Separation of Clay Minerals Using Polyethylenimine-coated Magnetic Nanoparticles

June-Hyun Kim[1,2], Sung-Man Kim[1], In-Ho Yoon[1], Sang-June Choi[2], and Il-Gook Kim[1,*]

[1] Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, Republic of Korea

[2] Kyungpook National University, 80, Daehak-ro, Buk-gu, Daegu, Republic of Korea

[*]ilgook@kaeri.re.kr

1. Introduction

Radioactive Cs released by nuclear accident such as Fukushima Daiichi Nuclear has resulted in severe soil contamination. According to Horie et al. (2017), after Fukushima Daiichi Nuclear accident, the total quantity of contaminated soils discharged through the work is expected to be 16~22 million m^3 [1].

Radioactive Cs was mainly adsorbed on topsoil within 5 cm of the area round due to strong affinity with clay minerals. It was reported that clays account for approximately 7% within the surface 10 cm of the soil near to the Fukushima area [2]. Therefore, separation of clay minerals from soil is necessarily needed for soil waste volume reduction.

Cs is strongly and selectively adsorbed onto especially 2:1 type clay minerals such as illite (ILT) that have high selective adsorption property of Cs, due to their negatively charged surface and frayed edge site.

For selective clay mineral separation, the surface properties of clay minerals are considered for a key role. Therefore, the surface-modified magnetic nanoparticles (MNPs) by polyethylenimine (PEI) which is known for its high density of positive charge, were used to separate clay mineral having a negative charge. PEI-coated magnetic nanoparticles were applied to separate clay mineral. Also, several primary parameters that affect the separation of clay mineral were investigated.

2. Materials and Methods

2.1 Synthesis of Naked MNPs

Naked MNPs were synthesized by co-precipitation method. The concentration of MNPs suspension were represented by the concentration of the total Fe determined by contrAA 700 (F-AAS).

2.2 Synthesis of PEI-coated MNPs

1 mL of 5% (w/w) PEI solution was mixed with different mass ratio (0.01:1, 0.02:1, 0.04:1, 0.05:1, 0.06:1, 0.08:1, 0.1:1) of MNPs solution, and the mixture was sonicated for 30 min. In order to remove residual PEI, PEI-MNPs were separated from the solution by magnetic separation and washed with DI water for seven times.

2.3 Clays Separation

The naked MNPs and PEI-MNPs were mixed with different mass ratio (0.005:1, 0.01:1, 0.05:1, 0.1:1, 0.2:1, 0.4:1, 0.8:1, 1:1) of clay mineral (ILT). Clay separation efficiency (SE%) was calculated using SE% =100% - ($m_f/m_0 \times 100\%$), where m_0 is the initial clay mineral mass in the suspension and m_f is the final clay mineral mass in the suspension.

3. Results and Discussion

3.1 MNPs Physicochemical Properties

Increasing PEI to MNPs mass ratio, zeta potential of PEI-coated MNPs have more and more positive charge, which is maximum level at the 0.1 of PEI to MNPs mass ratio (Fig. 1 (a)). Also, PEI-coated

MNPs (mass ratio 0.1) have positive charge at a wide pH range, whereas naked MNPs have positive charge above pH 6, and clay mineral has negative charge (Fig. 1 (b)). These results imply that PEI-coated MNPs are likely to adsorb on clay mineral because of the electrostatic attraction against naked MNPs.

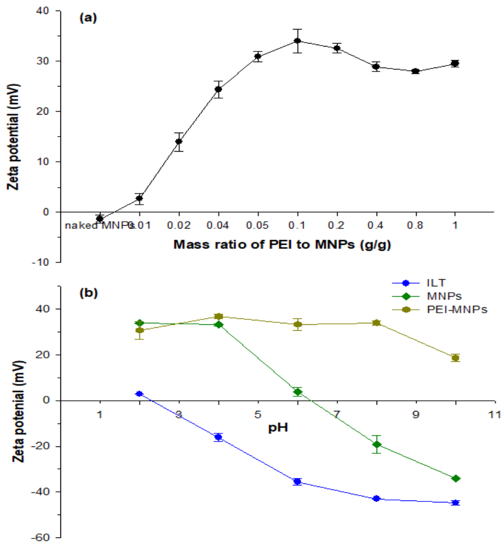

Fig. 1. Zeta potentials of (a) PEI-MNPs at different mass ratio of PEI to MNPs (g/g) at pH 7, (b) naked MNPs, PEI-MNPs (mass ratio 0.1) and clay mineral at different pH.

3.2 Effect of PEI Coating on Clays Separation.

Fig. 2 indicates that the separation efficiency (SE%) of clay minerals increased with the increase of the mass ratio between the both naked MNPs or PEI-MNPs and clay minerals.

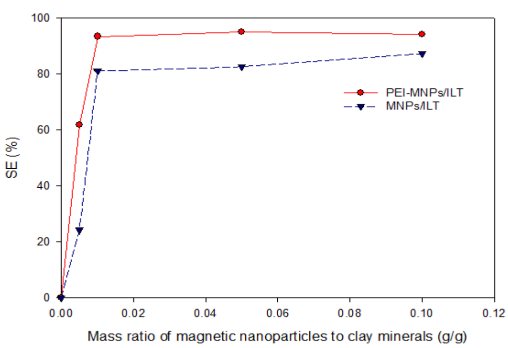

Fig. 2. Clay separation efficiency (SE%) as a function of the mass ratio of magnetic nanoparticles to clay minerals at pH 7. The initial clay mineral mass was 50 mg.

When the mass ratio of naked or PEI-coated MNPs to ILT was 0.01 and 0.1 g/g, the maximum separation efficiency of 94.3% and 87.3% was achieved, respectively. This result shows that the PEI coating significantly reduces the dose demand to separate clay minerals compared to naked MNPs.

4. Conclusion

PEI-coated MNPs which were synthesized at 0.1 of the mass ratio (g/g) PEI to MNPs to separate clay minerals. When the mass ratio PEI-MNPs to clay mineral exceeded 0.1 g/g, maximum separation efficiency was obtained. Hence, the PEI-coated MNPs with magnetic separation provide a promising method for efficient separation of clay minerals.

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