Regeneration of Waste Edible Oil by the Use of Virgin and Calcined Magnesium Hydroxide as Adsorbents

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Abstract: In this study, we prepared virgin (S, L) and calcined (S-380, S-1000, L-380, L-1000) magnesium hydroxide for regeneration of waste edible oil. Deterioration of soybean oil, rapeseed oil, and olive oil was achieved by heat and aeration treatment. The properties of the different adsorbents were investigated using specific surface area measurements, scanning electron microscopy, X-ray diffraction analysis, thermogravimetric-differential thermal analysis, and surface pH measurement. Moreover, the relationship between the changes in acid value (AV) and carbonyl value (CV) and the adsorbent properties were evaluated. The specific surface areas of S-380 and L-380 were greater than that of other adsorbents. In addition, the XRD results show that S-380 and L-380 contain both magnesium hydroxide and magnesium oxide structures. The decreases in AV and CV using S-380 and L-380 were greater than achieved using other adsorbents. The correlation coefficients between the decrease in AV and CV and specific surface area were 0.947 for soybean oil, 0.649 for rapeseed oil, and 0.773 for olive oil, respectively. The results obtained in this study suggest that a physical property of the adsorbent, namely specific surface area, was primarily responsible for the observed decreases in AV and CV. Overall, the results suggest that S-380 and L-380 are useful for the regeneration of waste edible oil.

Key words: magnesium hydroxide, magnesium oxide, calcination, deterioration, waste edible oil

1 INTRODUCTION

Waste disposal problems continue to increase and endanger the environment. Recycling of used frying oils could not only reduce the problems associated with waste disposal, but, more importantly, could also increase the effective usage of food and agricultural resources. However, oil deteriorating during frying, through the effects of heat, air, and moisture, has a negative impact on the usability of these edible oils. These degradation processes lead to polymerization, oxidation, and hydrolysis, which in turn lead to the formation of various polar compounds and polymers that adversely affect human health. These changes are influenced by the frying temperature and by the presence of emulsifiers, trace metals, food scraps, free fatty acids, and alkaline-reacting materials in the frying oil. Therefore, regeneration of waste edible oil is very important.

Several methods have been employed to purify used frying oils. These methods are active and passive filtration, membrane processing, and supercritical carbon dioxide extraction. A number of adsorbents, including activated carbon, clay, aluminum hydroxide, charcoal, celite, silica gel, silicon dioxide, oyster shell, ceramic plate, aluminum oxide, and others have been used to regenerate frying oils for subsequent reuse. In addition, we previously reported that calcium silicate, a food additive, decreases the acid value (AV) and carbonyl value (CV) of deterioration oil. Food additives have evidences of safety for human health. However, the mechanism by which this decrease in AV and CV occurred had not been reported. On the other hand, Chang et al. reported that the efficiency of bleaching is unaffected by the specific surface area of the adsorbent when the pore diameter was less than 50 Å but does vary with specific surface area when the pore diameter is larger than 50 Å. These findings suggest that the physical properties (e.g., specific surface area, pore size distribution, etc.) of the adsorbents were related to the bleaching efficiency.

Therefore, it is important to elucidate the mechanism by which adsorbents can decrease AV and CV. Elucidation of
the regeneration mechanism of deteriorated oil by adsorbent treatment can lead to application in a wide range of fields and can prove useful for developing novel regeneration treatments for waste edible oil.

On the other hand, our earlier studies indicated that the degree to which AV and CV are decreased in waste rape-seed oil by magnesium oxide is greater than when magnesium hydroxide is used as the adsorbent. This indicates that the changes in the physical and chemical properties on changing from magnesium hydroxide to magnesium oxide led to improvement in the regeneration of deteriorated oil. Moreover, magnesium hydroxide and magnesium oxide are food additives, and approval for adding to foods. Previous studies have reported the regeneration of deteriorated oil by food additives (magnesium hydroxide and magnesium oxide), but the regeneration mechanism for these additives has not been described.

In this report, we describe our evaluation of virgin and calcined magnesium hydroxide as adsorbents for regeneration of waste edible oil (soybean oil, rapeseed oil, and olive oil). The microstructures of the adsorbents were analyzed by scanning electron microscopy, X-ray diffraction, thermogravimetric-differential thermal analysis, and specific surface area measurements. In addition, the decreases in AV and CV after adsorbent treatment were also examined.

2 EXPERIMENTAL

2.1 Materials

Magnesium hydroxide (‘S’ particle size <10 μm; ‘L’, particle size ≥10 μm) was purchased from Tomita Pharmaceutical Co. Ltd., Japan. Calcined magnesium hydroxide was prepared by treating magnesium hydroxide in a muffle furnace at either 380°C (S-380, L-380) or 1000°C (S-1000, L-1000) for 2 h. Specific surface area measurement and thermogravimetric-differential thermal analysis (TG-DTA) were carried out on a NOVA4200e specific surface analyzer (Yuasa Ionics, Japan) and a TG8120 (Rigaku, Japan), respectively. X-ray diffraction (XRD) analyses were performed using a Mini Flex II (Rigaku, Japan). SEM images were obtained using a JSM-5200 scanning electron microscope (JEOL, Japan). The pH of a solution after the addition of adsorbents was measured using the following method: after adding 1.0 g of adsorbent to 50 mL of distilled water (pH = 7.0), the suspension was stirred for 2 min. The suspension was filtered using a 0.45 μm membrane filter (Advantec MFS, Inc.), and the pH of the filtrate was measured using a digital pH meter LAQUA (HORIBA Ltd.).

Edible shirahime soybean oil, rapeseed oil, and olive oil were purchased from Showa Sangyo Co. Ltd. and J-OIL MILLS, Inc. Deterioration of the oils was carried out by both heat and aeration treatments[10]. Untreated edible oil (200 mL) was heated at 180°C while stirring for 250 rpm for 7 h/day (total of 4 days) while maintaining an aeration oxygen flow of 300 mL/min. The adsorbent materials were individually added to each waste oil at a concentration of 1% (w/w), mechanically stirred for 15 min at 100°C, and filtered through a 0.45 μm membrane filter (Advantec MFS, Inc.). The AV and CV, as well as concentrations of free fatty acid and tocopherol, were then determined for the filtered oil, as described in Sections 2.2 and 2.3 respectively.

2.2 AV and CV estimation

Samples (2 g) of filtered oil were dissolved in 100 mL of a mixture of ethanol:ether (1:1), and the solution was titrated with 0.1 mol/L potassium hydroxide (phenolphthalein was used as the indicator). AV was calculated according to equation (1):

\[ AV = 5.611aF/M \]

where \( a (\text{mL}) \) is the amount of potassium hydroxide (0.1 mol/L) required for the titration, \( F \) is the factor of potassium hydroxide (0.1 mol/L), and \( M (\text{g}) \) is the mass of the edible oil sample[12].

Samples (0.25 g) of filtered oil were dissolved in 25 mL of 1-butanol. Subsequently, 1 mL of sample solution and 1 mL of 2,4-dinitrophenyl hydrazine were mixed for 20 min at 40°C. Potassium hydroxide (8%; 8 mL) was added to the mixtures, and the samples were centrifuged at 3,000 rpm for 5 min using a KUBOTA 3100 centrifuge (KUBOTA Co., Ltd.). The supernatants were analyzed using a UV-1200 spectrophotometer (Shimadzu). The absorbance was measured at 420 nm[13]. All reagents were purchased from Wako Pure Chemical Industries, Japan.

2.3 Analysis of free fatty acid (FFA) and tocopherol contents

Benzene (0.5 mL) and 14% (w/w) boron trifluoride-methanol (1 mL) were mixed with the samples (10 mg) of filtered oil, and the suspensions were heated for 2 h at 80°C. Subsequently, 5 mL of n-hexane and 15 mL of distilled water were added, and the sample in the n-hexane layer was analyzed using a gas chromatograph equipped with a flame ionization detector (GC-2014; Shimadzu). The measurement conditions were as follows: capillary column, FAMEWAX (30 m × 0.25 mm ID; Shimadzu GLC Ltd.); carrier gas, He; column temperature, 200°C; flow rate, 0.6 mL/min; and injection volume, 1 μL.

The tocopherol concentration was estimated by diluting the samples in a mobile phase (hexane:ethyl acetate, 7:3) followed by analysis by high-performance liquid chromatography (HPLC; SPD-10A VP, Shimadzu). The measurement conditions were as follows: column, Inertsil NH2 (250 mm × 4.6 mm, GL-Science); column temperature, 30°C; flow rate, 1.0 mL/min; wavelength of detection, 290 nm; and injection volume, 10 μL.
2.4 Statistical analysis

All data are presented as mean ± S.D. of 2-3 experiments, and multiple groups were evaluated by one-way ANOVA. The p values less than 0.05 were considered significant.

3 RESULTS AND DISCUSSION

3.1 Properties of adsorbents

The specific surface areas of the studied adsorbents are shown in Fig. 1. The specific surface areas for S, S-380, and S-1000 were 37.0, 88.9, and 9.8 m²/g, respectively, while those for L, L-380, and L-1000 were 41.0, 103.0, and 8.1 m²/g, respectively.

The specific surface areas for S-380 and L-380 were greater than that of other adsorbents. The SEM images of the adsorbents, shown in Fig. 2, confirm the larger particle size of L compared to that of S. In addition, the appearance of the adsorbent surface and the particle size of the adsorbents were not significantly altered by calcination treatment.

The pH values of distilled water (pH = 7.0) after the addition of S, S-380, S-1000 were 10.4, 10.9, and 10.0 respectively, while those after the addition of L, L-380, and L-1000, were 10.4, 10.8, and 10.1, respectively.

Figure 3 shows the XRD patterns of the adsorbents. The patterns for S and L are consistent with the crystal structure of magnesium hydroxide, whereas the patterns for S-1000 and L-1000 are consistent with the crystal structure of magnesium oxide. In contrast, the patterns for S-380 and L-380 have elements of the crystal structures of both magnesium hydroxide and magnesium oxide, which indicated that S-380 and L-380 were intermediates. Sato et al. reported that the crystal structure of magnesium oxide produced from magnesium hydroxide calcined at 380°C is distorted cubic but becomes cubic when calcined at 600°C. Therefore, calcination at 380°C is very important for obtaining the intermediate. Hamano reported the changes in the crystal structure of magnesium hydroxide in detail, and showed that calcination of magnesium hydroxide at 380°C produces the most random crystal structure (unstable structure), which leads to a higher specific surface area. In this study, the specific surface areas of the intermediates (S-380 and L-380) were greater than that of other adsorbents. The unstable structures of S-380 and L-380 may be responsible for their reactivity. The results obtained in this study were similar to the trends reported previously.

TG-DTA thermograms of the adsorbents are shown in
The endothermic peak at approximately 380°C in L and S indicates that magnesium oxide was produced from magnesium hydroxide by a dehydrating decomposition reaction. As L-380, L-1000, S-380, and S-1000 had all been previously calcined at 380°C or 1000°C, their endothermic peaks were smaller than those for L and S. S-380 and L-380 have different structures according to XRD analysis, the peak of magnesium hydroxide in S-380 was stronger than that in L-380. These results suggest that the dehydration (endothermic reaction) of S-380 is greater than that of L-380. We confirmed the dehydration (endothermic reaction) of S-380 and L-380 according to TG-DTA analysis.

3.2 Changes in AV and CV after adsorbent treatment

The decrease in AV and CV after adsorbent treatment is shown in Figs. 5 and 6. After deterioration, the AV was 0.90, 1.26, and 1.39 mg/g for soybean oil, rapeseed oil, and olive oil, respectively (the initial AV of virgin soybean oil, virgin rapeseed oil, and virgin olive oil was 0.31, 0.34, and 0.56 mg/g, respectively). The AV of deteriorated edible oil did not reach a hygienic value (2.5 mg/g). In addition, after deterioration, the CV of the oils was 74.30, 81.23, and 44.35 μmol/g for soybean oil, rapeseed oil, and olive oil, respectively (the initial CV of virgin soybean oil, virgin rapeseed oil, and virgin olive oil was 38.68, 6.72, and 9.31 μmol/g, respectively). With the exception of waste olive oil, the CV of
all the waste edible oils reached a hygienic value (50 μmol/g) after deterioration treatment. The method used in this study for deterioration of edible oil using heat and aeration could be useful for preparing waste edible oil.

The amount by which AV decreased for soybean oil after treatment with either L-380 or S-380 was greater than for any of the other adsorbents (L-1000 < L-380 and S-1000 < S < S-380). Similar trends were observed using rapeseed oil and olive oil. On the other hand, the decreasing CV was different by three oil species.

Recently, Ichikawa reported the determination of the deterioration of waste edible oils using AV, CV, and peroxide value, because these values can be used to simultaneously evaluate the amount of fatty acid peroxide, aldehyde, and carboxylic acid produced by the deterioration of the edible oil (unit: meq/kg, the sum of each analytical value). This means that the extent of oxidative degradation and the contents of the products can be elucidated. The components of the oils used in this study (soybean oil, rapeseed oil, and olive oil) were different, which means that the progress of oxidative degradation and the products produced by the deterioration of the edible oils were also different. Therefore, it is necessary to evaluate the overall deterioration. In this study, the percentage decrease in the sum of AV and CV using L, L380, L-1000, S, S-380, and S-1000 was 24.9, 32.0, 20.3, 21.1, 32.4, and 15.1%, respectively for soybean oil; 9.5, 16.5, 10.2, 8.2, 10.0, and 9.7%, respectively for rapeseed oil; and 11.4, 21.9, 14.3, 21.3, 28.3, and 10.4%, respectively for olive oil.

Next, we evaluated the relationship between the decrease in AV and CV and specific surface area (Fig. 7). The correlation coefficients using soybean oil, rapeseed oil, and olive oil were 0.947, 0.649, and 0.773, respectively. These findings suggest that the decrease in AV and CV depended on the specific surface area, i.e. the physical properties of the adsorbents. Figure 8 shows the relationship between the decrease in AV and CV and surface pH. The correlation coefficients using soybean oil, rapeseed oil, and olive oil were 0.949, 0.728, and 0.868, respectively. The decrease in AV and CV using virgin or calcined magnesium hydroxide was related to the properties of the adsorbent surface. The use of activated carbon, aluminum hydroxide, silica gel, and organic and inorganic adsorbents has been previously investigated for the regeneration (decreasing AV or CV) of waste edible oil. Polar compounds generated during the deterioration of edible oil were removed by the adsorbents because of van der Waals interactions. In addition, calcium silicate, a food additive, is also useful for decreasing the AV, CV, and FFA. The mechanism of adsorption of polar and non-polar compounds generated in waste edible oil by calcium silicate was related with the presence of silica gel molecules in calcium silicate. In this study, the decrease in AV and CV using virgin or calcined magnesium hydroxide mainly appears to be related to the specific surface area (a physical property) but a chemical property (surface pH) could also be responsible for the observed decreases in AV and CV.

In addition, relationships between the decrease in AV (CV) and adsorbent properties or the oil components are statistically analyzed by one way ANOVA (Fig. 9). The decrease in AV was related to the adsorbent properties of chemical and physical properties (p < 0.0001). On the other hand, the decrease in CV was related to the oil species (p < 0.05). These data indicate that the oil species and adsorbents are very important factors for purification of waste edible oil.

3.3 Changes in tocopherol and FFA

The amounts of α-, β-, γ-, and δ-tocopherol were 10.00, 2.17, 189.49, and 59.97 mg/100 g for soybean oil; 83.01, 25.21, 226.43, and 4.35 mg/100 g of oil for rapeseed oil; and
48.68, 3.04, 4.78, and 0.00 mg/100 g of oil for olive oil. The amount of tocopherol in these edible oils decreased after deterioration by the combined heat and aeration treatment. After deterioration, the residual amounts of γ- and δ-tocopherol in soybean oil were 3.04 and 13.91 mg/100 g of oil, respectively, corresponding to residual percentages of 1.6 and 23.2%. Aladedunye & Przybylski have reported that the relative stability of α- and γ-tocopherols is temperature-dependent, with the loss of α-tocopherol being greater than that of γ-tocopherol. In addition, previous studies have reported that the radical scavenging activity is in the order δ < γ < β < α-tocopherol, whereas the trend of heat stability is opposite (α < β < γ < δ-tocopherol). Therefore, while residual amounts of γ and δ-tocopherols remain in soybean oil after deterioration, no tocopherols remain in rapeseed oil and olive oil.

The concentrations of FFA before and after deterioration are shown in Tables 1-3. FFA in soybean oil, rapeseed oil, and olive oil has an abundance of palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid (19.5, 19.5, 248.0, 752.8, and 48.9 mg/L, respectively for soybean oil; 79.7, 77.3, 749.3, 292.4, and 115.3 mg/L, respectively for rapeseed oil; and 116.7, 57.6, 877.7, 78.9, and 29.8 mg/L, respectively for olive oil). After deterioration, the concentrations of saturated fatty acid (palmitic acid and stearic acid) are observed to either increase or undergo no significant change. On the other hand, the concentrations of unsaturated fatty acid (oleic acid, linolenic acid, and linolic acid) decrease. Deterioration of polyunsaturated fatty acid (linoleic acid and linolenic acid) occurs more easily compared to that of monounsaturated fatty acids (e.g., oleic acid), which indicates that soybean oil and rapeseed oil were easily degraded by deterioration. In this study, the AV for soybean oil, rapeseed oil, and olive oil after deterioration was 2.90, 3.71, and 2.48 times higher, and similar increases were observed for the CV (1.92, 12.09, and 4.76 times, respectively). The ratio of monounsaturated fatty acid and polyunsaturated fatty acid in soybean oil, rapeseed oil, and olive oil was 1.0:3.2, 1.0:0.5, and 1.0:0.1, respectively. The components in edible oil affect the products produced by deterioration treatment. Moreover, the adsorbent treatment did not drastically affect the concentration of FFA, which indicates that virgin and calcined magnesium hydroxide were useful for the regeneration of waste edible oil.

4 CONCLUSION

Magnesium hydroxide (S and L) was calcined at 380 and 1000°C (S-380, S-1000, L-380, and L-1000). The specific surface areas for S-380 (88.9 m²/g) and L-380 (103.0 m²/g) were greater than that of other adsorbents. S-380 and L-380 contain both magnesium hydroxide and magnesium oxide structures, which indicates that S-380 and L-380 are unstable, and these unstable structures may be responsible for their reactivity. We carried out deterioration of oil by both heat and aeration treatment. Adsorbent treatments lead to decreases in AV and CV in soybean oil, rapeseed oil, and olive oil with the largest decreases being exhibited when using S-380 and L-380 as adsorbents. The observed decreases in AV and CV have been attributed to the adsorbent specific surface area and surface pH values. The correlation coefficient between the decrease in AV and CV and

![Fig. 9 Relationships between the decrease in AV(CV) and adsorbent properties or the oil species.](image-url)
Regeneration of waste edible oil by the adsorbents


<table>
<thead>
<tr>
<th>Table 1</th>
<th>Concentration of free fatty acid in soy bean oil.</th>
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<tbody>
<tr>
<td>Concentration (mg/L)</td>
<td>Palmitic acid</td>
</tr>
<tr>
<td>Virgin oil</td>
<td>92.0</td>
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<tr>
<td>Before treatment (After deterioration)</td>
<td>133.4 ± 3.8</td>
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<tr>
<td>L</td>
<td>128.6 ± 3.7</td>
</tr>
<tr>
<td>L-380</td>
<td>132.3 ± 3.8</td>
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<tr>
<td>L-1000</td>
<td>108.4 ± 3.1</td>
</tr>
<tr>
<td>S</td>
<td>132.9 ± 3.8</td>
</tr>
<tr>
<td>S-380</td>
<td>126.2 ± 3.6</td>
</tr>
<tr>
<td>S-1000</td>
<td>126.2 ± 3.6</td>
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<tr>
<th>Table 2</th>
<th>Concentration of free fatty acid in rape seed oil.</th>
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<tr>
<td>Concentration (mg/L)</td>
<td>Palmitic acid</td>
</tr>
<tr>
<td>Virgin oil</td>
<td>79.7</td>
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<tr>
<td>Before treatment (After deterioration)</td>
<td>77.3 ± 1.8</td>
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<td>L</td>
<td>74.8 ± 1.8</td>
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<tr>
<td>L-380</td>
<td>72.8 ± 1.7</td>
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<tr>
<td>L-1000</td>
<td>71.3 ± 1.7</td>
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<tr>
<td>S</td>
<td>78.4 ± 1.9</td>
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<tr>
<td>S-380</td>
<td>76.1 ± 1.8</td>
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<tr>
<td>S-1000</td>
<td>78.0 ± 1.9</td>
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<tr>
<th>Table 3</th>
<th>Concentration of free fatty acid in soy olive oil.</th>
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<tr>
<td>Virgin oil</td>
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<td>L</td>
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<tr>
<td>L-380</td>
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<tr>
<td>L-1000</td>
<td>157.7 ± 16.1</td>
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<tr>
<td>S</td>
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<tr>
<td>S-380</td>
<td>145.5 ± 1.5</td>
</tr>
<tr>
<td>S-1000</td>
<td>129.9 ± 15.1</td>
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Specific surface area was 0.947 for soy bean oil, 0.649 for rape seed oil, and 0.773 for olive oil, respectively. These findings suggest that S-380 and L-380 were useful for the regeneration of waste edible oil.

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