

## Removal of $\text{Co}^{2+}$ , $\text{Sr}^{2+}$ and $\text{Cs}^+$ from aqueous solution by phosphate-modified clay

Bin Ma, Won Sik. Shin\*, Sang-June. Choi  
 Kyungpook National University, Daegu702-701, Korea  
 (E-mail: phonix311@hotmail.com)

### 1. Introduction

The removal of radionuclides, such as Co, Sr and Cs which are frequently released from nuclear industrial wastewater (Low Level Radioactive water) is one of the most important issues of environment remediation. They will contaminate soil and groundwater if without any treatment, accumulate in food chain and have harmful effect on human health. As a result, numerous technologies have been applied in the removal of radionuclides [1]. Sorption is considered to be one of the most common processes for removal of heavy metal from wastewater and accordingly many types of adsorbents have been developed. Among the adsorbents, clays have been widely used due to their high specific surface area, high chemical and mechanical stability, and a variety of surface and structural properties. Montmorillonite is the main component of bentonite, which has 2:1 structure and permanent negative charge on their surfaces resulting from the isomorphous substitution of central atoms in the octahedral/tetrahedral by cations of lower valence. It has been proved to Montmorillonite have excellent performance of removal of heavy metals. Nevertheless, Montmorillonite can only provide weak affinity and have low metals holding capacity for metal ions compared with other adsorbents. However, this property can be improved by the modification.

Recent research suggests that chemically modified clay minerals represent a new and promising class of adsorbents for water purification and industrial wastewater treatment [2]. Modification with organic or inorganic matters has gained an attention because they can improve the structure and metal ion holding capacity. Modification of the clay by phosphate can enhance the cation-exchange capacity (CEC) of clay. The simple but cost effective method of modifying clay with phosphate has made phosphate-modified clay (PMC) a promising adsorbent in the removal of metal ions from aqueous solutions.

### 2. Materials and Methods

#### 2.1 Modification of clay sample

Clay samples (15g) were equilibrated with 1L of 2000 mg/L of  $\text{PO}_4^{3-}$  (from  $\text{KH}_2\text{PO}_4$ ) by rotary agitating for 24 h at room temperature. Thereafter, the clay samples were washed three times with 1L distilled and deionized water in order to remove excess  $\text{H}_2\text{PO}_4^-$  ions and then dried at 323K in an oven for 24 h.

#### 2.2 Single-solute adsorption

For sorption of single-solute metal ions, 1g PMC was mixed with 50mL of different concentrations of Sr, Co and Cs solutions in 50ml conical centrifuge tube (PE, SPL labware). The initial concentrations were ranged from 1 to 20mM. The pH was adjusted approximately to 5 using MES buffer solution. The dispersion was placed on a rotary shaker for 24h under 25°C. The supernatant obtained after centrifugation was analyzed by ICP-OES (PerkinElmer Optima 2100DV). The amount adsorbed was calculated by concentration difference.

#### 2.3 Bi-solute adsorption

Competitive sorption method was conducted following the same method of single sorption except that solution contains binary metal ions. The objective of competitive adsorption is to test the affinity of phosphate-modified clay for different metal ions in the mixed solution.

### 3. Results and discussions

#### 3.1 Single-solute adsorption

The increasing initial concentration from 1mM to 20mM resulted in an increase in the metal ions adsorbed on phosphate-modified clay. The adsorption behaviors of Co and Sr were similar to each other but different from Cs. The sorption affinity of Cs was higher than that of Co and Sr. The amount of adsorption by the PMC followed the order:  $\text{Cs} > \text{Co} > \text{Sr}$ .

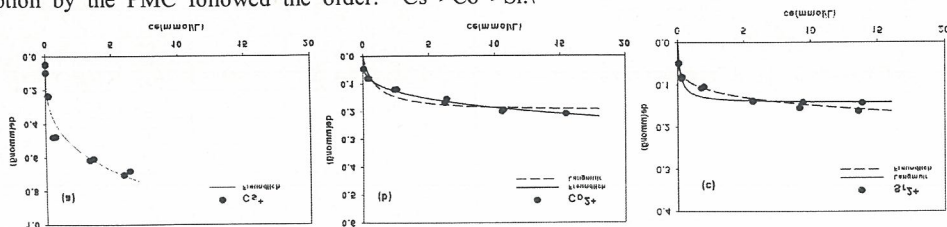


Fig.1 isotherm of adsorption of (a)  $\text{Cs}^+$ , (b)  $\text{Co}^{2+}$  and (c)  $\text{Sr}^{2+}$  on phosphate-modified clay

Table.1 parameters of single-solute adsorption of Cs<sup>+</sup>, Co<sup>2+</sup> and Sr<sup>2+</sup> fitted by Freundlich and Langmuir

	Freundlich			Langmuir		
	K	n	R <sup>2</sup>	q	b	R <sup>2</sup>
Cs	0.4348±0.0207	0.2751±0.0296	0.9859	-	-	-
Co	0.0997±0.0025	0.2726±0.0113	0.9985	0.2021±0.0146	1.1219±0.4439	0.9763
Sr	0.0957±0.003	0.1919±0.0149	0.9961	0.1434±0.006	5.0197±1.3317	0.9873

### 3.2 Bi-solute adsorption

The adsorption of Cs on PMC was not affected by the presence of Sr but by Co. This indicates that the adsorption behavior of Co and Cs is similar in some extent. Cs has very small hydration energy, thus the electrostatic attraction of Cs ions by clay particles is large and therefore are preferentially sorbed [3]. In addition to the dependence of Cs adsorption on phyllosilicate minerals, Cs adsorption was strongly correlated with CEC of the adsorbent [4]. The adsorption behavior of Co was not affected when Sr existed. It can be explained by the different mechanism of adsorption of Co and Sr on clay [5-6].

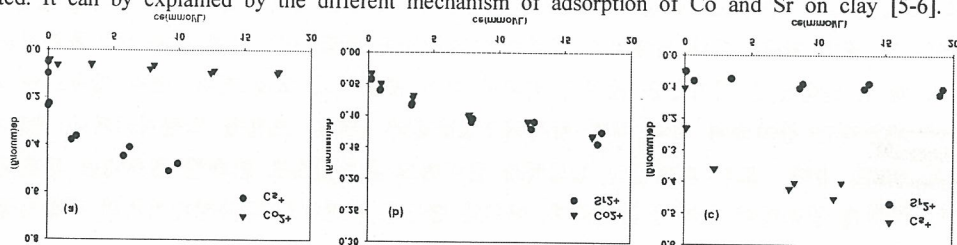


Fig.2 Bi-solute isotherm adsorption of (a) Co<sup>2+</sup>&Cs<sup>+</sup>, (b) Co<sup>2+</sup>&Sr<sup>2+</sup> and (c) Cs<sup>+</sup>&Sr<sup>2+</sup> on phosphate-modified clay

### 4. Conclusion

Modification of montmorillonite with phosphate has improved the adsorption ability. The PMC showed a high affinity for Cs and reach high amount of equilibrium (0.7mmol/g). The sorption of Cs is slightly affected by Sr or Co. This indicates the sorption mechanisms of Co, Sr and Cs have something in common.

### Acknowledgement

This research was supported by Korea Science and Engineering Foundation (KOSEF) grant funded by the Korean government, the Ministry of Education, Science and Technology (grant number: M20706000036-07M0600-03610).

### References

- [1] F. Giannakopoulou. Sorption behavior of cesium on various soils under different pH levels, *J. Hazard. Mater.*, 149 (2007) 553-556.
- [2] P. Malakul. Metal adsorption and desorption characteristics of surfactant-modified clay complexes, *Ind. Eng. Chem. Res.*, 37 (1998) 4296-4301.
- [3] N. L. Hakem. Sorption of cesium and strontium on Hanford soil, *J. Radioanal. Nucl. Chem.*, 246 (2000) 275-278.
- [4] A. Grutter. Sorption, desorption and exchange of cesium on glaciofluvial deposits, *Radiochim. Acta*, 50 (1990) 177-184.
- [5] N. Lu. Sorption-desorption behavior of strontium-85 onto montmorillonite and silica colloids. *Appl. Geochem.*, 16 (2001) 1653-1662.
- [6] L. Chen. Sorption and desorption of radiocobalt on montmorillonite-effects of pH, ionic strength and fulvic acid, *Water Res.*, 66 (2008) 288-294.