Reuse of Waste Oyster Shells as a SO$_2$/NO$_x$ Removal Absorbent


Department of Health Administration, Sorabol College, Gyeongbuk 780-711, Korea
*Department of Environmental Engineering, Kwangwoon University, Seoul 139-701, Korea
**Busan Center, Korea Basic Science Institute (KBSI), Busan 609-735, Korea
***Korea Institute of Energy Research, Daejeon 305-343, Korea
****Department of Environmental Engineering, Hanseo University, Chungnam 356-820, Korea

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Abstract: An enormous amount of waste oyster shells are dumped into public waters and landfills, which causes a bad odor as a consequence of the decomposition of organics attached to the shells. Marine pollution by waste oyster shells has become one of the most serious problems in the mariculture industry in Korea. To determine the feasibility of recycling waste oyster shells as desulfurization/denitrification sorbents, pretreating experiments and the SO$_2$/NO$_x$ removal activity were investigated. Through pretreating processes, such as calcination and hydration, the specific surface area and pore volume of waste oyster shells were increased over those of the fresh particles, making it possible to enhance the removal capacity in acid gases. XRD analysis of calcined waste oyster shells exhibited peaks characteristic of calcium oxide, whereas raw waste oyster shells showed that the main peaks were characteristic of calcium carbonate. The optimal temperatures for calcination and hydration were 800~850 and 90°C, respectively. SO$_2$/NO$_x$ removal experiments were undertaken to test the reactivity of absorbents in a fixed bed reactor. The SO$_2$ removal activity and reaction rate of the calcined/hydrated waste oyster shells were higher than those of calcined/hydrated limestone. This finding clearly indicates that absorbents prepared from waste oyster shells are substitutes for commercial limestone and can be applied directly to industries attempting to reduce their emissions of SO$_2$ and NO$_x$.

Keywords: absorbent, calcination, hydration, limestone, oyster shell

Introduction

Recently, due to the increase of seafood consumption and the residue of oyster farming, marine pollution by waste shells of shellfish has become one of the most serious problems in the mariculture industry in Korea. From among many waste shells of shellfish (oyster, mussel, clam, and short-necked clam), waste oyster shells (WOS) are the most predominant. In 2004, 275,490 tons of waste oyster-shells was produced [1], more than 50~70% of which were dumped into public waters and reclaimed lands, causing a nasty odor as a consequence of the decomposition of fresh remnants attached to the oysters [1-3]. Approximately 30~50% of the shells from harvested oysters were utilized and the remainder was disposed [3,4]. Thus, recycling of waste oyster-shells has arisen as an imminent issue in the mariculture industry. As recycling processes, many studies on the application of waste oyster shells to construction materials [3], laver farming, fertilizer [5], sludge conditioners [6], eutrophication control [4], and desulphurization sorbents [7] have been reported. Desulphurization systems can be divided into three groups: dry adsorption [8], wet scrubbing [9], and wet/dry systems [10,11]. It is well known that alkali sorbents, such as CaO, CaCO$_3$, Ca(OH)$_2$, NaOH, Na$_2$CO$_3$, NaHCO$_3$, KOH, MgO, Mg(OH)$_2$, dolomites, and dolomite limestones (CaCO$_3$/MgCO$_3$), can be used to remove SO$_2$ and acid gases in flue gas cleaning processes [7,12,13]. Of these sorbents, calcium-based alkali sorbents are the most widely used to remove SO$_2$, because calcium-based sorb-
Table 1. Pretreating and Experimental Conditions

<table>
<thead>
<tr>
<th>Experimental variables</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination temperature (°C)</td>
<td>700 ~ 1000</td>
</tr>
<tr>
<td>Hydration time (hr)</td>
<td>24</td>
</tr>
<tr>
<td>Hydration temperature (°C)</td>
<td>90</td>
</tr>
<tr>
<td>Slurrying velocity (rpm)</td>
<td>200</td>
</tr>
<tr>
<td>Absorbent drying time (hr)</td>
<td>24</td>
</tr>
<tr>
<td>SO2 concentration (ppm)</td>
<td>1800</td>
</tr>
<tr>
<td>NOx concentration (ppm)</td>
<td>250</td>
</tr>
<tr>
<td>O2 concentration (%)</td>
<td>6</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>150</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>10</td>
</tr>
</tbody>
</table>

ents have good reactivity toward acidic gases and lower cost compared to sodium-based alkali adsorbents.

According to the literature [14], the composition of the main component (CaO) in waste shells of different shellfish species is 53 ~ 54 wt%, which is comparable to that of commercial limestone. Clam shells are the most favorable SO2/NOx removal sorbents among the tested waste shells of different shellfish species. Even though the acidic gas removal capacity of oyster shells is slightly lower than those of clams and short-necked clams, the specific surface area is comparable to those of short-necked clams and commercial limestone [14] and oysters are the predominant source of waste shellfish shells in Korea. Nevertheless, the recycling processes of waste oyster shells are limited and experimental results are scarce in the literature. Therefore, alternative methods for recycling waste oyster shells must be found. The purpose of this study was to develop a means of converting waste oyster shells into a more-reactive absorbent and to evaluate the feasibility of using this absorbent as a SO2/NOx removal agent.

Experimental

The waste oyster shells from Tongyoung province around the South Sea in Korea were chosen as main materials. Salts and other organic substances were removed by washing with tap water and then the waste oyster shells were dried in a drying oven for ca. 2 days. The waste oyster shells were crushed two times by a Jaw crusher and a Ball mill after drying. Limestone from Jungsun province, which is used commercially in the flue gas desulphurization system, was selected for comparison of the physicochemical properties and the acid gas cleaning reactivity with those of the waste oyster shells. The physicochemical characteristics of the oyster shells and limestone were analyzed by ICP (ICPS-7500 Shimadzu, Japan), TGA (Perkin-Elmer, USA), BET (Micromeritics Co., USA), and SEM (JEOL superprobe JSM-5400, Japan). Surface areas of the samples were measured using the BET technique after pretreating to remove vapor at $1 \times 10^{-3}$ torr (vacuum) and 180.0 °C for 2 h.

To enhance the physicochemical properties of the waste oyster shells, pretreating techniques were applied to the samples before performing SO2/NOx removal tests. The goal of the pretreating process was to convert the relatively lowly reactive calcium component (in the form of calcium carbonate) into the forms of calcium oxide and calcium hydroxide that readily react with acid gases. These processing techniques are referred to as calcination and hydration, respectively.

To calculate the sorbent capacity, the SO2/NOx removal experiments were carried out using a fixed-bed reactor system [14] under atmospheric pressure at 150.0 °C. The fixed-bed quartz reactor (0.025-m diameter, 0.25-m height) was placed in a hot air bath and the temperature was controlled using a PID-type controller with the precision of ±1.0 °C. After the sample was placed on the reactor (1 g of sample) and the temperature was stabilized in a N2 flow, a reacting gas containing SO2, O2, and NOx was injected into the reactor using mass flow controllers (MFC, BROOKS Instrument, Inc., Model 5850 E, England). At the same time, water was also injected to the reactor using a syringe pump to maintain a steady vapor concentration in the simulated gas. A hygrometer and an SO2/NOx analyzer were used to measure the gas concentration; signals from the measuring instrument were recorded onto a personal computer equipped with an RS-232C interface. Table 1 shows the pretreating and experimental conditions.

Results and Discussion

The physicochemical compositions of the waste oyster shells and the commercial Jungsun limestone are summarized in Table 2. To perform XRF (X-ray fluorescence spectroscopic) analysis, samples were powdered after being dehydrated in a drying oven at 105.0 °C for 24 h. From the composition analysis, we found that oyster shells consist mostly of CaO, with some SiO2, MgO, Al2O3, and Fe2O3. The composition of CaO in the oyster shells was ca. 53.81 wt%, which is comparable to that of commercial Jungsun limestone and was in good agreement with the results of Yoon and coworkers [3], who reported that the CaO content of oyster shells was ca. 53.7 wt%.

X-ray diffraction (XRD) patterns of waste oyster shells, limestone, and calcined waste oyster shells (C-WOS) are shown in Figure 1. The patterns for waste oyster shells and limestone are nearly similar, and the diffraction
Table 2. Physicochemical Properties of Tested Absorbents

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>Chemical composition [wt%]</th>
<th>Pore volume [cc/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>WOS</td>
<td>0.40</td>
<td>0.22</td>
</tr>
<tr>
<td>Jungsun limestone</td>
<td>2.43</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Figure 1. XRD profiles of oyster shells and limestone; (a) limestone, (b) oyster shells, and (c) calcined oyster shells.

peaks of CaCO₃ as major phases are identified (Figures 1a and 1b). The patterns for calcined waste oyster shells exhibited peaks characteristics of CaO (Figure 1c).

To clarify the effect of temperature, thermogravimetric analysis (TGA) of the waste oyster shells and limestone was performed under a N₂ atmosphere using an Automatic Derivative Differential Thermo-balance (Figure 2). The heating rate in the calcination, which involved conversion from calcium carbonate to calcium oxide, was 10.0 °C/min in the temperature range 600.0 °C to 900.0 °C. As can be seen in Figure 2, calcination of the oyster shells started at 645.0 °C and was complete at 780.0 °C, whereas that of the Jungsun limestone started at a temperature over 680.0 °C and was complete at 845.0 °C. The masses of oyster shells and limestone in the calcinations under N₂ atmosphere decreased by 44.8 and 44.0 %, respectively. From this analysis, we confirmed that the mass decrease resulted from the reaction CaCO₃ → CaO + CO₂. Also, in the case of Jungsun limestone, the temperature of the calcinations should be above ca. 850.0 °C.

Figure 3 shows scanning electron micrographs (SEM) of various solid Jungsun limestones and oyster shells. Images (a) (a’) and (b) (b’) of Figure 3 show the scanning electron micrographs of the fresh and calcined samples, respectively. SEM images of the hydrated and calcined/hydrated samples are shown in (c) (c’) and (d) (d’) of Figure 3, respectively. Observation of the oyster shells morphology indicates some agglomeration of the particles/grains in the hydrated waste oyster shells (H-WOS), relative to those of the fresh oyster. However, as shown in Figure 3(b’), in the SEM image of the calcined sample, an enormous amount of agglomeration by sintering is observed.

Figure 4 shows the pore volume with respect to the pore diameter. The calcined oyster had a decreased pore volume relative to that of the fresh oyster.

The specific surface areas of oyster shells and limestone
Table 3. Kinetic Data of Tested Absorbents

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>$E_a$ [kJ/mole]</th>
<th>Order [n]</th>
<th>Sample wt. [mg]</th>
<th>Flow gas</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>WOS</td>
<td>176.1±8.90</td>
<td>0.42±0.10</td>
<td>15–16</td>
<td>N$_2$</td>
<td>Isothermal</td>
</tr>
<tr>
<td>Jungsun limestone</td>
<td>201.72±5.17</td>
<td>0.37±0.08</td>
<td>15–16</td>
<td>N$_2$</td>
<td>Isothermal</td>
</tr>
</tbody>
</table>

Figure 3. SEM micrographs of limestone and oyster shells; (a) fresh limestone, (a') fresh oyster shells, (b) calcined limestone at 850 °C, (b') calcined oyster shells at 850 °C, (c) hydrated limestone, (c') hydrated oyster shells, (d) hydrated limestone after calcination, and (d') hydrated oyster shells after calcination.

Figure 4. Cumulative pore volume curves for two types of waste oyster shells as a function of pore diameter.

Figure 5. Effect of calcination temperature on the surface area.

Plotted as a function of the calcination temperature are shown in Figure 5. The specific surface area of the oyster shell changed from 2.4465 m$^2$/g before calcination to 2.3950 m$^2$/g at 700.0 °C, 2.2810 m$^2$/g at 750.0 °C, 2.2120 m$^2$/g at 800.0 °C, 2.1209 m$^2$/g at 850.0 °C, 1.9510 m$^2$/g at 900.0 °C, 1.8000 m$^2$/g at 950.0 °C, and 1.7000 m$^2$/g at 1,000.0 °C. The specific surface area of the waste oyster shells was larger than that of the calcined oyster shells, and it decreased with increasing calcination temperature. This result indicates that some agglomeration by sintering blocked the specific surface area of the calcined oyster shells. In contrast, the specific surface area of limestone increased from 1.2368 m$^2$/g before calcination to 1.3100 m$^2$/g at 700.0 °C, 1.3200 m$^2$/g at 750.0 °C, 1.5100 m$^2$/g at 800.0 °C, 2.1544 m$^2$/g at 850.0 °C, 2.3205 m$^2$/g at 900.0 °C, 2.0210 m$^2$/g at 950.0 °C, and 1.2124 m$^2$/g at 1,000.0 °C. The specific surface area of limestone increased with increasing calcination temperature up to a maximum at 900.0 °C and then decreased slightly. The specific surface area at 850.0 °C was similar to that at 900.0 °C. Therefore, we conclude that the calcination temperature had a positive effect on the development of
The specific surface area for limestone, unlike the situation for the waste oyster shells.

The change in the surface area of the oyster shells and limestone after processing (calcination/hydration) is shown in Figure 6. The specific surface areas of oyster shells and limestone changed from 2.4465 and 1.2368 m$^2$/g, respectively, before calcination/hydration to 12.9789 and 11.3380 m$^2$/g, respectively, after pretreatment. From this result, we could expect that the sulfating reactivity of the oyster shell sample would increase by ca. five times after calcination/hydration because of the increase of specific surface area and pore volume, and because the acid gas removal capacity of absorbents is proportional to the specific surface area [14].

The desulfurization efficiency of the raw material is shown in Figure 7. From a comparison of the SO$_2$ removal quantities between waste oyster shells and limestone, the desulfurization capability of waste oyster shells was higher by ca. 50 % than that of Jungsun limestone. This result means that the SO$_2$ removal capacity of oyster shells was superior to that of the limestone because of the specific surface area, as can be seen in Figure 6 (left side).

In general, a power plant discharges SO$_2$ at 1800 ~ 1900 ppm, O$_2$ at 6 %, CO$_2$ at 13 %, N$_2$ at 74 %, a water content of 10 %, and NO at 600 ppm into the air during combustion. The SO$_2$/NOx removal capacity of the calcined/hydrated limestone (CH-L) and calcined/hydrated waste oyster shells (CH-WOS) was measured in a fixed bed reactor. As can be seen in Figure 8, the desulfurization capacity of the adsorbent was one order of magnitude higher than the denitrification capacity, regardless of the absorbent species. This phenomenon arose because the Henry’s Law constant and diffusion coefficient in the gas phase for SO$_2$ are much higher than those for NO [15]. Thus, the SO$_2$ and NOx removal quantities of CH-WOS were slightly higher than those of CH-L. It can be inferred that waste oyster shells are a good sorbent for the removal of SO$_2$ and NOx in flue gas cleaning processes. The SO$_2$ and NOx absorption mechanism on the absorbent can be explained by combining the following equations [16]:

\[
\begin{align*}
CaCO_3(s) + SO_2(g) + 2H_2O(l) & \leftrightarrow CaSO_3 \cdot 2H_2O(s) + CO_2(g) \\
CaO(s) + H_2O(l) & \leftrightarrow Ca(OH)_2(s) \\
Ca(OH)_2(s) + SO_2(g) + H_2O(l) & \leftrightarrow CaSO_3 \cdot 2H_2O(s) \\
CaCO_3(s) + 2NO(g) + 1/2O_2(g) & \leftrightarrow Ca(NO_2)_2(s) + CO_2(g) \\
Ca(OH)_2(s) + 2NO(g) + + 1/2O_2(g) & \leftrightarrow Ca(NO_2)_2(s) + H_2O(l)
\end{align*}
\]

The removal of SO$_2$ [Ca(OH)$_2$ conversion ratio] in the simulated flue gas by the CH-L and CH-WOS absorbents was examined under different reaction conditions to
study the effects of the coexistence of NOx in a flue gas (Figure 9). As depicted in Figure 9, the reaction rate of desulphurization by CH-WOS increased (ca. 30 % higher) relative to CH-L. In addition, the SO2 removal activity was enhanced in the presence of NOx, which might be due to its oxidizer role of SO2 [17].

Conclusions

The present study was conducted to develop a means of converting waste oyster shells into useful absorbents for the removal of SO2/NOx from industry. Through pre-treatment, such as calcination and hydration, the specific surface area and pore volume of the oyster shells increased relative to those of the fresh particles, which makes it possible to enhance the removal capacity of acid gases. The optimal temperatures for calcination and hydration were 800.0∼850.0 and 90.0 °C respectively. Pores in the absorbent were formed by the emission of CO2 during the high-temperature calcination, but it was agglomerated by sintering. Therefore, the specific surface area decreased and was completely different from that of the limestone.

SO2/NOx removal experiments were carried out to test the reactivity of the absorbents in a fixed bed reactor. The SO2 removal activity and reaction rate of calcined/hydrated waste oyster shells were higher than those of the calcined/hydrated limestone. The results clearly indicate the that waste oyster shells can be used as acid gas cleaning agents to reduce air pollution problems. Also, these materials can be applied directly to industries attempting to reduce their emissions of SO2 and NOx.

Acknowledgment

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References