플라이애쉬와 굴패각을 이용한 중금속 이온의 흡착특성에 관한 연구
Sorption Characteristics of Heavy Metal Ions on Fly Ash and Oyster Shell

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SYNOPSIS : 본 연구에서는 대표적인 산업부산물인 굴패각과 플라이애쉬를 활용한 흡착제를 개발하여 중금속 이온의 제거 기작을 평가하였다. 1차적으로 연구된 중금속 이온은 카드뮴, 납, 구리이며, 산업부산물을 활용하여 흡착특성을 평가하였고, 동시에 현장 적용성을 모사하기 위해 점성토와 화강풍화토에 대한 흡착실험도 함께 수행하여 각각의 흡착특성을 비교·평가 하였다. 실험 결과를 등온흡착식으로 분석하여본 결과 굴패각의 경우 카드뮴, 납, 구리이온의 용액 내 제거율이 해성점토나 화강풍화토를 사용한 흡착제에 비해 우수하므로 흡착제로서의 사용 가능성을 확인할 수 있었다.

Key words : sorption, heavy metal, byproducts, oyster shell, fly ash.

1. Introduction

Environmental pollution problems due to the wastes from various industrial facilities and activities have become a serious issue. The specific problem associated with heavy metals in the environment is their accumulation in the food chain and their persistence in nature. Conventional technologies for the removal of heavy metals such as chemical precipitation, membrane technology, electrolysis, ion exchange, evaporatory recovery, adsorption method, biological treatment method, and flotation method using surfactants are often inefficient or very expensive.

It is known that alkali absorbents such as CaO and $CaCO_3$ are used to remove heavy metals. Recently, a large amount of oyster shells have accumulated around the South Sea and caused a notorious smell and a pollution source. It should be also noted that these shells, one of the most representative sea wastes, consist of pure $CaCO_3$ with couples of thin membrane and SiO_2. A few researches are being carried out to develop these waste shells as a material for cleaning industrial wastewater.

A large amount of fly ash is generated annually from the combustion of coal in power plants. Only a small amount of fly ash is used as an additive to cement. However, most of that has been disposed of by dumping, which gives rise to serious environmental pollution. Consequently, the development of methods for greater utilization and production of high value compounds from waste fly ash has been the object of recent research.

In this study a method for the efficient utilization of byproducts such as oyster shell and fly ash, and evaluation of their potential for the removal of heavy metals, were investigated. In-situ application of byproducts was also studied by performing the sorption test on the clay and weathered soil as reference materials.

2. Isotherm equation

Adsorption can be defined as the interaction of a contaminant with a solid(Piwoni and Keeley, 1990). Adsorption is the process in which chemical compounds become associated with solid phase. Adsorption is extremely important because it may affect the fate of chemicals in the environment. Adsorption processes can be driven by a variety of forces and mechanisms as follows(Park et al., 1996). Hydrophobic sorption, hydrogen bonding, ion exchange, physical adsorption, coordination, and chemisorption.

One of the most important characteristics of an adsorbent is the quantity of adsorbate that it can accumulate. The constant temperature equilibrium relationship between the mass of adsorbate per adsorbent, S, and the equilibrium concentration of adsorbate in solution C_e is called the adsorption isotherm. The most common equation is the Freundlich equation, which has the form.

$$S = K_F C_e^{\frac{1}{n}} \tag{1}$$

If the slope of the Freundlich isotherm, 1/n, is found to be equal to 1, then the isotherm is said to be linear and the Freundlich coefficient K_F is identical to the distribution coefficient K_d. The constant K_F is related to the capacity of the adsorbent to sorb the compound, and 1/n is a function of the strength of adsorption.

The Langmuir isotherm is based on the concept that a solid surface possesses a finite number of sorption sites. When all the sorption sites are filled, the surface will no longer sorb solute from solution. The Langmuir isotherm is given by

$$\frac{C_e}{S} = \frac{1}{\beta_1 \beta_2} + \frac{C_e}{\beta_2} \tag{2}$$

The constant β_1 is an absorption constant related to the binding energy, and β_2 is the maximum amount of solute that can be absorbed by solid.

Some dissolved contaminants may interact with the soil solids encountered along the flow path through adsorption, ion exchange and other processes. These interactions result in the contaminants' distribution between the aqueous phase and the solids, diminution of concentration in the aqueous phase, and retardation of the movement of the contaminant relative to groundwater flow(Mackay and Roberts, 1985).

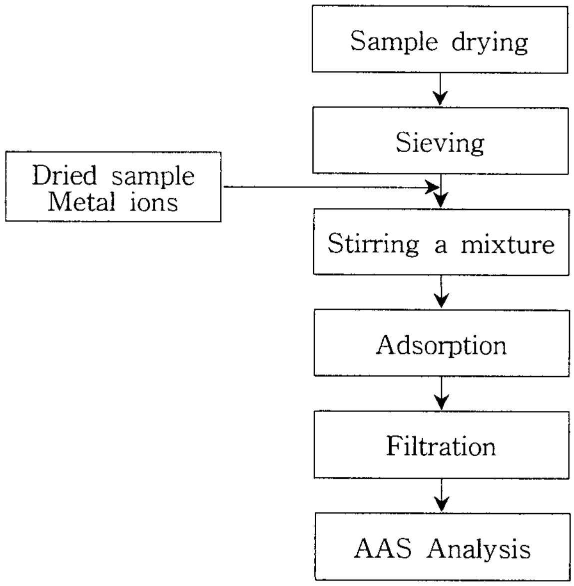

Fig. 1. Diagram of sorption test

3. Materials and methods

3.1 Experimental materials

Samples of oyster shell and fly ash used in this research was obtained at Tongyoung in Kyungnam and a power plant located at Taean in Chungnam, respectively.

Oyster shell was crushed and sieved to give the fraction of 10mesh, using ASTM standard sieves and fly ash was used with untreated natural state. As mentioned above, experiments were conducted with clay and weathered soil as reference materials, to evaluate in-situ applications of byproducts. Clay obtained at coastal area in Tongyoung is silty clay, and weathered soil was obtained a construction site at SNU. After drying in an oven at 105℃ overnight, the dried clay was crushed to use the test, and weathered soil was sieved to give the fraction of 10mesh. Three heavy metals such as cadmium, lead, copper were chosen for sorption tests because these heavy metals are major toxic contaminant groups.

3.2 Experimental methods

Laboratory batch tests were conducted to evaluate the adsorption behavior of three heavy metals(cadmium, lead, copper) on test adsorbents and test procedures shown in Fig. 1.

The mixture was stirred with adsorbents of 0.3g and solution of 30mL at 25±0.5℃, and filtered. Standard solution of 1000mg/L was used to prepare stock solutions which were diluted for use. The supernatant used for the determination of residual metal ion concentrations which were obtained by using atomic absorption spectrometer(AAS).

Laboratory adsorption tests included blank test, sorption equilibrium test and sorption isotherm test. Test methods were as follows.

Table 1. Results of blank test

Metal ions	C_e^*/C_0
Cadmium	0.995
Lead	0.994
Copper	0.997

C_e^* : Concentration of after 4 days

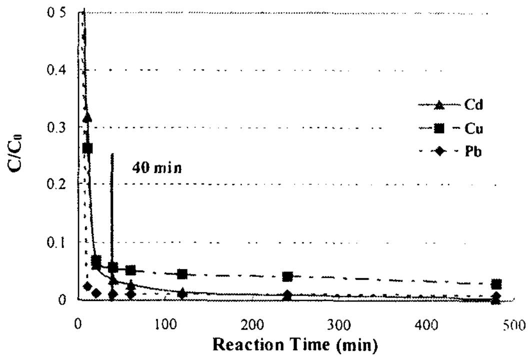

Fig. 2. Effect of reaction time of cadmium, lead and copper adsorption on Oyster Shell and of initial concentration of 40mg/L

3.2.1 Blank test

Blank samples were also prepared to ensure that the heavy metal was not being lost by any mechanism other than adsorption onto adsorbents, such as biodegradation, adsorption onto the walls of the vials and volatilization.

Pure solutions of 40mg/L containing no adsorbent were stirred at 25±0.5℃.

3.2.2 Sorption equilibrium test

Sorption equilibrium tests were carried out in establishing the adsorption equilibrium time required for adsorption of the each contaminant onto the oyster shell. Tests were carried with aqueous solutions of cadmium, lead and copper. Heavy metal solutions with a concentration of 40mg/L were prepared by dissolving standard solution in deionized distilled water. Mixture samples were withdrawn after 10, 20, 40, 60, 120, 240, 480 minutes of contact time. After an contact time, the mixture was filtered and the residual concentration of heavy metal in liquid phase was measured by AAS

3.2.3 Sorption isotherm test

Once the equilibrium time was established, isotherm tests for heavy metals were conducted, in which vials containing 0.3g of adsorbent and 30mL of aqueous contaminant solution varying in concentrations from 5 to 200mg/L were stirred for the desired equilibrium time and then filtered.

4. Test results

4.1 Blank test

Blank tests for each heavy metal, shown in Table 1, indicate that none of the heavy metals was adsorbed onto the side walls, volatilized or biodegradated.

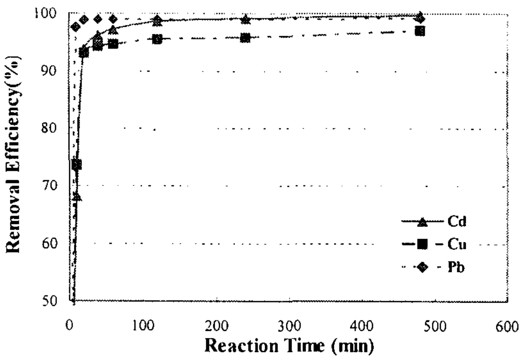

Fig. 3. Removal of cadmium, lead and copper on Oyster Shell at varying time and of initial concentration of 40mg/L

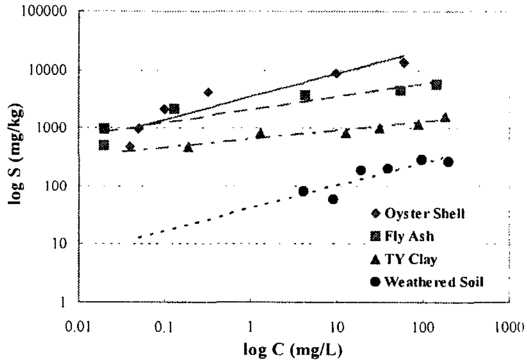

Fig. 4. Freundlich adsorption plots of adsorbents for cadmium

4.2 Sorpton equilibrium test

The results of equilibrium tests on oyster shell shown in Fig. 2. The initial aqueous solution concentration was 40mg/L and the mass of the adsorbent was 0.3g. The sorption occurs rapidly in the early stage. As time goes by, it reaches equilibrium within 40 minutes. Fig. 3 showed that the removal efficiencies of cadmium, lead and copper in oyster shell were 97~99%.

The equilibrium time of 48 hours was selected for further sorption testing for enough time.

4.3 Sorption isotherm test

Adsorption isotherm tests with varying concentrations were conducted to observe general adsorption characteristics of the heavy metals. Test was analyzed after the time of 48 hours. Freundlich isotherm test result of oyster shell, fly ash, clay and weathered soil in Fig. 4. Table 2 summarizes the Freundlich isotherm test parameter K_F and 1/n for each contaminant.

Because the K_F values in the Freundlich isotherm equation (2) are related to the capacity of the adsorbent for the adsorbate, and 1/n is a function of the strength of adsorption(Snoeyink, 1990), the isotherm data given in Table 2 indicate the potential difficulty of removing the heavy metals attached on the soil particles. As 1/n becomes smaller, the adsorption bond becomes stronger, which means that desorbing the contaminants from the particle becomes more difficult. Lead has the smallest value of 1/n for the most part, which means the bond between the lead and the particle is stronger than any of the other heavy metals. The removing ability of oyster shell was higher than any of the other absorbents and ordered as cadmium, lead and copper.

Table 2. Parameters of Freundlich equation for adsorption of heavy metals on adsorbents

Metal ions	Oyster Shell		Fly Ash		TY Clay		Weathered Soil	
	K_F	1/n	K_F	1/n	K_F	1/n	K_F	1/n
Cd	3482.1	0.397	2076.3	0.227	648.6	0.149	41.4	0.393
Pb	3093.6	0.337	1840.3	0.257	948.7	0.084	153.2	0.161
Cu	1913.1	0.398	2195.9	0.171	854.4	0.097	17.3	0.536

5. Conclusions

Based on the experimental data obtained during the investigation, the following conclusions can be drawn as:

1. Blank tests for each heavy metal indicate that none of the heavy metals was adsorbed onto the side walls, volatilized or biodegradated.
2. The results of equilibrium tests on oyster shell shows that sorption occurs rapidly in the early stage and reaches equilibrium within 40 minutes.
3. Lead has the smallest value of 1/n for the most part, which means the bond between the lead and the particle is stronger than any of the other heavy metals.
4. The removing ability of oyster shell was higher than any of fly ash, clay and weathered soil and ordered as cadmium, lead and copper, which means that oyster shell can be well used as an adsorbent for heavy metals.

Reference

1. Benefield, L. D. and Morgan, J. M., "Chemical Precipitation", Water Quality and Treatment, Pontius, F. W. (Ed.). McGraw-Hill Inc., New York, pp. 641-708 (1990)
2. Blanchard,G., Maunaye, M. and Martin, G., "Removal of Heavy Metals from Waters by Means of Natural Zeolites", Wat. Res., 18, 1501 (1984)
3. Corapcioglu, M.O. and Huang, C.P. "The Adsorption of Heavy Metals onto Hydrous Activated Carbon", Wat. Res., 21, 9, pp.1031-1044 (1987)
4. Dae Haeng Lee and Hee Moon, "Adsorption Equilibrium of Heavy Metals on Natural Zeolites", Korean J. Chem. Eng., 18(2), 247-256 (2001)
5. Dimitrova, S.V. and Mehandgiev, D.R. : Wat. Res., Vol. 32, No. 11 (1998)
6. Min-Gyu Lee, et al., "Conversion of Coal Fly Ash into Zeolite and Heavy Metal Removal Characteristics of the Products", Korean J. Chem. Eng., 17(3), 325-331 (2000)
7. Ruthven, D.M., "Principles of Adsorption and Adsorption Processes", John Wiley & Sons, New York (1984)
8. Upmeier. M.W. et al., "Use of natural clinoptilolite for the optimization of mineral clay liners for waste deposits", Prog. in zeolite & microporous materials studies in surface sci. & catalysis, Vol. 105, pp. 1633-1639 (1997)