

Effect of ionic strength on cadmium adsorption onto kaolinite in single- and multi-element systems

Prashant Srivastava^{A, B}, Balwant Singh^C

^A Faculty of Agriculture, Food and Natural Resources, University of Sydney, NSW 2006, Australia

^B Current Address: Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, Environmental Sciences Building (X), University of South Australia, Mawson Lakes, SA 5095, Australia, Email Prashant.Srivastava@crccare.com

^C Faculty of Agriculture, Food and Natural Resources, University of Sydney, NSW 2006, Australia, Email Balwant.Singh@sydney.edu.au

Abstract

Cadmium (Cd) adsorption on kaolinite was studied at three ionic strengths (I) viz., 0.01, 0.1 and 0.5 using NaNO_3 as a background electrolyte and at an equilibrium pH 6. Applied concentration of Cd ranged from 16.7 to 950.0 μM in the single-element system, whereas, applied concentration of Cd and other metals (Cu, Pb and Zn) ranged from 4.2 to 237.5 μM each in the multi-element system. Cd adsorption increased with increase in equilibrium concentration at any ionic strength and decreased with increase in ionic strength at any given equilibrium concentration in both single- and multi-element systems. At $I = 0.5$, the adsorption isotherm approached linearity, whereas, at $I = 0.01$, the adsorption isotherms reached a plateau at higher equilibrium concentrations in both single- and multi-element systems. The difference between Cd adsorption $I = 0.5$ and $I = 0.1$ was greater in the single element system than the multi-element system. A similar pattern was observed for difference between Cd adsorption at $I = 0.1$ and $I = 0.01$, however the magnitude of the difference was much greater in the latter case.

Key Words

Cadmium, adsorption, kaolinite, ionic strength

Introduction

Cadmium is one of the most toxic and commonly occurring heavy metals in contaminated environments. Use of phosphatic fertilizers in crop production is the major source of Cd contamination in agricultural soils (Syers and Cisse 2000). Other sources of Cd contamination in soils include metal plating, smelting and mining industries, cadmium-nickel battery manufacturing, paints and pigments and alloy industries (Kadirvelu and Namasivayam 2003). Cadmium is known to have toxic effects on plants, animals and humans even at low concentrations (Nriagu 1980). For example, Cd poisoning causes damage to lung, liver and kidney, bone lesions, cancer and hypertension, and dreaded *itai-itai* disease (ATSDR 1999).

Clay minerals in soils act as a natural scavenger of contaminants from soil through various ion exchange and adsorption-desorption reactions (Singh *et al.* 2000; Jobstmann and Singh 2001). Kaolinite is a 1:1 non-swelling clay mineral that is predominant in tropical weathered soils, and can exist as mobile or immobile colloid (Kaplan *et al.* 1995). Factors such as pH, ionic strength, equilibration period, temperature, adsorbate and competing ions are very critical in governing the adsorption behaviour of Cd in soils (Srivastava *et al.* 2005). Under a given set of conditions, Cd can be expected to behave differently when it is present in single- and multi-element systems due to varied degrees of competition in the system. The effects of factors other than ionic strength have been studied widely on various substrates; however, information on the ionic strength effects on metal adsorption on kaolinite is scarce, especially in multi-element systems (Srivastava 2005). In the present study, Cd adsorption on kaolinite as a function of ionic strength was studied in the single-element system, when Cd was present alone, and in a multi-element system, when Cd was present along with other commonly occurring heavy metals - Cu, Pb and Zn.

Methods

Cadmium adsorption isotherm experiments were conducted in single- and multi-element systems at three ionic strengths (I) viz., 0.01, 0.1 and 0.5, using 6.67 g/L kaolinite and NaNO_3 as the background electrolyte at pH 6. Cadmium concentration was varied between 16.7 and 950.0 μM in the single-element system and Cd, Cu, Pb and Zn concentrations varied between 4.2 and 237.5 μM each in the multi-element system. The molar concentration of each metal in the multi-element system was a quarter of the Cd concentration in the single-element system, and therefore the total metal concentration remains the same (16.7 to 950.0 μM) in both systems. This was done to evaluate the competition between Cd and other metals at similar total metal

concentrations for adsorption sites. The mineral and metal(s) suspension was stirred for 1 h after which a 10 mL aliquot was removed from the suspension. The removed aliquot was centrifuged at 3000 rpm for 20 min and filtered through Whatman No. 1 filter paper. Concentrations of Cd and other metals in the supernatant solutions were analysed using flame-atomic absorption spectrometer (Varian SpectraAA-220FS).

Results and discussion

Cadmium adsorption increased with increase in equilibrium concentration for all ionic strengths and decreased with increase in ionic strength at any given equilibrium concentration in both single- and multi-element systems (Figure 1). At the highest ionic strength ($I = 0.5$), Cd adsorption isotherms approached linearity in both single- and multi-element systems. At the intermediate ionic strength ($I = 0.1$), Cd adsorption followed a linear path, when present alone at equilibrium concentrations of up to 0.8 mM, after which the adsorption curve appeared to plateau, however, in the multi-element system, Cd adsorption did not reach plateau even at the highest equilibrium Cd concentration used in the experiment. At the lowest ionic strength ($I = 0.01$), Cd adsorption in both single- and multi-element systems appeared to plateau after a rapid initial adsorption for equilibrium concentrations of up to 0.3 mM in the single-element system, and for concentration up to 0.06 mM in the multi-element system.

The difference in the amount of Cd adsorbed at $I = 0.5$ and $I = 0.1$ was greater in the single-element system than in the multi-element system. Similar pattern occurred for the difference between Cd adsorption at $I = 0.1$ and $I = 0.01$, however, the magnitude of the difference was much greater in the latter case, which could be attributed to the difference in the ionic strength, and a well established fact that the lower the ionic strength, the greater the metal adsorption.

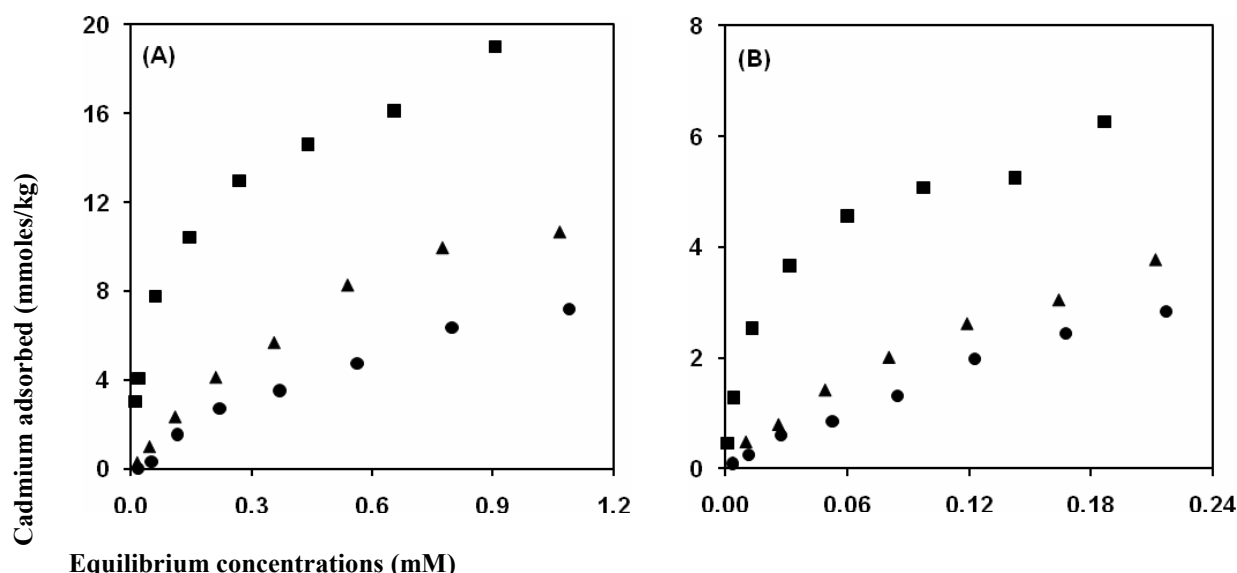


Figure 1 Cadmium adsorption isotherms in (A) single- and (B) multi-element (Cd, Cu, Pb and Zn) systems as a function of ionic strength ($I = \blacksquare$ 0.01, \blacktriangle 0.1 and \bullet 0.5). The equilibrium pH of the system was 6 and the background electrolyte was NaNO_3 . The metals were introduced in the solution in their nitrate forms.

The decrease in Cd adsorption in the single-element system due to increase in ionic strength of the equilibrium solution could be attributed to increased competition for adsorption sites between Cd^{2+} ions and Na^+ ions present in the background electrolyte (Doula *et al.* 2000). In the multi-element system in addition to competition from Na^+ ions, Cd experienced increased competition with other metals (Cu, Pb and Zn) present in the system, which tended to adsorb more strongly at kaolinite surface at pH 6 (Srivastava *et al.* 2005). Additionally, increase in solution ionic strength could have led to the formation of ion pairs between Cd^{2+} and other cations and anions (NO_3^-) present in the electrolyte that reduced the activity of free Cd^{2+} ions in the solution, especially in the multi-element system (Guo-Song 1994; Mattigod *et al.* 1979).

Conclusion

Cadmium adsorption decreased with increase in ionic strength, and behaved differently in single- and multi-element systems. The study showed that Cd availability might vary when it is present alone, or mixed with other metals, cations and anions, which is generally expected in the contaminated soil environments. Since typical contaminated sites often contain multitude of cations and anions, the physico-chemical properties of

soil solution, such as pH, electrical conductivity and ionic strength must be taken into account in predicting Cd availability and devising different remediation strategies for a given contaminated site.

References

- ATSDR (1999) Toxicological profile for cadmium, US Department of Health and Human Services, Public Health Services (Agency for Toxic Substances and Disease Registry), Atlanta, GA.
- Doula M, Ioannou A, Dimirkou A (2000) Thermodynamics of Copper Adsorption-Desorption by Ca-Kaolinite. *Adsorption* **6**, 325-335.
- Guo-Song H (1994) Adsorption kinetics of Pb^{2+} and Cu^{2+} on variable charge soils and minerals: V. effects of temperature and ionic strength. *Pedosphere* **4**, 153-164.
- Jobstmann H, Singh B (2001) Cadmium sorption by hydroxy-aluminium interlayered montmorillonite. *Water Air and Soil Pollution* **131**, 203-315.
- Kadirvelu K, Namasivayam C (2003) Activated carbon from coconut coirpith as metal adsorbent: adsorption of Cd(II) from aqueous solution. *Advanced in Environmental Research* **7**, 471-478.
- Kaplan DI, Bertsch PM, Adriano DC (1995) Facilitated transport of contaminant metals through an acidified aquifer. *Ground Water* **33**, 708-718.
- Mattigod SV, Gibali AS, Page AL (1979) Effect of ionic strength and ion pair formation on the adsorption of nickel by kaolinite. *Clays and Clay Minerals* **27**, 411-416.
- Nriagu JO (1980) Cadmium in the Environment. John Wiley and Sons, New York.
- Singh B, Alloway BJ, Bochereau FJM (2000) Cadmium sorption behavior of natural and synthetic zeolites. *Communications in Soil Science and Plant Analysis* **31**, 2775-2786.
- Srivastava P (1995) Competitive adsorption-desorption of Cd, Pb, Cu and Zn on kaolinite. PhD Thesis. University of Sydney, Australia.
- Srivastava P, Singh B, Angove M (2005) Competitive adsorption behaviour of heavy metals onto kaolinite. *Journal of Colloid and Interface Science* **290**, 28-38
- Syers JK, Cisse L (2000) Regional differences in the inputs of cadmium to soils. In 'SCOPE Workshop on Environmental Cadmium in the Food Chain: Sources, Pathways, and Risks'. Belgian Academy of Sciences, Brussels, 13-16 September, 2000.