Removal of Heavy Metals(Pb, Cr) Using Waste Eggshell

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Abstract

The calcination characteristic of waste eggshell were examined by thermal gravimetric analysis (TGA), qualitative and quantitative analysis by X-ray fluorescence, and microstructural analysis by scanning electronic microscopy(SEM). The calcined sample was lager grain and pore size.

Keywords : Thermal gravimetric analysis(TGA), Eggshell, Scanning electronic microscopy(SEM), X-ray fluorescence(XRF)

1. Introduction

Energy is a driving force in recent industries and the primary sources of energy are oil, coal petroleum. From many industrial activity as well as personal living purposes, a lot of energy and products are widely used and causes mass-production of several types of wastes. In the industrial wastewater, heavy metals are commonly contaminated after several industrial processes. Therefore, if the wastewater containing toxic heavy metals is not treated with a suitable process or leaked from storage tanks, it can causes a serious environmental problem in the natural eco-system. In this case, human body will be contaminated with accumulated metal ions such as lead, cadmium, and mercury through direct intake or food chains (Yoo *et al.* 2002). Because of its toxicity, heavy metal contamination should be prevented before it reaches to the natural environments (Kam *et al.* 2002; EPA 1991).

In order to regenerate the precious material or to remove toxic species, several treatment methods have been suggested and investigated in several countries. Although chemical precipitation, coagulation, ion exchange, solvent extraction, filtration, evaporation, membrane methods have been applied in this purposes, most techniques have limitations such as requirement of pre-treatment process, secondary treatment process or are less effective and requires higher cost (Kam *et al.* 2002; Kim 2002; Volesky 1990). Generally activated carbon, silica gel, activated alumina, and ion exchange resin have higher capacity in the removal of toxic heavy metals. However, their utilization is not common and confined to special treatment due to high installation and operating cost. Therefore, mass-preparation of economical adsorbent has much attention and studied (Kim 2002; Mukami 1981; Kam *et al.* 1999). Jo *et al.* (1993) studied

adsorption of heavy metals with rice hulls and leaf of persimmon. And Lee (1994) and Jo (1994) reported adsorption results of heavy metals on the shell of crab and shell of shrimp, respectively. From the removal of lead by shell of crab, Lee and Suh (1996) suggested potential possibility of regenerated wastes as adsorbents. In addition, applicability of wastes such as scoria, fly ash, zeolite, chitosan, corbicular japonica and ostrea virginica has been studied by many authors (Lee and Suh 1996; Lee *et al.* 2000; Kim et al. 1996; Choi and Ahn 1990; Park *et al.* 2001). Also, by simple treatment, plausible application of sawdust, oil cake, and coal as ion exchangers has been reported (Hwang and Meng 1980; Kim *et al.* 1981; Kim *et al.* 1995).
Important issues in the industrial process are minimization of wastes, recovery of precious material, and maximum regeneration of wastes and energy. Eggshell waste is widely produced from house, restaurant, and bakery. Eggshell has a little developed porosity and pure $CaCO_3$ as an important constituent. In this work, reuse of eggshell was investigated in the viewpoint of recycle of wastes and minimization of contaminants. Physical and chemical properties of eggshell were investigated and potential possibility of adsorbent in the removal of heavy metals was studied.

2. Materials and Methods

2.1 Materials

Eggshell sample was collected from bakeries in Busan city in Korea. To remove impurity and interference material such as organics and salts, the sample was rinsed with deionized water. Then the sample was dried 24 hours at 100°C in the dry oven after filtration of the sample with 0.45 μm membrane filters. Calcination was performed in the furnace at 800°C and for 2 hours after crushing of the dried sample. Finally samples having 40~100 mesh were used.

2.2 Methods

In order to characterize calcination of eggshell, Thermal Gravimetric Analyzer (DuPont Instruments Co, TGA-951 Series, USA) was used. A portion of samples previously removed impurity and interference material such as organics and salts were loaded in the TGA analyzer and then pyrolysis of the sample was performed up to 900°C at an elevation of temperature 40°C/min with continuous injection of N_2.
X-ray Fluorescence (XRF-1500, SHIMADZU, Japan) was used in the qualitative and quantitative analyses of the samples. Scanning Electron Microscope (Topcon, SM-300, Japan) was used in the analysis of size and structure of grain samples with 25 KV and 3000-times magnification.
All synthetic solutions of heavy metals (Pb and Cr) were prepared with dilution of 1000 ppm standard solution (Sigma, USA). In order to do adsorption experiments, 20.0 g of eggshell was mixed with 800 mL solution containing heavy metals at 200 rpm and at room temperatures (23~25°C). A portion of supernatant was removed from solution at a constant time interval and then each dissolved metal ion was measured with Induced Coupling Plasma (ICP, GBC XMP).

3. Results and Discussion

3.1 Property of calcinations

TGA was used to characterize calcination of eggshell. TGA profile of raw eggshell with variation of temperature was shown in Figure 1. When the sample was burned up to 800°C at a heating speed of 40°C/min, calcination of eggshell begin approximately at 650°C and then near complete calcination was observed at 770°C, resulting in phase-change in the sample. As most organics and humidity was removed during the pre-treatment process, major composition of sample was present as pure $CaCO_3$ in a temperature ranging from 0~640°C. When temperature was between 670°C and 750°C, both $CaCO_3$ and CaO was important composition of the sample. As a TGA curve was parallel with X-axis after 750°C, it was assumed that most fraction of the sample was changed to CaO by final pyrolysis.

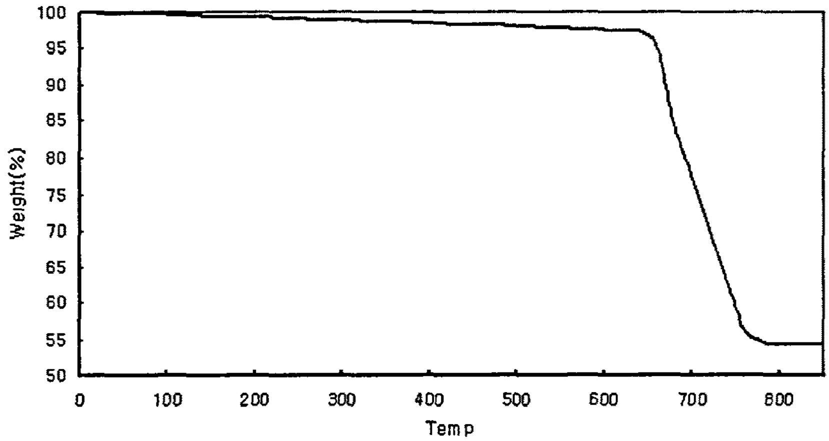

Fig. 1. TGA profile of raw eggshell due to thermal decomposition.

3.2 Composition of sample

Before calcinations, Ca as lime (91.94%) and Si (4.30%) was most inorganic composition of eggshell. After calcinations, major inorganic composition was Ca as lime (99.63%) and K, P, and Sr was identified as minor compositions. This indicates that the compositions of eggshell can be changed by calcinations as shown in Table 1. This result suggests that relatively pure sample can be obtained from eggshell by removing of mere organic compositions with less heating time and temperature.

Table 1. The composition of eggshells(natural and calcined)

Compound	Natural (%)	Calcined (%)
Ca	91.94	99.63
Si	4.30	-
Al	1.44	-
Na	0.53	-
K	0.48	0.14
F	0.42	-
P	0.32	0.06
Cl	0.25	-
Sr	0.16	0.16
Fe	0.09	-
Zn	0.07	-
Zr	0.01	-
Total	100 %	100 %

X-ray diffraction spectrums of natural and calcined samples were measured with $Cu_{K\alpha}$ radiation(λ =1.5406Å) at KV=30, MA=16, Scan Speed=8.0 Θ/min, and Scan Range=10~90 Θ. Figure 2 shows a X-ray diffraction spectrum of natural eggshell. Main peak appeared at 2Θ=29.4. In addition, the X-ray diffraction spectrum shows several peaks at 2Θ=23.05, 39.40, 43.15, 47.50, and 48.50. Table 2 shows peak information of XRF on natural eggshell. From JCPDS file, the major peak was corresponded with Ca as limestone. Figure 3 shows a X-ray diffraction spectrum of calcined eggshell at 800℃ for 2 hours. Main peak appeared at 2Θ=37.4. In addition, several peaks appeared at 2Θ=32.2, 53.9, 64.1, and 64.4. Compared with the JCPDS file, the composition of the calcined sample was identified as lime (CaO). As the peak of Ca as limestone (2Θ=29.4) appeared on natural eggshell in Figure 2 peak was not shown, most limestone ($CaCO_3$) might be transformed to lime (CaO). Compared to other results with chitosan, corbicular japonica and ostrea virginica, eggshell has a higher conversion efficiency into lime (CaO).

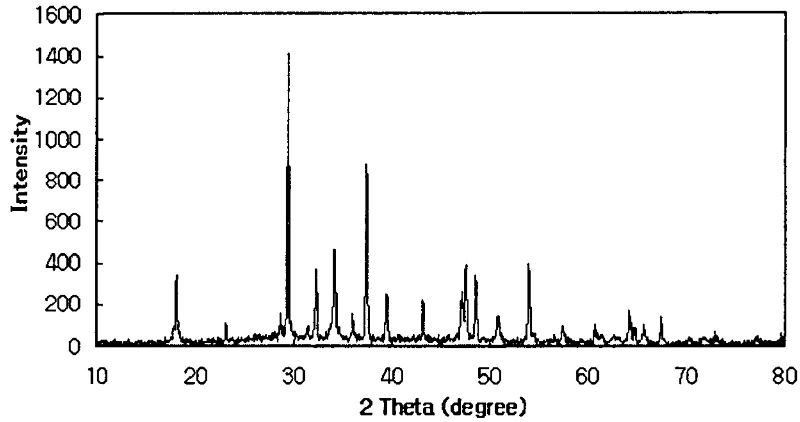

Figure 2. The x-ray diffraction spectrum of natural eggshell.

Table 2. Chart list of XRF on natural eggshell

Peak No.	d-value	Intensity	2theta
1	2.7774	36	32.202
2	2.4059	100	37.345
3	1.7009	54	53.852
4	1.4505	16	64.149
5	1.3888	16	67.370
6	1.2026	6	79.659
7	1.1037	6	88.517

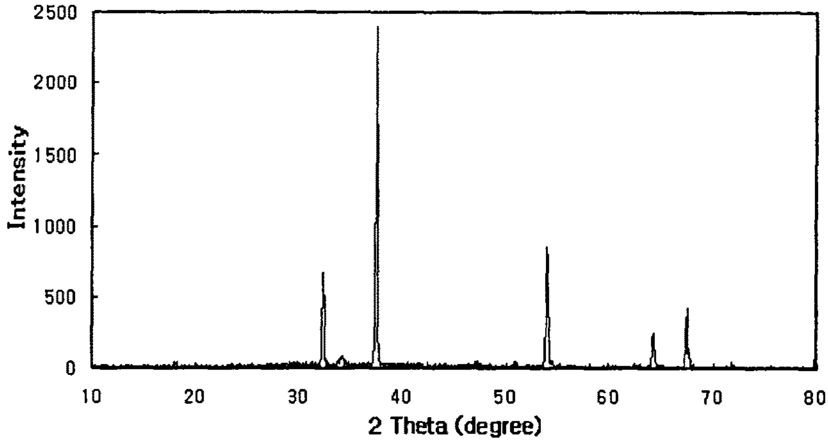

Figure 3. The x-ray diffraction spectrum of calcined eggshell.

Table 3. Chart list of XRF on calcined eggshell

Peak No.	d-value	Intensity	2theta
1	3.0355	998	29.398
2	1.8753	232	48.501
3	1.9124	218	47.503
4	2.2846	201	39.406
5	2.0944	160	43.155
6	2.4948	147	35.967
7	1.6041	118	57.394
8	3.8548	89	23.053
9	1.4404	84	64.655
10	1.9274	70	47.111
11	1.1538	68	83.762
12	1.5252	66	60.663

3.3 Surface analysis of calcined sample

SEM of eggshell sample before and after calcination was shown in Figures 4 and 5, respectively. Before calcination, natural eggshell had a generally irregular crystal structure. After calcination at 800°C for 2 hours, the crystal structure has been changed and the resultant image of SEM was shown as in Figure 5. From the emission of CO_2, much developed pore was observed in the calcined sample.

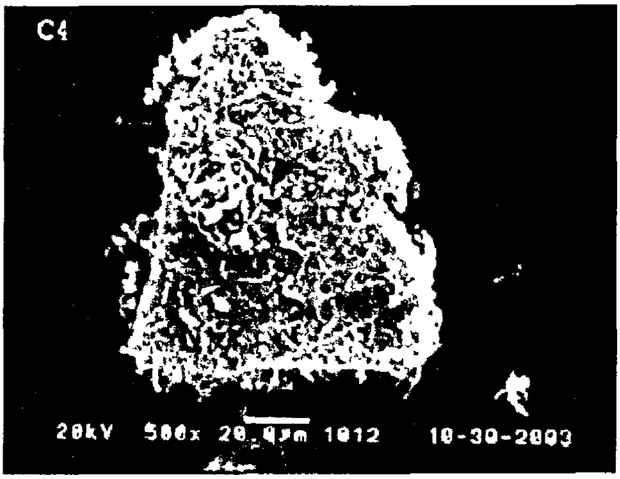

Figure 4. The picture of natural eggshell by SEM.

Figure 5. The picture of calcined eggshell by SEM.

3.4 Removal of heavy metal

Removals of Pb and Cr as a function of time are shown in Figures 6~8. Removal of Cr with calcined eggshell was quite faster than that with natural eggshell. In the calcined samples, above 99% removal of Cr was observed, respectively, after 10 minutes. Although natural eggshell also had removal capacity of Cr, the removal rate was quite slow and complete removal was difficult even after 60 minutes. Removal of Cr with natural eggshell was approximately 24% and 30%, respectively, after 10 minutes. However, removal of lead was favorable with natural eggshell. Removal of lead was 86% after 10 minutes and then reached 100% after 40 minutes. While removal of lead with calcined sample was quite slow and showed approximately 70% removal even after 1-hour.

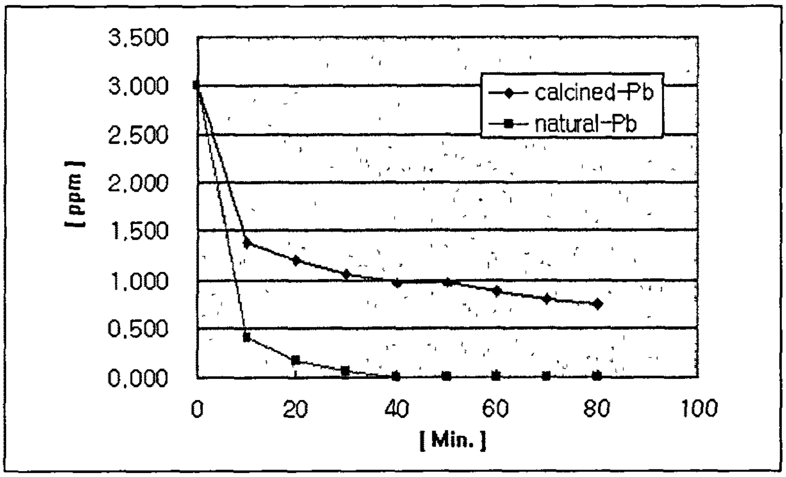

Figure 6. Removal of Pb with variation of time.

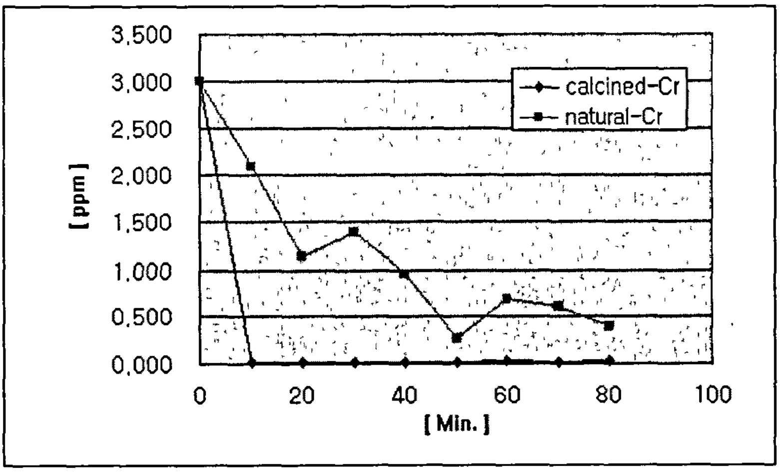

Figure 7. Removal of Cr with variation of time.

4. Conclusions

Preparation of adsorbent from eggshell was studied for the purpose of removal of toxic heavy metals with reused wastes. TGA, XRF, and SEM analyses were used to monitor changes of the eggshell properties after calcination.

1. After calcination, most composition of eggshell was transformed to lime (CaO) as well as

enlargement of pore and grain was observed. These results strongly suggest plausible reuse of calcinated eggshell.

2. Removal of Cr was much enhanced with calcined eggshell, however, removal of lead was efficient with natural eggshell rather than calcined eggshell. This may be related with different major composition in the sample before and after calcination.

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