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Evaluation of the Nitrate Anion in Recon Extract by Adsorbents

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ABSTRACT : The amount of nitrate in the tobacco leaf has been shown to be correlated with the levels of alkaloids and nitrosamines. Also the nitrate content of the tobacco correlated closely with the smoke delivery of nitric oxide and tobacco-specific nitrosamines (TSNAs). These are related with the effect of the reconstituted tobacco leaf(Recon) using the tobacco stems. Adsorption process is gaining interest as one of the effective processes of advanced liquid treatment for liquid containing unnecessary materials. This study is focused on the evaluation of four anion exchangers, a cation exchanger and an activated carbon, as adsorbents for reduction of nitrate anion from Recon extract. In order to analyze the nitrate anion, the IC method used in this work was carried out with a Dionex ICS-2000 system. The effects of dosages of adsorbents and concentration of extract on the removal of nitrate anion were examined. Experimental results showed that for nitrate-anion exchanger, nitrate-cation exchanger and nitrate-activated carbon adsorption system, approximately 70 %, 10 %, and 4 % removal efficiencies were achieved at the Brix 10 and the 20 % addition. Although the activated carbon was little efficient for removal of nitrate ion, the removal of nicotine was very efficient at given conditions.

Key words **: Reconstituted tobacco leaf, ion exchanger, activated carbon, nicotine, nitrate**

Nitrate and nitrite occur naturally in the environment in both plant and animal tissues. The amount of nitrate in the tobacco leaf has been shown to be correlated with the level of alkaloids and nitrosamines. Also the nitrate content of the tobacco correlated closely with the smoke delivery of nitric oxide and nitrosamines. Different methods have been applied to the removal of nitrite and nitrate. These include adsorption, biological denitrification, ultrafiltration and electrodialysis(Afkhami, 2006; Dursun, 2004).

Adsorption process in general, is gaining interest as one of the effective processes of advanced liquid treatment for liquid containing unnecessary materials. Extensive studies have shown that activated carbon is efficient in adsorption of numerous bio-resistant organic pollutants from aqueous system(Faust, 1987). In recent years, there has been a continuous search for locally available adsorbents for the replacement of activated carbon for removal of a variety of organic compounds(Swamy, 1997). Several papers have been published concerning the reduction of smoke delivery in cigarette to apply adsorbents such as ion exchanger and activated carbon (Lee, 2004).

Ion exchanger is capable of selective removal in liquid. The advantage of the ion exchanger is

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the control of the pore size, various functional groups and capacity. Ion exchanger can apply to entire fluid because of expectation of high adsorption efficiency in spite of short collision. Also, it has good selective adsorption properties to specific substance that is expected to be removed by introducing functional group(Wachinski, 1997; Helfferich, 1962).

The present work involves investigation of the use of four anion exchangers, a cation exchanger and an activated carbon, as adsorbents for reduction of nitrate from Recon extract. The adsorption properties of ion exchanger on nitrate ion in Recon extract were evaluated according to extract concentration and addition amount.

MATERIALS AND METHODS

Materials

All chemicals and reagents used were of analytical grade. All experiments were conducted using deionized water(18 MΩcm resitivity at room temperature). All the experiments were conducted at room temperature. The Recon extract having high nitrate content was collected from the local company producing reconstituted tobacco leaf. The ion exchangers and activated carbon used in this work were purchased from Sigma chemical Co. in USA and Sin-Gang Co. in Korea, respectively. The characteristics of these six adsorbents are listed in Table 1. The conditions applied this experiment are listed in Table 2.

Sample preparation and Ion chromatographic analysis

Recon extract with four concentrations such as Brix 10, 20, 30, 47 were applied in this study. Six types of adsorbents were applied in Recon extract by 20 % and 40 % addition. After being shaken on a reciprocating type horizontal mechanical shake method for one hour, the mixed extract was filtered with a glass-fibre filter. The filtered extract was then transferred to an

Table 1. Characteristics of adsorbents

Sample name	Type	Particle size (mesh)	Base	Matrix	Functional Group
A1	Anion exchanger	40 ~ 60	Weakly basic	Styrene-DVB	Polyamine
A2	Anion exchanger	16 ~ 50	Strongly basic	Styrene-DVB	Dimethyl-ethanolamine
A3	Anion exchanger	16 ~ 50	Strongly basic	Styrene-DVB	Quaternary ammonium
A4	Anion exchanger	50 ~ 100	Strongly basic	Styrene-DVB	Tertiary ammonium
CI	Cation exchanger	50 ~ 100	Strongly acidic	Styrene-DVB	Sulfonic acid

Sample name	Type	Particle size (mesh)	Surface area (m^2/g)	Pore volume (cm^3/g)
Carbon	Activated carbon	40 ~ 80	1100	0.5

Table 2. Design of experiment

Experimental condition	type
Concentration of Recon extract (Brix)	10, 20, 30, 47
Addition amount of adsorbents (by weight)	20 %, 40 % (Carbon 5 %, 10 %)

Erlenmeyer flask and was extracted with 300 mL deionized water. Extraction time was 30 min and was followed by filtering through a 0.45 μm disc filter. This solution was analyzed by IC and quantified against an external calibration curve. The IC method used in this work was carried out with a Dionex ICS-2000 system(Dionex Corporation, USA)composed of a ICS-2000 isocratic pump, AS40 autosampler, conductivity detector and ASRS-Ultra II (4 mm) anion self-regenerating suppressor under software control. The chromatographic separations were obtained with a standard IonPac AS18(4 x 250 mm) column. The chromatographic conditions applied were a flow-rate of 1.0 mL/min, injection volume of 25 μL , 30.5 mM KOH as eluent and 80 mA current. The anions such as fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate were separated less than 15 min. The results by the IC analysis are showen in Fig. 1. As an analysis of IC method, the anions in Recon extract was chloride, nitrate, phosphate, sulfate among seven anions analyzed. The largest portion among anions of Recon extract was composed of the nitrate ion.

RESULTS AND DISCUSSION

The largest portion among anions of Recon extract is composed of the nitrate ion, therefore we have to deal with discussing the removal of nitrate ion. The removal percentage of nitrate ion as function of adsorbents type by the additional amount of adsorbents and the low concentrations (Brix 10 and 20) of Recon extract are shown in Fig. 2. The anion exchangers among the adsorbents makes it possible to take significantly effect for the removal of nitrate ion in Recon extract. In case of low concentration of recon extract, there was 70% reduction in the removal of nitrate ion. However, both the cation exchanger and the activated carbon were little efficient for removal of nitrate ion. To confirm the physical adsorption of nitrate ion for the anion exchanger, we used the cation exchanger that has the same physical properties such as particle size, base and matrix. As the result, the physical adsorption amount of nitrate ion by cation exchanger was less than 20 %, regardless of the concentration of Recon extract. Consequently, the removal of the nitrate ion by the cation exchanger could be caused by the phenomena of the physical adsorption. The result indicated that the removal of the nitrate ion could be passible by the phenomena of the chemical adsorption.

The removal percentages of nitrate ion as functions of adsorbents type by the addition amount of adsorbents and the high concentrations(Brix 30 and 47) of Recon extract are shown in Fig. 3. The reduction for nitrate

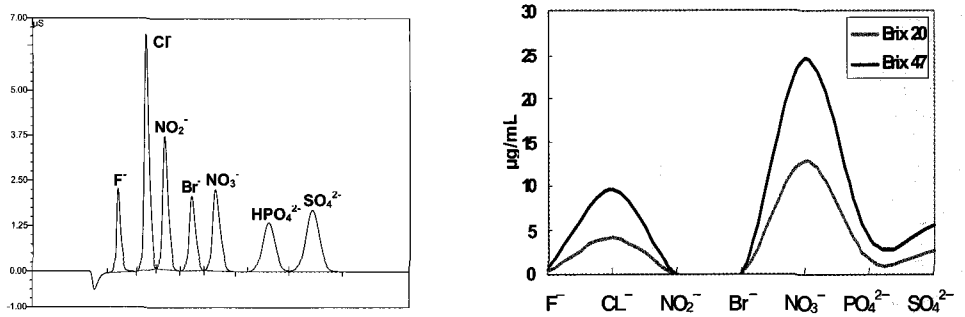
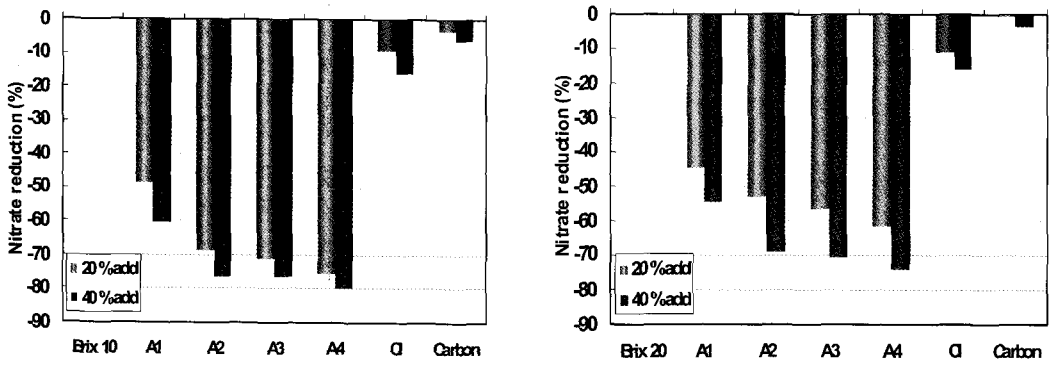


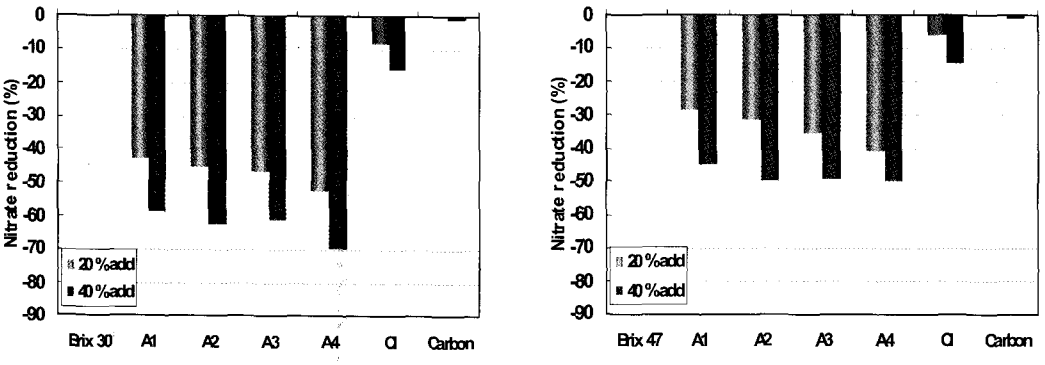
Fig. 1. The result of seven anion standard(a) and Recon extract anions from Brix 20 and Brix 47(b) to the IC analysis.



(a) (b)

Fig. 2. Comparison of reduction of nitrate ion by adsorbent types, addition amount and low concentration(Brix 10(a) and Brix 20(b)) of Recon extract. (Carbon bar : Activated carbon was the addition of 5 % and 10 %)

ion was decreased from 70 % to 30 % as increased concentration of Recon extract. Those results are not shown that total amount of adsorbed nitrate ion at high concentration in adsorbent were lower than those at low concentration of Recon extract. Just as much of the low concentration of Recon extract, both the cation exchanger and the activated carbon were little efficient for removal of nitrate ion at high concentration. Those result indicated that the chemical adsorption of nitrate ion is more effective than physical adsorption of nitrate ion. Therefore we considered the anion exchanger as the adsorbent for the removal of nitrate ion in Recon extract. Also, the results indicated that the type of anion exchangers such as the particle size, matrix and functional group has not affected the removal of the nitrate ion.



(a) (b)

Fig. 3. Comparison of reduction of nitrate ion by adsorbent types, addition amount and high concentration(Brix 30(a) and Brix 47(b)) of Recon extract. (Carbon bar : Activated carbon was the addition of 5 % and 10 %)

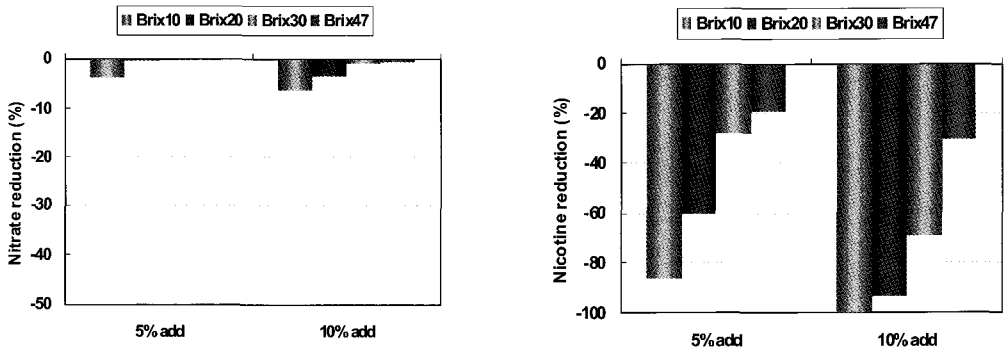
Additionally, supplemental experiment was performed on the activated carbon. Although the activated carbon was not effective for the removal of nitrate ion, it was effective for the removal of nicotine. Nicotine is an alkaloid organic compound, occurring naturally in the nightshade family of plants such as tobacco. During the combustion reaction that occurs when cigarettes are lit, a fraction of nicotine present in the tobacco is transferred to the inhaled smoke. The removal percentages of the nitrate and nicotine as functions of the addition amount of activated carbon and the concentration(Brix) of Recon extract are shown in Fig. 4. In case of the low concentration(Brix 10 and Brix 20) of Recon extract, there was almost 60 ~ 100 % reduction on the removal of nicotine. However the removal of nicotine at Brix 47 was less than 30 %. Such a result is considered as the fact that initial concentration of nicotine in high concentration of Recon extract is relatively high in comparison with initial concentration of nicotine in low concentration of Recon extract. The activated carbon could be suitable for the physical absorption of nicotine. The removal efficiency of nicotine is involved to the pore structure and the specific surface area of activated carbon.

CONCLUSIONS

We applied absorbents such as ion exchangers and activated carbon to Recon extract whether they have selective adsorption properties about nitrate ion or not. The summary of results is as follows.

The effect of adsorbent on the nitrate ion reduction

The removal efficiency of nitrate ion with adsorbent was in the order of A4 > A3 > A2 > A1 > CI. We found that anion exchanger was the most effective adsorbent for nitrate reduction by chemical adsorption. In case of Brix 10 to 30 of Recon extract, 20 % addition of adsorbents could achieve about 50 % reduction of nitrate ion. In case of Brix 47 of Recon extract, 40 % addition of adsorbents could results in about 50 % reduction of nitrate ion. These results indicate that the chemical adsorption on the removal of nitrate ion is more effective than physical adsorption on that of nitrate ion. We concluded that the anion exchanger as the adsorbent for the removal of nitrate ion could be applied to Recon extract.



(a) (b)

Fig. 4. Comparison of nitrate(a) and nicotine(b) reduction ratio according to addition amount of activated carbon and concentration(Brix) of Recon extract.

The effect of adsorbent on the nicotine reduction

For the reduction of nicotine, the activated carbon worked effectively. The activated carbon having much more micro pore and macro pore was effective on the removal of nicotine by the physical adsorption. However, the ion exchangers having much more meso pore were not effective on the removal of nicotine and nitrate by the physical adsorption.

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