

## EFFECTS OF PRETREATMENTS ON CALCIUM ACCUMULATION ONTO GAC

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### ABSTRACT

The effect of coagulation and ozonation as pretreatments for granular activated carbon (GAC) filtration on calcium accumulation onto GAC was studied. Three kinds of FA solutions extracted from commercial leaf mold for horticulture were used: FA itself, FA after coagulation (FA-c) and FA after ozonation (FA-oz). Coagulation used as pretreatment before GAC filtration significantly decreased calcium accumulation onto GAC while ozonation caused a small increase on calcium accumulation onto GAC. Acidic functional groups into GAC introduced by adsorption of fulvic acid controlled accumulation of calcium onto GAC. Significant decrease of calcium accumulation onto GAC by coagulation was caused by the removal of the fraction with acidic functional groups from FA.

### KEYWORDS

Calcium, granular activated carbon (GAC), pretreatment, coagulation, ozonation, dissolved organic carbon (DOC), fulvic acid (FA).

### INTRODUCTION

Granular activated carbon (GAC) filtration is a promising process that removes harmful or odorous organic compounds from water and wastewater. Natural water and wastewater contain not only organic matter but inorganic ions such as calcium, magnesium, sodium iron and others. It was found that these metals accumulate onto GAC used for water and wastewater treatment [Knappe *et al.*, 1992; Lehmann *et al.*, 1999; Lee *et al.*, 2003; Miño *et al.*, 2005]. Calcium (Ca) is known to be one of the major inorganic materials accumulated onto GAC. The mechanisms for the buildup of calcium onto GAC include precipitation as calcium carbonate (CaCO<sub>3</sub>) [Knappe *et al.*, 1992; McCafferty *et al.*, 2000; Lee *et al.*, 2003], adsorption of calcium-organic complexes in the presence of natural organic matter (NOM) [Knappe *et al.*, 1992; McCafferty *et al.*, 2000; Nowack and Cannon, 1997; Lee *et al.*, 2003] and ion exchange between calcium and surface functional groups of GAC [Leboda *et al.*, 1998].

One of the problems caused by calcium accumulation onto GAC is that large amounts of calcium accumulated decrease the adsorption capacity of it for organic contaminants [Lee *et al.*, 2003]. Another problem occurs during regeneration process of GAC [Cannon *et al.*, 1993; Knappe *et al.*, 1992]. The accumulated calcium can

catalyze the regeneration reaction to accelerate internal mass loss and convert micropores to mesopores [Mazyck and Cannon, 2000]. In natural aquatic systems, inorganic ions are rarely present as free hydrated ions [Buffle, 1988]. Complex formation is one of the most important reactions of inorganic ions in aquatic systems and NOM is an important complexing agent for inorganic ions and therefore for calcium [Schmitta *et al.*, 2003; Christensen *et al.*, 1996]. It has been proven that calcium accumulation onto GAC is negligible in the absence of NOM. On the other hand, large amounts of calcium are accumulated on GAC when both NOM and calcium are present in the solution [Lee *et al.*, 2003; Frederick and Cannon, 2001]. Therefore the presence of DOC such as NOM in water and wastewater has a strong influence on the calcium accumulation through adsorption of complex of DOC with Ca.

Lee *et al.* [2003] reported that calcium accumulation onto GAC in a column operated for 5.0 years for drinking water treatment from an eutrophic reservoir was 36.6 mg Ca/g GAC. The amounts of calcium accumulated onto GAC in eight different drinking water treatment plants were reported to range from 10 to 68 mg Ca/g GAC (time of operation is not shown) [Knappe *et al.*, 1992]. On the other hand, Miño *et al.* [2005] reported that the amounts of calcium accumulated onto GAC used for landfill leachate treatment was only 8.6 mg Ca/g GAC for two-year operation. The amounts of calcium accumulated onto GAC for landfill leachate treatment are smaller than those in the drinking water treatment, even though DOC and calcium concentrations in the landfill leachate were around 12 and 55 times higher than those in the reservoir water reported by Lee *et al.* [2003], respectively. One major difference between them is pretreatment. Influent water for the GAC was ozonated after microfiltration in the study reported by Lee *et al.* [2003]. However it was coagulated after biological treatment in the study reported by Miño *et al.* [2005], suggesting that pretreatment of influent water affects calcium accumulation onto GAC. Although GAC treatment does not directly apply to raw water and wastewater, it is very important to study the effects of pretreatments on calcium accumulation onto GAC.

Frederick and Cannon [2001] reported that iron and aluminum coagulation decreased the amount of calcium accumulation onto GAC used for drinking water treatment at low DOC and calcium concentration. Especially, iron addition at pH 6 was effective on reducing calcium accumulation onto GAC. However, it is still unknown how coagulation process decreased the calcium accumulation onto GAC. The objective of this study is to clarify the effect of coagulation and ozonation as pretreatments prior GAC filtration on calcium accumulation onto GAC.

## MATERIALS AND METHODS

### **GAC**

GAC used in this study was Filtrasorb 400 from Calgon Corporation. It was sieved in order to obtain grains with the average diameter ranging from 1.0 to 1.4 mm. GAC was washed several times by distilled water, dried for 24 h at 105°C and stored in a desiccator.

### ***Preparation of fulvic acids***

Aquatic NOM represents a wide range of structurally complex compounds derived from the chemical and biological degradation of plants and animals. The major fractions of NOM are humic and fulvic acids (humic substances, HS) which comprise over 50% of the carbon in NOM, and are mainly responsible for the colour in natural waters [Linhua et al., 2001]. Fulvic acids (FA) generally exhibit the lower equivalent weight and a corresponding higher charge density that is mostly created by acidic functional groups, carboxyl and hydroxyl functional groups, while humic acids tend to have higher equivalent weights and lower charge densities; also humic acids are more susceptible than FAs to be removed by coagulation [Nowack and Cannon, 1997]. Since FA is a significant component of NOM that is capable of forming complexes with calcium [Frederick and Cannon, 2001], three kinds of FA solutions extracted from commercial leaf mold for horticulture, i.e. FA itself, coagulated FA (FA-c) and ozonated FA (FA-oz), were used to determine the effect of pretreatment on calcium accumulation onto GAC.

Five hundred grams of commercial leaf mold were dried at room temperature and sieved through 60 mesh screen. To extract HS, the sieved leaf mold was placed in 3,000 ml of 0.1 N NaOH solution and boiled at 100°C for 40 min. The extract was separated by filtration through Whatman GF/D filters (pore size = 2.7 µm). The extraction was repeated on the residue using 3,000 ml of 0.1 N Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> solution [Kumada, 1987]. The two extracts were mixed and the pH was decreased to 1.5 using 3 N HCl. The solution was centrifuged at 5,000 rpm for 10 min to separate the supernatant. The supernatant was filtered through membrane filter (pore size = 0.45 µm). The pH of the supernatant was adjusted to 7.0 by 3 N NaOH and used as FA solution.

### ***Coagulation and ozonation for FAs***

The FA solution was coagulated using polyaluminum chloride (1.3 mg Al/mg DOC) for 3 min by rapid mixing at 125 rpm. The coagulated mixture was centrifuged at 5,000 rpm for 10 min to separate the supernatant. The pH of the supernatant was adjusted to 7.0 by 3 N NaOH and used as FA after coagulation (FA-c) solution. The FA solution had an initial DOC of about 1,400 mg/l, and after coagulation it decreased around 80 % to be about 265 mg/l.

The FA solution was diluted to a DOC concentration of 300 mg/l and then ozonated with 2.5 mg O<sub>3</sub>/mg DOC. The pH of the ozonated solution was adjusted to 7.0 by 0.1 N NaOH and used as FA after ozonation (FA-oz) solution. DOC of FA-oz solution was approximately 220 mg/l.

### ***Evaluation of calcium accumulation onto GAC***

Five hundred milliliters of each FA solution were adjusted at DOC concentration of 100 mg/l and calcium chloride was added to reach a concentration of 1,000 mg Ca/l. The pH was adjusted to 7.0. Six grams of GAC were added into the solution and shaken at 100 rpm. The solution was renewed periodically every 24 h. Amount

of DOC adsorbed into GAC was determined from the difference between the initial and final DOC concentrations in the solution.

### ***Analysis***

GAC sample was ashed at 600°C for 24 hours to determine inorganic materials onto GAC. The ash was mixed with 25 ml of 1 N HCl. After 24 hours of shaking, the solution was filtered through an acid-resistant, ash-free cellulose acetate membrane (pore size = 0.45 µm). The filtrate was then diluted to 250 ml with distilled water and a portion was transferred to a glass bottle. The concentration of Ca in the solution was determined by inductively coupled plasma (ICAP-575II, Nippon Jarrell-Ash).

The amount of calcium carbonate (CaCO<sub>3</sub>) fixed in GAC was evaluated by quantifying carbon dioxide (CO<sub>2</sub>) released by acidification [McCafferty *et al.*, 2000]. Most of the CO<sub>2</sub> released from GAC must originate from CaCO<sub>3</sub>, because the accumulated inorganic ions except calcium were low and FA on GAC was not decomposed by the acidification method [Lee *et al.*, 2003]. The amount of CO<sub>2</sub> released was determined by gas chromatography (GC-8A, Shimadzu with TCD detector). The recovery efficiency as CO<sub>2</sub> from analytical grade CaCO<sub>3</sub> was confirmed to be 100% in the above mentioned procedure.

Total acidic functional groups consisting of carboxyl and hydroxyl functional groups adsorbed into GAC were determined from GAC samples. They contained both free acidic functional group and acidic functional group forming complex with Ca. GAC was washed with 0.1 N hydrochloric acid in order to remove calcium accumulated onto GAC. The amount of hydroxyl groups adsorbed into GAC was obtained from the subtraction of the amount of carboxyl groups adsorbed into GAC from the amount of total acidic functional groups adsorbed into GAC. Carboxyl and total acidic groups adsorbed into GAC were quantified by 0.2 N NaHCO<sub>3</sub> and 0.2 N NaOH, respectively. The suspension of GAC was shaken at 25°C for 24 h. After shaking the solution was kept at 25°C for 96 h. After filtering the solution, the filtrate was back-titrated with 0.2 N HCl. Hydroxyl groups were quantified subtracting the value of carboxyl groups from total acidity [Boehm *et al.*, 1964; Morinaga *et al.*, 2003].

The concentration of aluminum (Al) in the different FA solutions was determined by inductively coupled plasma (ICAP-575II, Nippon Jarrell-Ash). DOC concentration in solutions was determined by TOC analyzer (TOC-V CSN, Shimadzu).

## **RESULTS AND DISCUSSION**

### ***Effect of pretreatments on calcium accumulation onto GAC.***

Figure 1 shows the effect of coagulation and ozonation on calcium accumulation onto GAC as a function of

adsorbed FA in batch experiments for FA, FA-c and FA-oz solutions. The amount of calcium accumulated onto GAC with approximately 20 mg C/g GAC was about 3 times lower in FA-c solution than in FA and FA-oz solutions. Lower accumulation of calcium onto GAC in FA-c solution is possibly because Al ions occupy the sites of FA where Ca forms complexes. Table 1 shows the Al concentrations in FA and FA-c solutions before calcium addition. Aluminum concentration in FA-c solution (0.06 mg/l) was much lower than in FA solution (0.19 mg/l). This means that Al did not form complexes with FA and the sites to form complexes with calcium would be available.

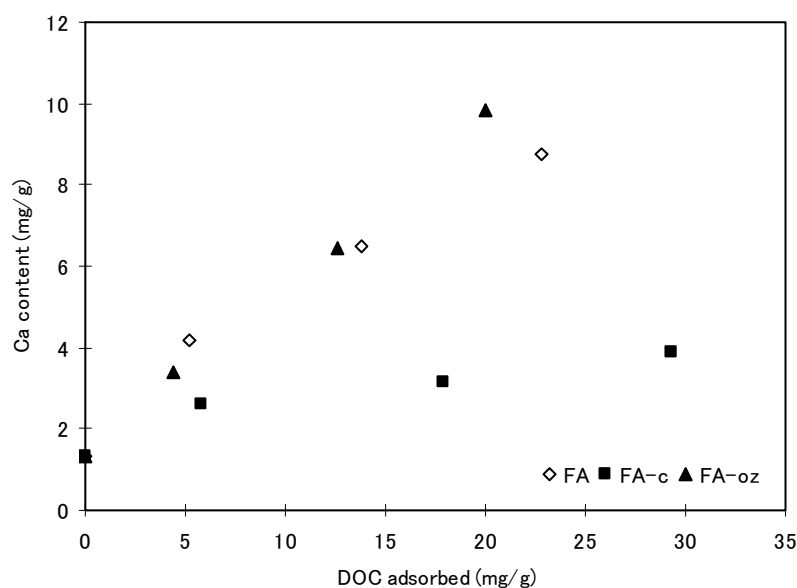


Fig. 1. Calcium accumulation onto GAC in different FA solutions.

Table 1. Al concentration in FA and FA-c solutions of 100 mg/l DOC.

Solution	Al (mg/l)
FA	0.19
FA-c	0.06

### *Calcium species accumulated onto GAC.*

Figure 2 shows calcium species accumulated onto GAC as  $\text{CaCO}_3$  and calcium forming complexes with DOC for the three solutions (FA, FA-c and FA-oz) in the case of the largest DOC adsorption for each solution. Calcium as  $\text{CaCO}_3$  represented less than 10 % of total calcium accumulated onto GAC in all 3 solutions and most of the calcium accumulated onto GAC was calcium forming complexes with DOC. It indicates that adsorption of DOC controls calcium accumulation and may suggest that the characteristics of FA affect DOC-calcium complex formation and the amount of calcium accumulation onto GAC. Coagulation may alter some characteristics of FA such as molecular weight and content of carboxyl and hydroxyl groups. Since 80 % of DOC was reduced by coagulation of FA, there is a possibility that the fraction of FA which could form complexes with calcium could be selectively removed by coagulation.

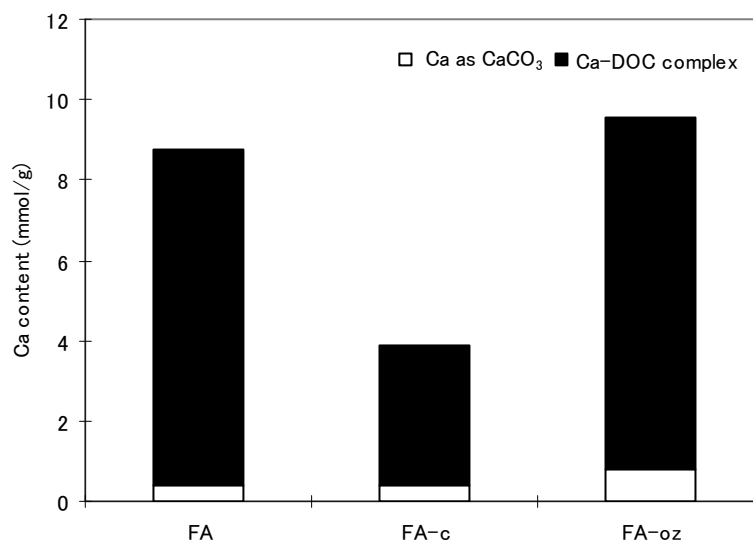


Fig. 2. Calcium species accumulated onto GAC used for different FA solutions.  
(DOC: 100 mg/l, Ca: 1000 mg/l)

#### ***Effect of acidic functional groups on calcium accumulation onto GAC.***

The increase in acidic functional groups on GAC with the increase in DOC adsorbed is shown in Fig. 3. For all 3 solutions, carboxyl and hydroxyl groups adsorbed on GAC represented around 65 and 35 % of total functional acidic groups adsorbed, respectively. Total amount of acidic functional groups on GAC before adsorption of FAs was 0.43 mmol/g. Total amount of acidic functional groups on GAC proportionally increased with the increase in DOC adsorbed. However, the rates of total acidic functional groups adsorbed on GAC were 0.037, 0.051 and 0.007 mmol/mg for FA, FA-oz and FA-c, respectively. This result suggests that coagulation removed the fraction with much acidic functional groups from FA. Ozonation caused small increase in acidic functional groups adsorbed on GAC.

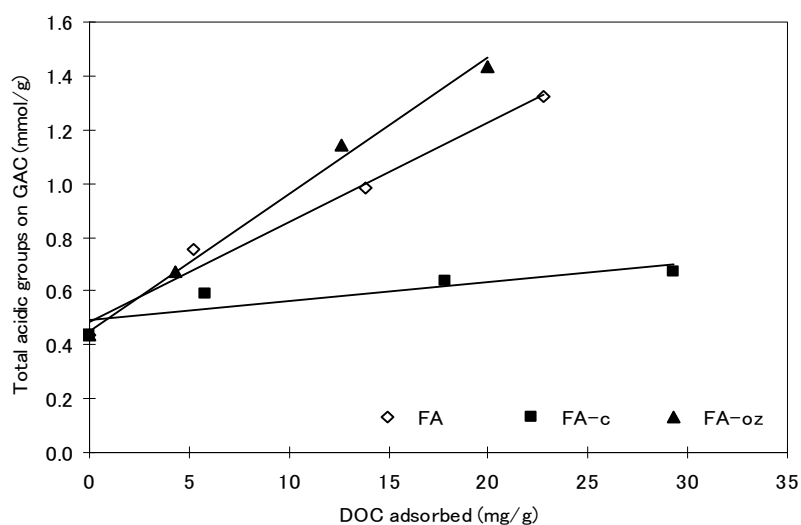


Fig. 3. Relation between DOC and total acidic groups of different FA solutions adsorbed into GAC.

Figure 4 shows the relationship between acidic functional groups on GAC and calcium accumulation. We can find a good relationship between calcium accumulation and acidic functional groups on GAC for all data from FA, FA-c and FA-oz. The acidic functional groups adsorbed on GAC introduced by adsorption of FAs controlled the accumulation of calcium. Stoichiometrically, 2 mol of acidic functional groups are needed for each mol of calcium. About 5 mol of acidic functional groups were adsorbed per mol of calcium accumulated onto GAC in our study, suggesting that not all acidic functional groups formed complex with calcium. This agrees with the results obtained by Frederick *et al.*, [2001]. They mentioned that not only the number but also the position of acidic functional groups affect calcium accumulation. Organic compounds containing carboxyl and hydroxyl functional groups at the ortho position enhanced calcium accumulation onto GAC. In their research, calcium accumulation for organic compounds containing adjacent carboxyl and hydroxyl functional group was approximately up to 15 times higher than that for organic compounds with either carboxyl or hydroxyl groups. Overall coagulation and ozonation as pretreatment processes change the acidic functional groups adsorption on GAC, which dictates the amount of calcium to be accumulated onto GAC.

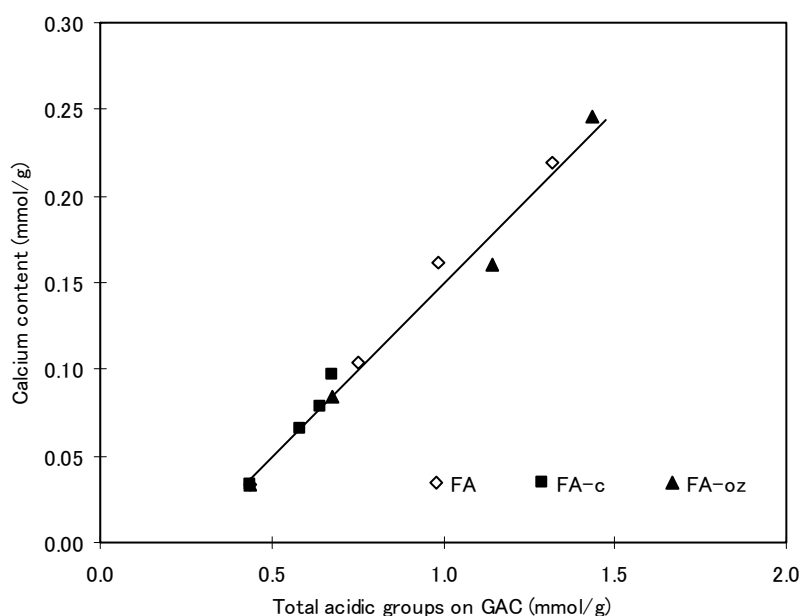


Fig.4. Effect of acidic functional groups adsorbed on calcium accumulation onto GAC.

### Conclusions

1. Coagulation used as a pretreatment before GAC filtration significantly decreased calcium accumulation onto GAC while ozonation caused a small increase of calcium accumulation onto GAC.
2. Acidic functional groups into GAC introduced by adsorption of FA controlled calcium accumulation onto GAC.
3. Significant decrease of calcium accumulation onto GAC by coagulation was caused by the removal of the fraction with acidic functional groups from FA.

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