Adsorption and Desorption of Thallium(I) by Soils

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INTRODUCTION

Thallium is highly toxic and the annual release of Tl to the environment is estimated to be 2000-5000 t. In Taiwan, the application of Tl in semiconductor and optoelectronic industries have resulted in the occurrence of elevated levels of Tl in farmland soils near those industrial areas. However, the maximum contamination level of Tl has not been regulated by the Environmental Protection Agency due to its unknown environmental risk.

Adsorption reaction plays an important role in determining the mobility and bioavailability of contaminants in soils. However, to the best of our understanding, the adsorption of Tl by soils and the key factors determining the adsorption reaction have not been understood. In this study, the adsorption reactions of Tl by permanent-charge and pH-dependent-charge soils were investigated. Permanent charges come from isomorphic ionic substitution in the structure of clay minerals and are unaffected by the change of soil pH (Sposito, 2008). Comparatively, pH-dependent charges result from the proton association and dissociation of surface functional groups on soil particles and are subject to the change of soil pH. These two types of soils were presumed to exhibit different Tl(I) adsorptivity due to their differences in their surface charge properties. Therefore, in this research, adsorption and desorption of Tl(I) by soils with different charge properties were investigated to provide information that is critical for understanding the environmental risk of Tl in soil.

MATERIALS AND METHODS

Adsorption experiment

(a) Permanent-charge soils

Chang-bin (Cp), Tung-wei (Btw) and Chih-shang (CS).

(b) pH-dependent charge soils

Lu-tsuo (Lv), Chen-tsuo (Ce) and Pu-sin (Pu)

- 0.1 g Soil sample + 20 mL of varying concentrations of Tl in 0.01 M $NaNO_3$ solution.
- Initial concentrations:

  Permanent-charge soils: Tl ranged from 0 to 3 mM.

  pH-dependent charge soils: Tl ranged from 0 to 1.2 mM

Desorption experiment

- After adsorption experiment, the desorption experiments were conducted immediately.
- Using 10 mL 0.01 M $NaNO_3$ re-suspended the residues and shake for 2 hr. Then the suspensions were centrifuged and 10 mL supernatant was withdrawn from the tube .This process was repeated five times.
- Using AAs to determine the equilibrium Tl concentration after each desorption step.

RESULTS AND DISCUSSION

Tl adsorption isotherms

- Adsorption capacities:

  Permanent-charge soils > pH-dependent charge soils
- The max adsorption capacities (q_{max})

  CS > Btw > Cp
- The ratio of Tl(I) adsorption maximum to CEC of soils:

  Permanent-charge soils: about 0.5 to 0.6

  pH-dependent charge soils: about 0.2 to 0.4

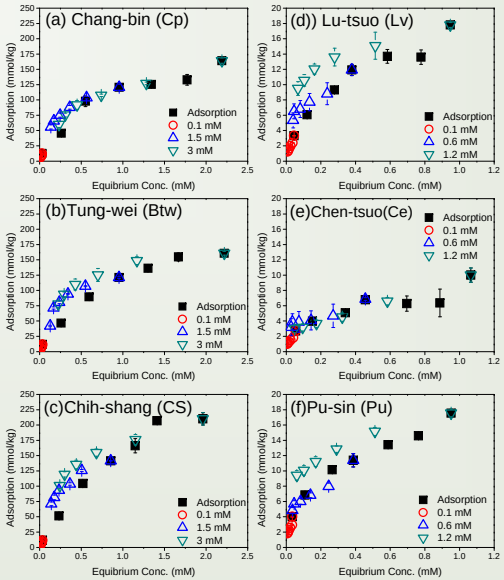

Fig. 1. Thallium adsorption isotherms and desorption isotherms in permanent-charge and pH-dependent-charge soils.

Table 1 The parameter values for Lagmuir equation by fitting on Tl adsorption isotherms in permanent-charge soils system and pH-dependent charge soils systems.

	Lagmuir Isotherm			CEC	q_{max}/CEC
	q_{max} (mmol/kg)	K_L	R^2	(mmol/kg)	
Cp	202.15±18.46	1.50±0.40	0.96	369	0.55
Btw	219.56±14.16	1.27±0.21	0.98	430	0.51
CS	340.41±31.37	0.88±0.16	0.96	320	1.06
Lv	21.17±2.19	3.30±0.96	0.95	55	0.38
Ce	9.67±1.82	4.21±2.89	0.84	43	0.22
Pu	19.67±1.71	4.60±1.40	0.96	67	0.29

Tl desorption isotherms and hysteresis coefficient

- Hysteresis:

  $n_{des}/n_{ads} \leqq 1$, reversible

  Low initial concentration < High initial concentration

Table 2 The parameter values for Freundich equation by fitting on Tl adsorption and desorption isotherms in permanent-charge soils system and pH-dependent charge soils systems.

	Freundlich Isotherm			
Soil	Initial conc. (mM)	n_d	n_d/n_a	R^2
Cp	0.1	1.62±0.21	0.98±0.17	0.951
	1.5	2.59±0.17	1.56±0.19	0.987
	3.0	2.39±0.21	1.60±0.19	0.990
Btw	0.1	1.20±0.11	0.78±0.10	0.973
	1.5	2.20±0.57	1.43±0.39	0.826
	3.0	3.22±0.43	2.09±0.34	0.947
CS	0.1	1.12±0.05	0.83±0.06	0.994
	1.5	2.66±0.23	1.98±0.23	0.978
	3.0	3.06±0.26	2.27±0.26	0.978
Lv	0.1	1.82±0.24	0.96±0.17	0.950
	0.6	3.37±0.56	1.77±0.37	0.920
	1.2	4.29±0.17	2.26±0.22	0.995
Ce	0.1	2.37±0.43	0.89±0.27	0.908
	0.6	4.81±1.40	0.85±0.42	0.896
	1.2	2.54±0.45	0.95±0.29	0.911
Pu	0.1	2.21±0.51	0.94±0.22	0.855
	0.6	3.25±0.56	1.39±0.25	0.916
	1.2	4.25±0.26	1.82±0.15	0.989

CONCLUSIONS

- The max adsorption capacities of permanent-charge soils are much higher than those of pH-dependent charge soils.
- The adsorption/desorption hysteresis of Tl(I) indicates that Tl(I) is more mobile at lower concentrations.
- The reversibility of Tl(I) adsorption reveals a high environmental risk of Tl(I) pollution in soil.