Research article

Removal of Nitrate Nitrogen in Activated Carbon with Calcium Treatment

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Received 6 February 2010 Accepted 25 July 2010

Abstract As chemical fertilizers have been applied to farmlands beyond the environmental capacity, leaching of nitrate nitrogen (NO_3-N) have been causing severe problems, such as groundwater contamination or eutrophication in water systems of watersheds. Also, high concentration of nitrate nitrogen in groundwater happens to affect human health, especially on infant. So, research interests have been focused on the effective measures for eliminating nitrate nitrogen leaching from farmlands. This study dealt with the strategy on removal of nitrate nitrogen from farmlands through the column experiment using activated carbon (charcoal) with calcium chloride ($CaCl_2$) treatment. In the experiments, 2 types of activated carbon were prepared; one was activated carbon with calcium chloride ($CaCl_2$) treatment and the other activated carbon without treatment. The experiment was conducted to corroborate the removal of nitrate nitrogen between 2 types of activated carbon and to quantify the amounts of activated carbon added for certain amounts of nitrate nitrogen removal. Glass beads, around 1.1 mm in diameter, were used as an alternative soil and incorporated with activated carbon at 10, 20 and 30% by volumetric basis. The experimental results indicated that average adsorption ratio of the columns with 20% and 30% of $CaCl_2$ treated carbon was larger than that of other columns, as initial adsorption ratio of the columns with 20% and 30% of $CaCl_2$ treated carbon was much higher than other columns. However, decreasing tendency in adsorbing NO_3-N of the columns with $CaCl_2$ treated carbon was comparatively higher than that of other columns.

Keywords $CaCl_2$ treatment, nitrate nitrogen, activated carbon, ground water, glass beads

INTRODUCTION

Nitrate nitrogen, which is a component in chemical fertilizers, discharges from farmlands and caused environmental problems such as groundwater contamination or eutrophication. Also, nitrate nitrogen is a cancer causing substance known as carcinogenic substance. In addition, nitrate nitrogen is toxic particularly to human infant resulting fatal anoxia. Although there are some measures to extract nitrate nitrogen component in water, such as reverse osmosis membrane method, ion-exchange membrane method, biological method etc., appropriate ones being economically reasonable and easy handleing for treating agricultural discharges are still not developed.

Removal of nitrate nitrogen using charcoal treated with $FeCl_2$ (Mori et al., 1995) was advanced by Yokoyama et al. (2008). In this study, the raw material of carbon was treated with $CaCl_2$ and then re-burned. The charcoal treated with $CaCl_2$ having high capacity to adsorb hydrochloric acid was more effective to remove nitrate nitrogen than $FeCl_2$ treated charcoal. However, the preparation procedure of $CaCl_2$ treated charcoal was so complicated that the method was not popularized. For simplifying the preparation procedure of $CaCl_2$ treated charcoal, Ota (2009) selected activated carbon for $CaCl_2$ treatment. However, attentions have been paid to the sustainability adsorbing NO_3-N with $CaCl_2$ treated charcoal.

Accordingly, the objectives of this study were to evaluate the sustainability adsorbing NO_3-N with $CaCl_2$ treated activated carbon (charcoal) and to discuss the appropriate amount of activated carbon applied in site.

MATERIALS AND METHODS

Granules of charcoal known as activated carbon at less than 2.0 mm in diameters were used in this study. This activated carbon was derived from coconut shell as it was the most effective activated carbon to adsorb nitrate nitrogen comparing to other kinds of charcoal (Ota, 2009). Two types of activated carbon were used in this experiment; one was the $CaCl_2$ treated and the other the untreated activated carbon.

In the initial stage of the pretreatment process, the the activated carbon was dipped into 1000 ml of 3 mol L^{-1} $CaCl_2$ aqueous solution for 1 hour. And then, the $CaCl_2$ treated activated carbon was rinsed with distilled water. These steps were repeated until the electric conductivity became below 10 mS/m. In the last stage, the cleansed activated carbon with $CaCl_2$ treatment was dried in the oven at 100℃ for 24 hours.

Columns made from plastic vinyl chloride pipe at 5.6 cm in diameter and 25 cm high were prepared. Glass beads about 1.1 mm in diameter were used instead of soils. As shown in Fig. 1, column A was filled with only glass beads as a control, columns B, C and D were filled with glass beads and untreated activated carbon (hereinafter, UAC) by volume ratios at 9:1, 8:2 and 7:3, respectively. Glass beads with $CaCl_2$ treated activated carbon (hereinafter, TAC) were added to columns E, F and G at the same ratios as column B, C and D.

Aqueous solution of nitrate nitrogen (NO_3-N) at 20 mg/L was continuously dripped into each column at 0.05 ml/sec for 3 hours, which equaled 547 ml per day. And then the discharged water from the bottom of the column was collected for analyzing the amounts of NO_3-N discharged. The experiment was repeated 5 times.

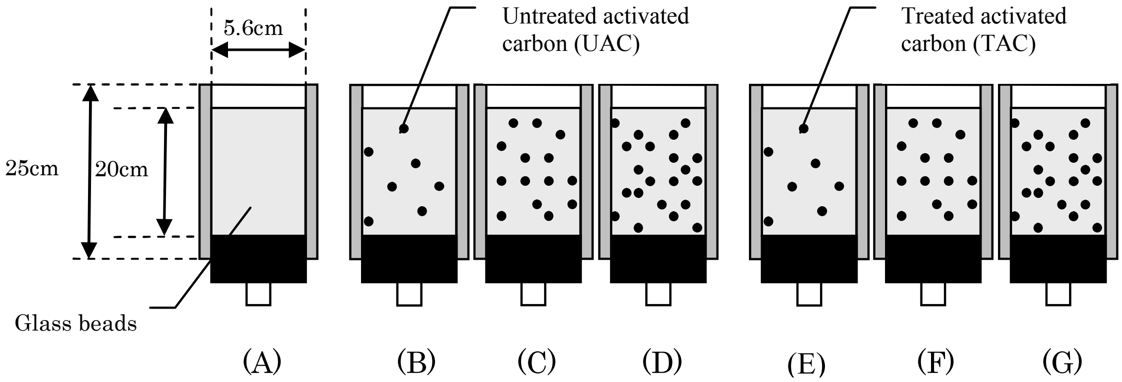

Fig. 1 Experimental columns filled up with glass beads and activated carbon
Controlled (0% UAC added) (A), 10% UAC added (B), 20% UAC added (C), 30% UAC added (D), 10% TAC added (E), 20% TAC added (F), and 30% TAC added

RESULTS AND DISCUSSION

As mentioned above, UAC or TAC was mixed at 10, 20 and 30% for columns B, C and D or columns E, F and G (Fig. 1), respectively. The changes in nitrate nitrogen concentration with water discharged are shown in Fig. 2. The concentration of nitrate nitrogen of water discharged from the column with TAC was remarkably smaller than that with UAC or control. However, there was a tendency for the concentration of nitrate nitrogen to increase with the amounts of water discharged. In case of TAC 30% (Fig. 2 (C)), although the initial concentration of NO_3-N was almost 0 mg/L, the concentration increased to 6.25 mg/L with the amounts of water.

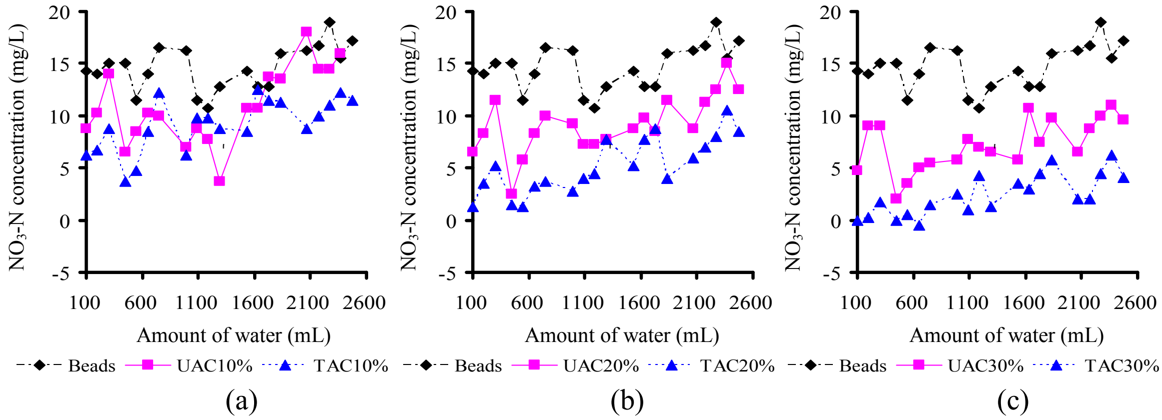

Fig. 2 Changes in nitrate nitrogen concentration with amounts of water discharged
Control, UAC 10%, TAC 10% (a), Control, UAC 20%, TAC 20% (b), and Control, UAC 30%, TAC 30% (c)

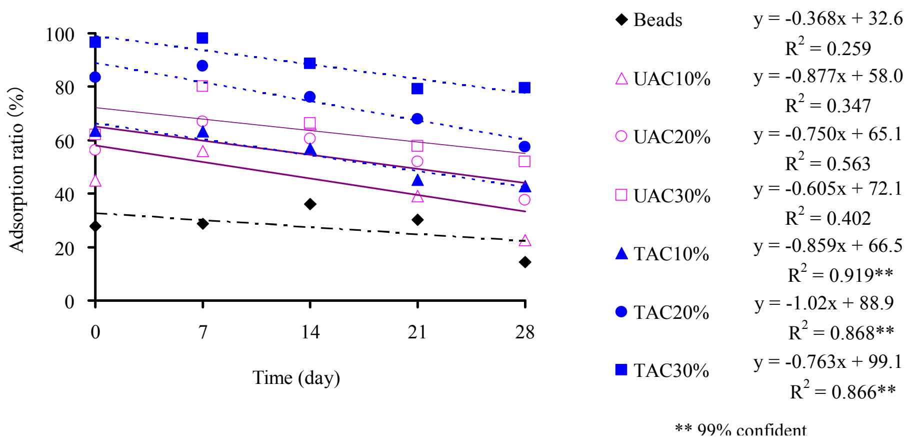

Fig. 3 Changes in adsorption ratio of each column with time

Adsorption ratio was calculated based on the equation (1). The changes in average adsorption ratio for every 7 days of 7 columns were summarized in Fig. 3. There was a tendency that adsorption ratio of every column decreased after 2 weeks passed. The highest adsorption ratio appeared for TAC 30% column, in which adsorption ratio was almost 100% in the initial stage but decreased to 80% after 28 days passed.

$$Adsorption\ ratio = \frac{C_i - C_o}{C_i} \times 100 \qquad (1)$$

where C_i was NO_3-N concentration of inflow and C_o was NO_3-N concentration of inflow.

The changes in adsorption ratio of each column were expressed with the linear regression formula of y=ax+b as shown in Fig. 3. Also, the values of slope (a in y=ax+b) and the values of intercept point (b in y=ax+b) were summarized in Fig. 4 (a) and (b), respectively.

The values of slope in the regression line, a in y=ax+b, of TAC columns with 20% and 30% of $CaCl_2$ treated activated carbon tended to be smaller than that of UAC columns with 20% and 30% of untreated activated carbon as shown in Fig 4 (a). It means that adsorption capacity of TAC columns diminishes earlier than UAC columns.

On the other hand, the values of intercept point in the regression line, b in y=ax+b, of TAC columns were remarkably higher than that of UAC columns as shown in Fig 4 (b). It means that initial adsorption capacity of TAC columns with $CaCl_2$ treated activated carbon is much higher than that of UAC columns with untreated activated carbon.

Through four weeks experiments, it was considered that TAC columns particularly with 20% and 30% of $CaCl_2$ treated activated carbon showed the highest adsorption ratio among all columns in the initial stage. However, there was a tendency for adsorption capacity of TAC columns diminishes earlier than UAC columns.

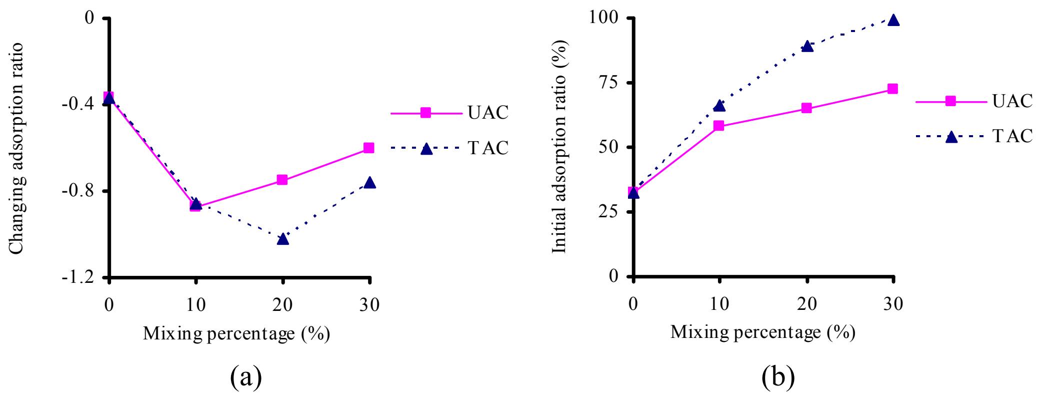

Fig. 4 Summarized values from linear regression formula

Changing adsorption ratio of UAC and TAC columns based on slope in formula (a) and initial adsorption ratio of UAC and TAC columns based on intercept value in formula (b)

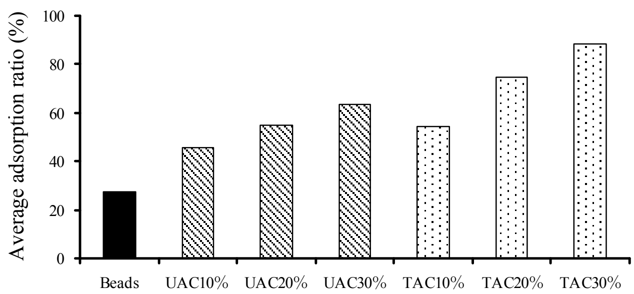

Fig. 5 Average adsorption ratio of each column

According to the experimental results for 28 days, average adsorption ratio of each column was calculated (Fig. 5). Average adsorption ratio of UAC and TAC columns was remarkably higher than that of control column with glass beads. Also, there was a tendency for average adsorption ratio of TAC columns with 20% and 30% of $CaCl_2$ treated activated carbon to be larger than that of other columns. Accordingly, it was considered the strategy adding $CaCl_2$ treated activated carbon even at 20% is the effective to adsorb NO_3-N and to eliminate the nitrate nitrogen leaching from farmlands.

CONCLUSION

This study dealt with the effects of activated carbon (charcoal) added on nitrate nitrogen removal. Two types of activated carbon were employed in this study; one was activated carbon with calcium chloride ($CaCl_2$) treatment and the other carbon without treatment. The column experiment was conducted to corroborate the removal of nitrate nitrogen between 2 types of activated carbon. The columns were filled with glass beads at 1.1 mm in diameter incorporated with activated carbon at 10, 20 and 30% by volumetric basis. The experimental results indicated that average adsorption ratio of the columns with 20% and 30% of $CaCl_2$ treated carbon was larger than that of other columns, as initial adsorption ratio of the columns with 20% and 30% of $CaCl_2$ treated carbon was much higher than other columns. However, decreasing tendency in adsorbing NO_3-N of the columns with $CaCl_2$ treated carbon was comparatively higher than that of other columns.

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