (Cd) and zinc (Zn) are heavy metals with similar chemical characteristics and mineralogical origin. Much of the physiological effect of cadmium has been attributed to chemical similarity to zinc (Hamon *et al.* 1998). Soil contamination by both metals resulted from adsorption may impact on the plant growth process and may later enter into the food chain thus posing a great health risk to humans (Alloway 1990). Cd is more mobile in the sorption process than Zn and tends to form stable ionic species in soil solution at a wide range of soil pH. Due to heterogeneity of the real surface, sorption affinity varies across the surface. The high affinity sorption sites will be occupied at low concentration, whereas at higher concentrations sites of lower affinity are also occupied. The partition coefficient of metal in soil is not constant, but depends on the conditions in the solid and the solution (Sauve *et al.* 2000). Furthermore, metal adsorption can vary significantly between the competitive systems (multiple metals present in a soil) and monometal adsorption systems (the corresponding individual metal in the same soil) (Christensen 1984).

In this work, metal a solution mapping method was used to examine adsorption behaviour of a Cd and Zn in either none competitive sorption, i.e., mono metal system or competitive dual metal system on two Australian soils with different acidity. The variation in distribution behaviour of Cd and Zn in mono and dual metal adsorption systems can be attributed to the competition between both metals in soil systems..

Methods

Materials

Two virgin soils, one acidic loamy soil and one alkaline sandy soil, were collected from different location in Australia. Both soils were sampled vertically between 0-20 cm from the A horizon. The collected samples were air dried, sieved to 2 mm fraction and stored in plastic containers in an ambient temperature before used for this study. Prior to the adsorption study, characterization of both soils was conducted (Table 1) to gain general knowledge on both soils and to ensure minimum interference from the soil substrates for adsorption results.

Sorption study

Batch studies of heavy metal sorption on both soils were performed according to widely used procedures (Ravi *et al.* 1994). 1.000 gram of less than 2 mm soil was weighed into a 50ml PE centrifuge tube followed by adding 30 ml 0.01 M $\text{Ca}(\text{NO}_3)_2$ as background electrolyte containing various concentrations of individual metal ion from 0 to 2×10^{-4} M. Samples were then equilibrated using a spinning shaker for 24 h at 25 °C. At the end of the shaking period, the suspensions were centrifuged at 3000 rpm for 30 min and filtered through

Table 1. General characteristics of the soil.

Sample name	Unit	PB	AT
Soil type		Alfisols	Ultisols
pH	in H ₂ O	7.95	3.80
	in 0.01M CaCl ₂	8.44	5.34
EC	uS/cm	520	26
CEC	cmol/kg	11	9.47
Surface Area	m ² /g	9.97	0.91
Organic Content	%	1.32	0.56
Clay content	Clay %	8.46	19
	Silt %	0.53	39
	Sand %	91	42
Soil Texture		Sandy	Loamy

a 0.22 mm Millipore filter before metal analysis. For both mono metal and mixed dual metal sorption experiments, the batch study for a particular concentration of metal was conducted simultaneously on all soils, while also using a blank sample (no soil), so that the results would be comparable. The solution before and after sorption was analysed by an Agilent 7500C inductively coupled plasma-mass spectrometer (ICP-MS) (Agilent, USA).

Calculation

For monometal adsorption study, sorption at equilibrium was fitted using the Freundlich adsorption isotherm expressed as follows:

$$C_{\text{sorb}} = k(C_{\text{soln}})^n$$

Where, $C_{\text{Pb}_{\text{sorb}}}$ is the sorbed Pb concentration in soil and $C_{\text{Pb}_{\text{soln}}}$ is the Pb concentration in solution phase. k is the slope constant and also estimated to be the partition coefficient K_d (K_d ; also known as the sorption distribution coefficient). n is a constant for a particular sorption system. For competitive dual metal adsorption, 3D graphs were used to display sorption behaviour as Freundlich adsorption isotherm is no longer suitable to describe the sorption behaviour of a competitive metal sorption.

Results

Adsorption isotherms of Cd and Zn in single metal adsorption systems are listed in Figure 1. Both metals sorption behaviour in either acidic AT or in alkaline PB are generally well fitted with Freundlich adsorption equation with correlation coefficients are all close to 1 except Zn in acidic soil AT. In the acidic soil AT, the of both metals uptake by soil showed a great mobility in solution phases with only small difference in which Zn was just slightly higher bondable to soil ($K_d=9.640$ L/kg) than Cd did ($K_d=1.211$ L/kg). In contrast, Cd and Zn uptake in alkaline soil PB showed significant changes in sorption behaviour to those in acidic soil as an increase in metal concentration in solution resulted in decreasing slope of the sorption curve. The mobility of both Cd and Zn in alkaline soil PB was reduced dramatically. The difference in partition coefficient of Cd and Zn, i.e., the distribution ratio between solid and soil solution, in alkaline soil is 174 and 180 times greater than for corresponding metals uptake by acidic soil. The difference for Zn and Cd uptake in acidic soil was relatively small, but it became much larger for both metals in the alkaline soil PB which showed about 15 times more Zn adsorbed in PB than for Cd.

The variation in metal concentration in soil phases among mixed dual metal adsorption in acidic soil and alkaline soil are displayed as 3D graphs in Figure 2. In addition, a mesh surface provides information regarding the trend of variation in individual metal concentration in the system. The distribution behaviour of both metals in solid phase in alkaline soil displayed a similar behaviour. If the total Zn concentration in soil remains constant, increase total Cd concentration in soil will result in increases in amount of Zn or Cd sorbed in soil. The similar trend was also observed when total Cd concentration remains constant with increasing total Zn concentration. At constant high concentration of total Cd; however, uptake of Cd soil was deviated slightly from a linear increase with a slight drop in uptake but increased as total Zn concentration increased further. In fact, a similar variation in Zn uptake in soil at high total Zn concentration was also observed at a much smaller extent. This kind of variation beyond normal adsorption behaviour (single metal adsorption) implies interference from other factors to reduce the sorbed metal species in the soil phase. Much greater variation in the soil phase for uptaked both metal were exhibited. When the total Zn concentration in the

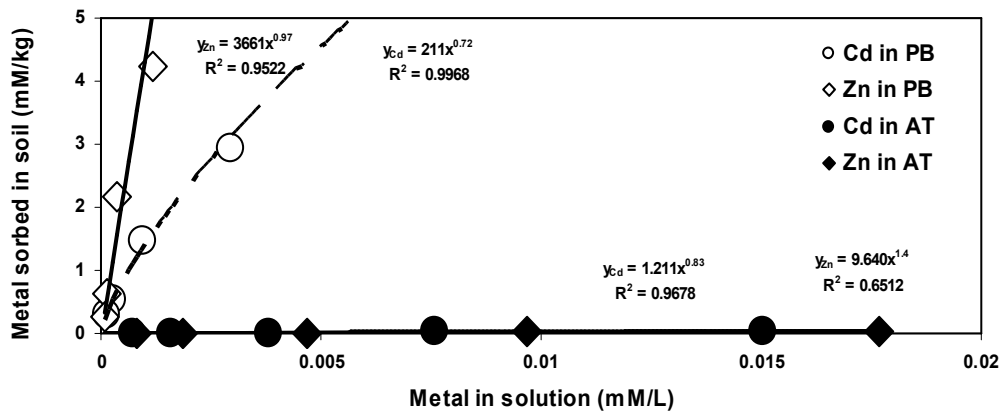
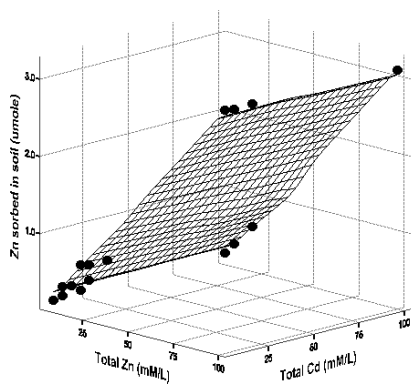
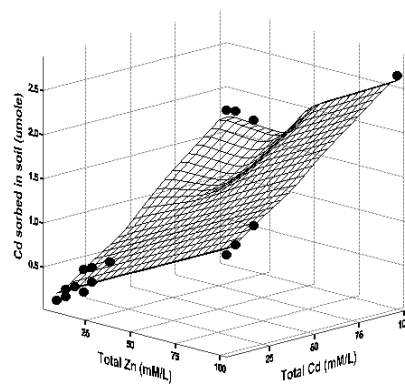


Figure 1. Variation in adsorption behaviour of single metal Cd and Zn sorbed on acidic soil AT and alkaline soil PB.

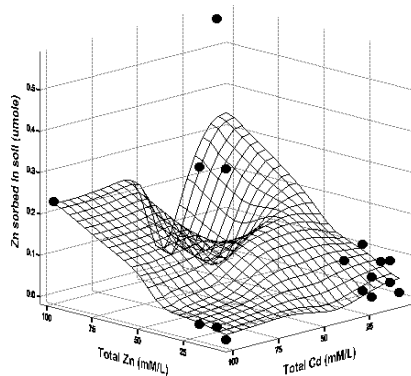
system remains constant with increase in total Cd concentration, the sorbed Zn will decrease slowly at low total Zn concentration but drop dramatically in uptake of Zn when the total Zn concentration becomes high (10^{-4} M total Zn). Under the similar condition for both Cd and Zn, the Cd sorption will generally increase. In contrast, when total Cd concentration remain constant with an increase in total Zn concentration, the adsorbed Zn in soil will increase nearly linearly at low total Zn concentration until total Cd concentration become very high (10^{-4} M Zn) with a big jump in adsorbed Zn. Adsorbed Cd in soil under the same conditions did not change a lot until the total Cd concentration was very high (10^{-4} M) so that Cd uptake changed from very high to dropping sharply and increasing again at high total Zn concentration (Figure 3D). As no such a distribution behaviour occurred for the single Cd sorption system or at low total Cd concentration, it is most likely due to present of large amount of Zn in soil preventing the normal adsorption process, i.e. metal competition in the sorption system.



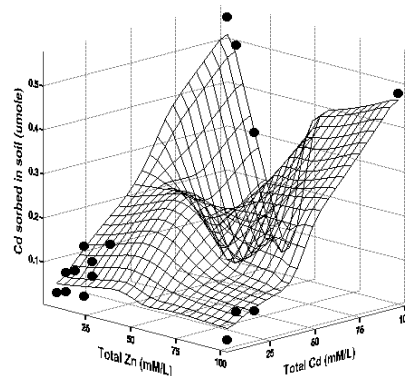
Zn sorbed in alkaline soil



Cd sorbed in alkaline soil



Zn sorbed in acid soil



Cd sorbed in acid soil

Figure 2. Cd-Zn competition for acidic soil and alkaline soil

Conclusions

The adsorption behaviour of Cd(II) and Zn(II) onto two virgin Australian soils with different pH was studied. Zn exhibited a greater affinity with alkaline soil PB ($K_d=3661$ kg/L) than Cd ($K_d=211.1$ kg/L) but much lower reactivity in acidic soil AT with only a marginal difference in distribution behaviour between Zn ($K_d=9.641$ kg/L) and Cd ($K_d=1.211$ kg/L). For the competitive dual metal sorption system, the sorption preference for both metals in alkaline soil is Zn slightly over Cd, but Cd slightly over Zn in acidic soil. Furthermore, for the dual metal sorption system, variations in sorption behaviour were strong in acidic soil but weakly in alkaline soil suggesting competition of two metals was dependent upon the nature of the soil.

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