Removal of Fluoride Ions from Water by Adsorption onto Carbonaceous Materials Produced from Coffee Grounds

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Abstract: Carbonaceous material for the removal of fluoride ions from water was prepared from coffee grounds (CGs) by calcination and subsequent HCl treatment. The characteristics of the CGs, including the surface area, mean pore diameter, pore volume, and surface functional groups were determined, and the morphological characteristics were evaluated using scanning electron microscopy. The adsorption isotherms, saturated amount of fluoride ions adsorbed, and the effect of contact time and temperature on the adsorption of fluoride ions were investigated for a sample of tap water. The specific surface area of CG calcined at 600°C (CG600) was larger than that of CGs calcined at 400, 800, and 1000°C. Phenolic, lactonic, and carboxyl groups were detected on the CG600 surface. The adsorption capacity of the carbonized CGs for fluoride was ranked in the order CG400 < CG1000 < CG800 < CG600 (where the numeral indicates the carbonization temperature), whereas virgin CG and CG600-NAT (not treated with hydrochloric acid solution) did not exhibit any adsorption ability for fluoride ions. The amount of fluoride ions adsorbed onto CG600 increased with increasing temperature and was consistent with chemical adsorption. The mechanism of adsorption of fluoride ions onto CG600 proceeded via ion exchange with chloride ions (1:1) present on the surface of CG600. The adsorption isotherms were fitted to the Freundlich and Langmuir equations. Moreover, CG600 showed an acceptable adsorption capacity for fluoride ions present in tap water.

Key words: coffee grounds, biomass, fluoride ion, carbonaceous material

1 INTRODUCTION

Fluorine is considered to be essential for the maintenance of human health. To maintain a healthy level of fluorine in the body, the optimal fluorine level in drinking water should be between 0.5 and 1.0 mg/L\(^{1}\). Concentrations higher than this can lead to a disorder known as fluorosis. Excessive fluoride intake is responsible for dental fluorosis\(^2\), skeletal fluorosis\(^8\), mottling of teeth\(^8\), ossification of tendons and ligaments\(^4\), and in several cases, stunted growth and neurological damage\(^5\). According to the World Health Organization (WHO), the maximum acceptable fluoride concentration for drinking water is 1.5 mg/L, while the permitted fluoride level in Japan is 0.8 mg/L\(^{10}\). Fluoride is used in many industrial processes such as aluminum manufacturing, stainless steel pickling, and cleaning of semiconductor parts and liquid crystal panels; consequently, fluoride effluents are often released into nearby water bodies\(^{10}\). Moreover, in parts of Africa and China that are rich in fluorite and fluorapatite, the concentration of fluoride ions in the groundwater is greater than the permissible value. Therefore, the removal of fluoride ions from wastewater is important from the perspectives of environmental conservation and human health.

Several techniques for fluoride removal have been developed, including membrane filtration\(^7\), ion exchange\(^6\), electrocoagulation\(^9\), precipitation\(^10\), nanofiltration\(^11\), and adsorption\(^12\). Because of its low cost, simplicity of design, and ease of operation, the adsorption technique has been the most extensively used of these techniques. Several adsorbents including natural, synthetic, and biomass materials such as activated carbon\(^13\), fly ash\(^14\), activated alumina\(^15\), metal oxide\(^16\), zeolite\(^17\), and chitosan beads\(^18\) have been reported. The high cost and limited pH range for adsorption of fluoride of these adsorbents makes them unsuitable for industrial application. Therefore, the development of an effective and low cost fluoride adsorbent is warranted.

Approximately 80,000 tons of coffee grounds (CGs) are

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generated in Japan as waste every year. Waste recycling is very important for achieving sustainable development. Although a portion of the CGs (biomass) is dumped in landfills, most of the CGs are incinerated; hence, a more suitable recycling process is required. CGs are generated in both advanced and developing countries; efficient utilization of these CGs would thus provide extensive benefits. Carbonaceous materials produced from CGs have many applications such as degradation of acidic dyes\textsuperscript{20}, adsorption of ammonia\textsuperscript{20}, and removal of heavy metals\textsuperscript{21}. Moreover, we have previously reported the adsorption of fluoride ions onto carbonaceous materials produced from biomass\textsuperscript{22}. Recently, Yokoyama \textit{et al.}\textsuperscript{23} reported a new and highly efficient technique for recycling waste that involves ion exchange.

In this study, we investigated the application of the ion exchange technique proposed by Yokoyama \textit{et al.}\textsuperscript{23} to CGs and measured the amount of fluoride ions adsorbed onto the carbonaceous material produced from the treated CGs. Moreover, this carbonaceous material was used to adsorb fluoride ions from tap water.

### 2 EXPERIMENTAL PROCEDURES

#### 2.1 Materials

Extracted CGs were obtained from UCC Ueshima Coffee Co., Ltd. Sodium fluoride and potassium chloride of special grade were used (Wako Pure Chemical Industries, Co., Ltd.). Surface modification of the CGs was performed according to the method reported by Yokoyama \textit{et al.}\textsuperscript{23} Virgin CGs (40 g) were added to 500 mL of 1 mol/L calcium chloride solution (Wako Pure Chemical Industries, Co., Ltd.) and stirred for 24 h at room temperature. The suspensions were filtered using a 0.45-μm membrane filter (Advantec, MFS, Inc.); the CG residues were dried for 5 h at 110°C. The CGs were then carbonized in a muffle furnace by heating for 2 h at 400, 600, 800, and 1000°C under a nitrogen gas inflow. Following carbonization, the CGs were added to 100 mL of 6 mol/L hydrochloric acid solution. Following carbonization, the CGs were dehydrated for 2 h at 400, 600, 800, and 1000°C, respectively. The suspensions were shaken at 100 rpm for 24 h, at 25°C. The adsorption of fluoride ions onto the CGs was calculated using Eq. (1):

\[
q = (C_0 - C_e) \times V/W
\]

where \(q\) (mg/g) is the amount of fluoride ions adsorbed onto the CGs, \(C_0\) (mg/L) is the initial concentration, \(C_e\) (mg/L) is the equilibrium concentration, \(V\) (L) is the solvent volume, and \(W\) (g) is the weight of the CGs.

The morphology of the CGs was analyzed using a JSM-5200 scanning electron microscope (JEOL, Japan), and the pH of the solution after the addition of CGs was measured using the activated carbon testing method (JIS K 1474) (The pH of the solution: 5.6).

#### 2.2 Characteristics of CGs

The yield percentage of the CGs was calculated using the weight of the CGs before and after carbonization. The specific surface area, pore volume, pore distribution, and mean pore diameter were measured on the basis of nitrogen adsorption/desorption isotherms using a NOVA 4200e (Sysmex, Japan) system\textsuperscript{24}. The surface functional groups were determined using the methods reported by Boehm \textit{et al.}\textsuperscript{25, 26}. CGs (0.1 g) were mixed with 20 mL of NaHCO\textsubscript{3}, Na\textsubscript{2}CO\textsubscript{3}, NaOH, and HCl solutions (0.05 mmol/L), respectively. The suspensions were shaken at 100 rpm for 24 h, at 25°C. The excess base or acid in 5 mL of the filtrate, obtained using a 0.45-μm membrane filter, was titrated using 0.01 mmol/L HCl or NaOH. The surface acidity or basicity was calculated based on the assumption that NaHCO\textsubscript{3} neutralizes only carboxyl groups; Na\textsubscript{2}CO\textsubscript{3} neutralizes only carboxyl and lactonic groups; NaOH neutralizes all acidic groups including carboxyl, lactonic, and phenolic groups; and HCl neutralizes all basic groups. Special grade NaHCO\textsubscript{3}, Na\textsubscript{2}CO\textsubscript{3}, NaOH, and HCl were used (Wako Pure Chemical Industries, Co., Ltd.).

#### 2.3 Fluoride ion adsorption isotherms using CG adsorbents

CGs (0.05 g) were added to 50 mL fluoride ion solution at different initial concentrations (5-50 mg/L). The suspensions were shaken at 100 rpm for 24 h, at 25°C (15 or 35°C). The suspensions were then filtered using a 0.45-μm membrane filter. The concentration of fluoride ions was measured using ion chromatography (Prominence HIC-NS, Shimadzu). The measurement conditions were as follows: column: Shim-pack IC-A3 (Shimadzu); mobile phase: 8.0 mmol/L p-hydroxybenzoic acid, 3.2 mmol/L bis-tris, and 50 mmol/L boric acid (1:1:1); flow rate: 1.2 mL/min; temperature: 40°C; detector: CDD-6A (Shimadzu); and injection volume: 50 μL. The amount of fluoride ions adsorbed onto the CGs was calculated using Eq. (1):

\[
q = (C_0 - C_e) \times V/W
\]

In addition, the efficacy of the CGs for fluoride ion removal was evaluated using tap water containing 5-50 mg/L fluoride ions. The amount of fluoride ions adsorbed onto the CGs was measured in the same manner as presented above.

#### 2.4 Saturated amount of fluoride ion adsorbed onto CGs

CGs (0.05 g) were added to 50 mL of a fluoride ion solution at an initial concentration of 300 mg/L. The suspensions were shaken at 100 rpm for 24 h, at 25°C. The satu-
3 RESULTS AND DISCUSSION

3.1 Characteristics of CGs

The physical properties of the CGs are listed in Table 1. The yield percentage of the CGs decreased with increasing carbonization temperature, which indicated that carbonization had occurred. Following carbonization (with the exception of CG600-NAT), the CGs were decomposed by hydrochloric acid treatment. The yield percentage of CG600-NAT (44.2%) was higher than that of CG600 (31.8%). CG600 had the highest specific surface area ($55.4 \text{ m}^2/\text{g}$), and the mean pore diameter of CG600 (76.5 Å) was smaller than that of the CGs carbonized at 400, 800, and 1000°C and CG600-NAT. The difference in the specific surface areas of CG600-NAT (5.0 m$^2$/g) and CG600 (55.4 m$^2$/g) indicates that the specific surface areas were influenced by the hydrochloric acid treatment carried out after carbonization. In general, as the number of pores increases, the specific surface area also increases; the higher specific surface area of CG600 was in agreement with this trend. The CG pores were classified into three categories on the basis of their diameter: micropores ($d<20$ Å), mesopores ($20<d<500$ Å), and macropores ($d>500$ Å). In this study, the pore volume of the CGs was determined using only micropores and mesopores.

The chemical properties of the CGs are listed in Table 2. The pH of each solution was 3.1-3.5 except for virgin CG (6.8) and CG600-NAT (7.0) (Table 2). The number of acidic functional groups decreased with increasing carbonization temperature. In the case of waste wood, the decomposition of organic components occurs as a result of carbonization; several surface functional groups were generated at different carbonization temperatures. For instance, phenolic groups and carboxyl groups were generated upon carbonization at 400-500°C; the number of these functional groups decreased on carbonization at 600-700°C. Moreover, hydroxyl and carboxyl groups disappeared at temperatures above 800°C. The trends in the changes in the surface functional groups of the CGs with varying carbonization temperature were similar to those of waste wood. The concentration of the basic functional groups of virgin CG and CG600-NAT were 0.15 and 0.68 mmol/g, respectively.

Scanning electron microscopy (SEM) images of the CGs are shown in Fig. 1. These images show that ramified structures were generated for CG400, CG600, CG800, and CG1000.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield (%)</th>
<th>Specific surface area (m$^2$/g)</th>
<th>Mean pore diameter (Å)</th>
<th>Pore volume (mL/g)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin CG</td>
<td>—</td>
<td>0.6</td>
<td>95.2</td>
<td>&lt;0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>CG400</td>
<td>53.7</td>
<td>2.1</td>
<td>748.1</td>
<td>&lt;0.001</td>
<td>0.015</td>
</tr>
<tr>
<td>CG600</td>
<td>31.8</td>
<td>55.4</td>
<td>76.5</td>
<td>0.003</td>
<td>0.097</td>
</tr>
<tr>
<td>CG800</td>
<td>25.9</td>
<td>31.5</td>
<td>139.3</td>
<td>0.017</td>
<td>0.104</td>
</tr>
<tr>
<td>CG1000</td>
<td>25.5</td>
<td>23.5</td>
<td>273.8</td>
<td>&lt;0.001</td>
<td>0.151</td>
</tr>
<tr>
<td>CG600-NAT</td>
<td>44.2</td>
<td>5.0</td>
<td>43.3</td>
<td>&lt;0.001</td>
<td>0.004</td>
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</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Total</th>
<th>Phenolic groups</th>
<th>Lactonic groups</th>
<th>Carboxyl groups</th>
<th>Basic functional groups (mmol/g)</th>
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</thead>
<tbody>
<tr>
<td>Virgin CG</td>
<td>6.8</td>
<td>2.31</td>
<td>0.76</td>
<td>0.07</td>
<td>1.48</td>
<td>0.15</td>
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<tr>
<td>CG400</td>
<td>3.1</td>
<td>3.79</td>
<td>0.81</td>
<td>0</td>
<td>2.98</td>
<td>0</td>
</tr>
<tr>
<td>CG600</td>
<td>3.4</td>
<td>3.74</td>
<td>1.13</td>
<td>0</td>
<td>2.61</td>
<td>0</td>
</tr>
<tr>
<td>CG800</td>
<td>3.5</td>
<td>2.65</td>
<td>0.27</td>
<td>0</td>
<td>2.38</td>
<td>0</td>
</tr>
<tr>
<td>CG1000</td>
<td>3.4</td>
<td>2.34</td>
<td>0</td>
<td>0</td>
<td>2.34</td>
<td>0</td>
</tr>
<tr>
<td>CG600-NAT</td>
<td>7.0</td>
<td>3.24</td>
<td>0.91</td>
<td>0</td>
<td>2.33</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Table 1: Physical properties of virgin CG and carbonized CGs.

Table 2: Chemical properties of virgin CG and carbonized CGs.
3.2 Fluoride ion adsorption isotherm using CG adsorbents

The amount of fluoride ions adsorbed onto the CGs is shown in Fig. 2. No adsorption of the fluoride ions was observed for virgin CG. The capacity of the carbonized CGs for fluoride ion adsorption was ranked in the following order: CG600-NAT < CG400 < CG1000 < CG800 < CG600. CG600 had the largest specific surface area of the samples, and the smallest mean pore diameter, which indicated that these functional properties influenced the amount of fluoride ions adsorbed onto the CGs.

However, the amount of fluoride ions adsorbed onto CG600-NAT was smaller than that adsorbed onto CG600, which indicated that the amount of fluoride ions adsorbed onto the CGs depended on the hydrochloric acid treatment after carbonization. On the basis of these results, it can be deduced that treatment of the CGs carbonized at different temperatures with hydrochloric acid generated additional adsorption sites for the fluoride ions on the surface of the CGs. After adsorption, the pH of the solution changed from 6.7 to a value between 3.9 and 4.9 for CG400-CG1000 (initial concentration of fluoride ions is 50 mg/L).

Moreover, the amount of fluoride ions (about 20.0 mg/g) adsorbed onto CG600 (about 30 mg/L) at the equilibrium concentration was greater than that onto commercial activated carbon (about 0.4 mg/g) or bone char (about 3.0 mg/g). The saturated amount of fluoride ions adsorbed onto CG600 was 74.0 mg/g. Tchomgui-Kamga et al. reported that the saturated amount of fluoride ions adsorbed onto charcoal that contained calcium compounds was 19.1 mg/g. The adsorbent produced from waste biomass (coffee grounds) in this study was more efficient than charcoal for the adsorption of fluoride ions.

3.3 Mechanism of adsorption of fluoride ions onto CGs

The relationship between the amount of fluoride ions adsorbed onto CG600 and the amount of chloride ions released is shown in Fig. 3. A linear plot with a correlation coefficient of 0.969 was obtained, which indicated that fluoride ions were exchanged with chloride ions with a 1:1 ratio. Nonetheless, the correlation coefficient of CG600-NAT was 0.283. These results indicated that chloride ions on the CG surface may or may not be exchanged with the fluoride ions. After carbonization, the surface of the CGs contained chloride ions, which were produced on treatment with hydrochloric acid (formula of the surface of the
Removal of Fluoride Ions from Water by Carbonaceous Materials

Many mechanisms have been reported for the adsorption or removal of fluoride ions; the relationship between fluoride ions and hydroxyl ions has been particularly discussed. Moreover, in those reports, the adsorption or removal of fluoride ions was found to be dependent on the pH of the solution, which showed that defluoridation depended on the charge of the adsorbent surface. A new method for the removal of fluoride ions is proposed herein, whereby the adsorption of fluoride ions depends heavily on the pH of the solution and the properties of the CG surface; additionally, the concentration of released chloride ions is below the permissible level stipulated by the Waterworks Law of Japan (below 200 mg/L).

Adsorption isotherms describe the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of adsorbate in the solution at equilibrium. Generally, the Freundlich and Langmuir isotherms are used to describe the adsorption characteristics of adsorbents used with water and wastewater. The experimental data fitted to the Freundlich equation, Eq. (2), and Langmuir equation, Eq. (3), respectively, as follows:

$$\log q = \log K + \frac{1}{n} \log C_e$$  \hspace{1cm} (2)

where $q$ is the amount of fluoride ions adsorbed onto the CGs (mg/g), $C_e$ is the equilibrium concentration (mg/L), $\log K$ is the Freundlich constant, indicative of the relative adsorption capacity of the adsorbent, and $1/n$ is the adsorption intensity.

$$C_eq = \frac{1}{a}Q_m + C_f/Q_m$$  \hspace{1cm} (3)

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Freundlich constants</th>
<th>Langmuir constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1/n$</td>
<td>$K$</td>
</tr>
<tr>
<td>CG600</td>
<td>0.42</td>
<td>5.90</td>
</tr>
<tr>
<td>CG800</td>
<td>0.37</td>
<td>6.84</td>
</tr>
<tr>
<td>CG1000</td>
<td>0.14</td>
<td>6.46</td>
</tr>
</tbody>
</table>

The goodness of fit of the experimental data obtained from the adsorption isotherms was verified for both models, and the results are summarized in Table 3. The Freundlich and Langmuir plots were linear with correlation coefficients of 0.975-0.994 and 0.982-0.997, respectively, suggesting that the data conformed to the models. Therefore, fluoride ions are believed to be adsorbed onto the CG surface according to monomolecular adsorption onto a heterogeneous surface.

3.4 Effect of temperature on the fluoride ion adsorption onto the CGs

Figure 4 shows the amount of fluoride ions adsorbed onto CG600 at different temperatures. ●: 5°C, ◆: 25°C, △: 35°C

![Graph showing relationship between amount of fluoride ions adsorbed and amount of chloride ion released using CG600.](image)

**Table 3** Freundlich and Langmuir constants for fluoride ion adsorption onto CGs.

- **Figure 3** Relationship between amount of fluoride ions adsorbed and amount of chloride ion released using CG600.
onto CG600 at 15, 25, and 35°C. The amount of fluoride ions adsorbed onto CG600 increased with increasing temperature. These results indicated that the adsorption of fluoride ions onto CG600 occurred by chemisorption, that is, the exchange of fluoride ions with chloride ions on the CG600 surface.

3.5 Application of CGs to fluoride removal from tap water

The amount of fluoride ions adsorbed onto the CGs from tap water containing fluoride ions is shown in Fig. 5. From this figure, the adsorption capacity of the CGs for fluoride ions was in the following order: CG1000 < CG800 < CG600. The amount of fluoride ions adsorbed from the tap water sample was less than that adsorbed from the control distilled water sample, suggesting the inhibition of fluoride ion adsorption onto the CGs by certain components of the tap water sample, such as other anions (nitrates, nitrites, sulfates, and phosphates) or organic compounds. The change in the pH of the tap water sample was similar to that of the distilled water sample (from 7.4 to 6.8-7.3).

4 CONCLUSION

Carbonaceous materials were prepared by calcination of coffee grounds at various temperatures, followed by HCl treatment. Ramified structures were generated by carbonization. A largest specific surface area and smallest mean pore diameter were obtained by carbonization at 600°C (sample CG600). Fluoride ion adsorption was higher with CG600 compared with the sample not treated with HCl (CG600-NAT), which indicated that the adsorption of fluoride ions was dependent on the presence of chloride ions generated by hydrochloric acid treatment. The mechanism of adsorption of fluoride ions involved exchange with chloride ions on the surface of CG600 (1:1). The adsorption isotherms were fitted to the Freundlich and Langmuir equations; the correlation with these equations suggested the occurrence of monomolecular adsorption on a heterogeneous surface. Fluoride adsorption with CG600 for a sample of tap water was lower than that for the control distilled water sample, which indicated that adsorption in tap water was inhibited by certain constituents, which may include other anions such as nitrates, nitrites, sulfates, phosphates, and organic compounds.

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