Property of Ion Exchange Resin having Tripropylamine as Functional Group for Development of Denitrogenation Process

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Abstract

Nitrate-selective ion exchange resins involving bulky trialkyl amine as functional group were synthesized by the reaction of chloromethylated polystyrene-divinylbenzene copolymer and the corresponding tripropylamine in ethanol. Fundmental properties such as bulk density, water content, effeative diameter, uniformity coefficient, appearance index, exchange capacity and particle size distribution were fully measured. The synthesized resins appeared to be good for nitrate selection.

Introduction

There are organic-N, NH_4^+-N, NO_2^--N, NO_3^--N, N_2, as types of nitrogen compounds existing in the nature. Though these nitrogen compounds are necessary in growth of microorganism, nitrate nitrogen and ammonium nitrogen are increasing through human lives, industry activities, and large-scale livestock industry, etc.. Especially, the water polluted in nitrate nitrogen in water is ion exchange that called the most practical and accessable technique when it comes to economical, technical and convenient way of handling. But the problems for removal the effective nitrate nitrogen by the method of ion exchange are how to remove the reproduced waste liquid exhausting by reproduction of anion exchange resin and the selection problem of ion by ion exchange resin. Water is including not only NO_3^- but also many other kinds of anions, SO_4^-, HCO_3^-, Cl^-, and they can remove by ion exchange resin. Therefore, we measured the material properties of ion exchange resin and the selection coefficient that have NPr_3 (Pr = $CH_2CH_2CH_3$) functional group among the third amines that do bulky that synthesized in this research, and we examined ion exchange property for mixed water included HCO_3^- and Cl^- as well as NO_2^- and SO_4^{2-} being condition such as general natural water.

Materials and Methods

Materials and Reagent - We used procursor of an anion exchange resin DIAION SA 10AP as chloromethylated stylene-divinylbenzene carrier of Cl type made by domestic SAMYANG Co., Ltd., we bought NMe_3, NEt_3, NPr_3, NBu_3, NPe_3, $N(EtOH)_3$ from Aldrich. We used KNO_3 and a commercial reagents without refining. The first grade distilled water applied to ion exchange reaction was filtered out by microfilter, then we made it as super pure state of 18MΩ by water purification system.

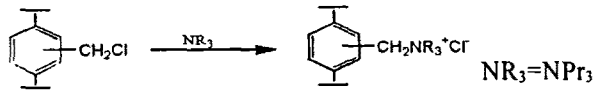
Instrument - UV/vis spectrophotometer; shimadzu(UV-240), Ion Chromatography; Dionex(DX-300), Peristaltic pump; cole-parmer(H-07553-85), Water bath; Dongyang science(0933), Water purification system; Millipore(Milli-Q).

Synthesis of Ion Exchange Resin - Nitrate-selective ion exchange resins which have bulky tripropyamine as functional group have been synthesized by the reaction of chloromethylated polystyrene-divinylbenzene copolymer and the corresponding tripropylamine in ethanol.

Experiment of Ion Exchange Resin Property - Ion exchange property of the synthesized ion exchange resin performed by continuous experiment.

Results and Discussion

Synthesis of ion exchange resin having tripropylamine as functional group - After ethanol solvent 250㎖ and tripropylamine 70㎖ dropped to flask of 500㎖, the reaction mixtures reflexed for 24hr with the speed of 100 rpm. After reaction, we got ion exchange resin having tripropylamine functional group to reaction in desiccator, after filted throught ion exchange resin after cool by room temperature and washed enough as water, after dried for 24hr in dry-oven of 70℃, (Table 1, Table 2).



NR_3=NPr_3

Table 1. Fundmental property of NPr_3

Terms		Analysis
Bulk Density (g/L)		637.0
Water Content (%)		40.2
Effeative Diameter (㎜)		0.512
Uniformity Coefficient		1.51
Appearance Index (%)	Sphere	85.2
	Half Sphere	0.4
	Crack	14.4
Exchange Capacity	meq/g-R	2.09
	meq/ml-R	1.33

Table 2. Particle size distribution of NPr_3

mesh(μ)	1180	850	710	600	425	300	300	TOTAL
mℓ		8.5	16.3	11.7	8.8	1.2	0.2	46.6
%		18.2	35.0	25.1	18.9	2.6	0.2	100.0
Σ%		18.2	53.2	78.3	97.2	9.8	100.0	

Property of ion exchange resin having tripropylamine as functional group - The concentration of NO_3^- in the manufactured natural water maked 124mg/l, and included SO_4^{2-}, Cl^-, HCO_3^- ion that is observed from general natural water that is polluted to NO_3^--N, and their ion concentrations were decided by 96mg/l, 40mg/l, 45mg/l being concentration that is observed from general natural water. The naturnal water in colunm chambered ion exchange resin 10g that have from tripropylamine functional group in 25℃ is flowed into 50ml/min. the result of breakthrough curve line by function of time 's existence showed NO_3^-, SO_4^{2-}, Cl^-, and HCO_3^- concentration and pH in the flowing out solution appeared to Fig. 2. In Fig. 2, SO_4^{2-} in breakthrough curved line of ion exchange resin having NPr_3 functional group is flowed out poured first and NO_3^- behind by action mourning, selectivity of ion is $NO_3^- > SO_4^{2-}$, and is expressing higher maxium value than the concentration of naturnal water in breakthrough curve line of SO_4^{2-}. Fig. 2 is appeared breakthrough curve line of NO_3^--N in Fig. 1. According to Weber theory yielding breakthrough capacity in breakthrough point that the breakthrough rate is 90%, breakthrough point of NO_3^--N on exchange resin having tripropylamine as functional group is showed 112mg/l and breakthrough capacity is showed about 150 minutes. polystyrene-divinylbenzene carrier 500g chloromethylated being the starting material reacted with the excess tripropylamine. At that time, Table 3 appeared reaction time, reaction temperature, quantity of ion exchange resin that is got by use solvent.

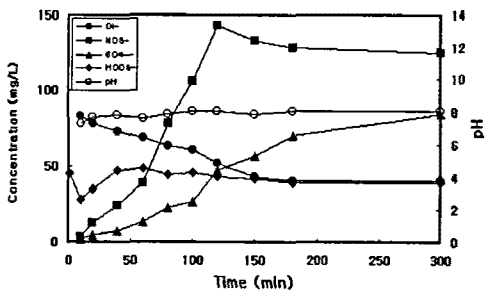


Fig. 1. Ion concentration profile by using NMe_3.

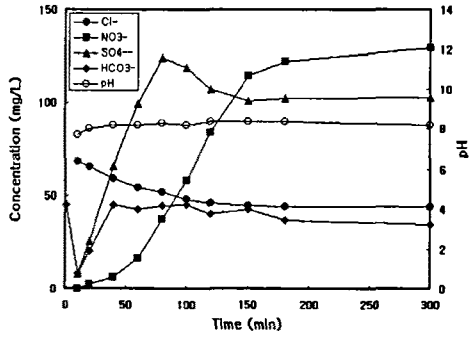


Fig. 2. Ion concentration profile by using NPr_3.

Table 3. Amount of product depending upon reaction condition

Run No.	Reaction Time(hr)	Temp (℃)	Solvent	Amount of product
1	1	50	EtOH	59.7
2	3	〃	〃	63.4
3	8	〃	〃	65.1
4	12	〃	〃	65.9
5	24	〃	〃	65.7
6	48	〃	〃	65.4
7	24	〃	EtOH	63.2
8	〃	〃	〃	65.9
9	〃	〃	〃	69.3
10	24	〃	H_2O	58.6
11	〃	〃	MeOH	65.8
12	〃	〃	EtOH	65.7
13	〃	〃	Toluene	67.2

*Weight of chloromethylated styrene-divinyl benzene is 50g.

Conclusion

Ion exchange resin having tripropylamine as functional group appeared to be more nitrate selective while commercial resin (trimethylamine) involving NMe_3 as functional group showed sulfate selective in low conentration of $NO_3^-/SO_4^{2-}/HCO_3^-/Cl^-$ mixed solution. NMe_3 showed 43% better in NO_3^- removal efficiency than NPr_3 under given experimental condition of this study and it was found that NO_3^- removal efficiency increase when Cl^- is included in the raw water.

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