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Potential of amberlite IRA 67 resin for deacidification of organic acids in noni juice

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ABSTRACT

Unpleasant odor of noni juice caused by organic acids has been a long standing problem. Adsorption using ion exchange resin has been found to be effective for the removal of organic acids. The ability of Amberlite IRA 67 resin to act as ion exchanger with the best adsorption efficiency were investigated by undergo characterization using FTIR and surface morphology using SEM. Results indicate that Amberlite IRA 67 resin treated using hydrochloric acid (HCl) has potential to be used in removing organic acids.

Keywords: Organic acid; ion exchanger; FTIR; SEM.

INTRODUCTION

Organic acids such as octanoic and hexanoic acid contained in noni fruit give undesirable odor which contributed by medium chain fatty acids [1]. Adsorption or ion exchange is a reliable technology to remove organic acids [2]. He also studied separation of organic acids from wastewater stream by using amine extractant. Other studies done by [3] recovered other carboxylic acids from fermentation broth by weak base polymer adsorbents.

Previous study also reported recovery of carboxylic acids from aqueous solution or fermentation broth by weakly basic ion exchange resins [2]. According to [4], they also found out that DIAION WA30 was a good adsorbent for recovery of organic acids from wine. Investigation of sorption equilibrium of of nine organic acids including monocarboxylic and monosulfonic acids on 16 anion exchangers has been conducted by [5,6].

The aim of this study is to investigate the best resin condition which has highest potential in removing organic acids.

MATERIALS AND METHODS

2.1 Resin

Anion exchange resin Amberlite IRA 67 used in this study is a commercial product purchased from Sigma-Aldrich (St. Louis, MO,USA). Amberlite IRA 67 resin was treated using different conditioning step as summarized in Table 2.

Resin	Chemical matrix	Functional group	Total exchange	Physical form	Particle size (mm)
		0 1	capacity (eq/L)	2	
Amberlite	Tertiary amine	≥ 1.60 (FB form)	≥ 1.60 (FB form)	Translucent white	0.50 - 0.75
IRA 67	•			spherical beads	

Table 1 Chemical and physical properties of resin used in this study

Table 2 Different conditioning step of Amberlite IRA 67

Condition 1	Condition 2	Condition 3	Condition 4	
Amberlite IRA 67	Amberlite IRA 67	Amberlite IRA 67	Amberlite IRA 67	
(0.5 g)	(0.5 g) + Deionized Water (15 ml) -	(0.5 g) + 4% NaOH (5 ml) - 45 min	(0.5 g) + 5% HCl	
\downarrow	45 min	\downarrow	(5 ml) – 45 min	
Dry in dessicator	\downarrow	Filter	\downarrow	
(24 hr)	Filter	\downarrow	Filter	
	\downarrow	Deionized Water	\downarrow	
	Dry in dessicator	(15 ml) - 2 hrs	Deionized Water	
	(24 hr)	\downarrow	(15 ml) – 2 hrs	
		Filter	\downarrow	
		\downarrow	Filter	
		Dry in dessicator	\downarrow	
		(24 hr)	Dry in dessicator	
			(24 hr)	

2.2 ATR-FTIR

FTIR spectroscopy technique was used to identify characteristic functional groups in resin. The infrared spectra of the resin were recorded on a spectrum $4000 - 650 \text{ cm}^{-1}$ FTIR spectrometer (Perkin Elmer, UK) using the attenuated total reflection (ATR) method for sample preparation technique. A mass of 0.5 mg of resin sample was used for all tests.

2.3 SEM

The surface morphology of the resin was studied using a Scanning Electron Microscope (SEM) with LEO 1450VP model. The sample was sputter-coated with gold before the observation.

RESULTS AND DISCUSSION

3.1 FTIR Characterization

o see what actually happened on resin (Amberlite IRA 67) during different conditioning step, Attenuated Total Reflection (ATR-FTIR) were used to characterize the resin. The effect of modification should also be observed in FTIR spectra in differences in intensity, shifts or extra bands. Fig. 1-4 showed the spectra of the resin and the wavenumbers of the band for each condition were compared to the spectra library [7,8].

As noticed in the spectra, the bands corresponding to the O-H groups (H-bonded alcohols or carboxylic acids) at 3287, 3286, 3282 and 3258 cm⁻¹ as in Fig.1 to 4, respectively. In Fig. 1, the band at 3075 cm⁻¹ is CH2 symmetric stretching of the alkanes. The bands at 2941 cm⁻¹ and 2863 cm⁻¹ are CH₂ and CH₃ asymmetric stretching of the alkanes (also C-H tertiary). The band at 2776 cm⁻¹ also C-H stretching from alkanes. The bands were still in the same range if compared to the spectra in Fig. 2 (3071, 2940, 2813, 2774 cm⁻¹) and Fig. 3 (3071, 2930, 2861, 2766 cm⁻¹), respectively.

The two strong bands at 1642 cm⁻¹ and 1541 cm⁻¹ are due to C=O and N-H bending of amide that produced from carboxylic acids and esters. The bands also appear in the spectra as in Fig. 2 (1642, 1537 cm⁻¹), Fig. 3 (1642, 1542 cm⁻¹) and Fig. 4 (1639, 1542 cm⁻¹), respectively. The bands at 1443 (CH₂ bending) and 1383 (CH₃ bending) of

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alkanes group. The similar bands with same range also noticed in Fig. 2 (1445, 1378 cm), Fig. 3 (1439, 1383 cm), Fig. 4 (1473 cm⁻¹, (no data, but the band appear in spectra), respectively.

The C-N bending of tertiary amine can be found at 1261, 1233, 1181, 1158 and 1098 cm (Fig. 1). The similar bands also appear in Fig. 2 (1261, 1232, 1181, 1157 and 1100 cm) and Fig. 3 (1261, 1233, 1183, 1157 and 1098 cm). Contrary to the bands in Fig. 4, the C-N bending of tertiary amine were showed at 2635, 2480, 2286 and 2052 cm . However, there were N-H merging at 1241 cm (from 1261 and 1233/1232 cm) and 1173 cm (from 1181/1183 and 1158/1157 cm). This resulted in modification of the resin structure when using HCl during conditioning step. It might due to the free amine (C-N) changed to the charged ammonium (N-H groups).

In Fig. 1, the bands at 1038 cm (strong) and 989 cm are due to the C-O from esters or carboxylic acids. The similar bands also shown in Fig. 2 (1038, 991 cm⁻¹). As can be seen in Fig. 3, only a strong band at 1039 cm⁻¹ (less intense) appeared and the second band was dissapeared. It might be because of COO interact with Na⁺ from NaOH. In Fig. 4, only a broad band at 1017 cm⁻¹ observed.

Overall, spectra in Fig.1 and 2 only gave minor changes. It indicated that the washing step for unconditioned resin did not give significant impact on the resin.



Fig. 1 The FTIR spectra of untreated Amberlite IRA 67 resin (Condition 1)

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Wl(l)	D I T	C	En mar Part (and)
wavenumber (cm)	Bond Type	Compound Type	Frequency Range (cm)
2287	O-H	H-bonded alcohols	3550-3200 (broad)
3287	O-H	Carboxylic acids	
3075	CH ₂	Alkanes (C-H symmetric stretching)	3000
2941	CH ₂ , CH ₃	Alkanes (C-H asymmetric stretching)	2926
2863	CH, CH	Alkanes (C-H symmetric stretching)	2853
	ČH Š	C-H tertiary	2890 (w)
2776	CH ₂	Alkanes (C-H)	
1642	C=O	Amides (Carboxylic acids)	1800-1650 (s)
1541	N-H	Amide (N-H bending)	1640-1550
1460	CH ₂	Alkanes (C-H bending)	
1443	CH ₂	Alkanes (C-H bending)	
1261	C-N	Tertiary aliphatic amine (C-N stretching)	1342-1266
1233	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1181	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1158	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1098	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1038	C-O	Esters or Carboxylic acids (C-O stretching)	

Table 3 IR vibration wavenumber and functional groups observed on untreated Amberlite IRA 67



Fig. 2 The FTIR spectra of untreated Amberlite IRA 67 resin (washed) (Condition 2)

Wavenumber (cm ⁻¹)	Bond Type	Compound Type	Frequency Range (cm ⁻¹)
3286	О-Н О-Н	H-bonded alcohols Carboxylic acids	3650-3200 (broad)
3071	CH ₂	Alkanes (C-H symmetric stretch)	3000
2940	CH ₂ , CH ₃	Alkanes (C-H asymmetric stretch)	2926
2865	CH ₂ , CH ₃ CH	Alkanes (C-H symmetric stretch) C-H tertiary	2853 2890
2774	CH ₂	Alkanes (C-H)	
1642	C=O	Amides (Carboxylic acids)	1800-1650 (s)
1537	N-H	Amide (N-H bending)	1640-1550
1445	CH ₂	Alkanes (C-H bending)	
1378	CH ₃	Alkanes (C-H bending)	
1261	C-N	Tertiary aliphatic amine (C-N stretching)	1342-1266
1232	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1181	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1157	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1100	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1038	C-O	Esters or Carboxylic acids	

Table 4 IR vibration wavenumber and functional groups observed on untreated Amberlite IRA 67 (washed)



Fig. 3 The FTIR spectra of treated Amberlite IRA 67 resin with NaOH (Condition 3)

Wavenumber (cm ⁻¹)	Bond Type	Compound Type	Frequency Range (cm ⁻¹)
3286	О-Н О-Н	H-bonded alcohols Carboxylic acids	3650-3200 (broad)
3071	CH	Alkanes (C-H symmetric stretching)	3000
2930	CH ₂ , CH ₃	Alkanes (C-H asymmetric stretching)	2926
2861	CH ₂ , CH ₃ CH	Alkanes (C-H symmetric stretching) C-H tertiary	2853 2890
2766	CH ₂	Alkanes (C-H)	
1642	C=O	Amides (Carboxylic acids)	1800-1650 (s)
1542	N-H	Amide (N-H bending)	1640-1550
1439	CH ₂	Alkanes (C-H bending)	
1383	CH	Alkanes (C-H bending)	
1261	C-N	Tertiary aliphatic amine (C-N stretching)	1342-1266
1233	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1183	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1157	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1098	C-N	Tertiary aromatic amine (C-N stretching)	1250-1000
1039	C-O	Esters or Carboxylic acids	

 Table 5 IR vibration wavenumber and functional groups observed on treated Amberlite IRA 67 with NaOH



Fig. 4 The FTIR spectra of treated Amberlite IRA 67 resin with HCl (Condition 4)

Wavenumber (cm ⁻¹)	Bond Type	Compound Type	Frequency Range (cm ⁻¹)
3258	O-H	H-bonded alcohols	3650-3200 (broad)
	O-H	Carboxylic acids	
2635	C-N	Tertiary amine	2700-2250
2480	C-N	Tertiary amine	2700-2250
2286	C-N	Tertiary amine	2700-2250
1639	C=O	Amide (N-H bending)	1680-1640
1542	N-H	Amide (N-H bending)	1640-1550
1473	CH	Alkanes (C-H bending)	
1241	N-H	Amines	
1173	N-H	Amines	

Table 6 IR vibration wavenumber and functional groups observed on treated Amberlite IRA 67 with HCl

3.2 Surface Morphology

The untreated and treated Amberlite IRA 67 resin as shown in Fig. 5 (a) and (b) were analysed using SEM. According to [9], SEM has been primarily used for determining the particle shape, and is particularly useful for characterizing fundamental physical properties including surface morphology of an adsorbent. Differences in surface morphology indicated that there was a chemical reaction in the ion exchange resin when the resin treated with HCl. Treated sample as shows in Fig. 5 (b) are mainly compose of irregular and porous particles. It might due to changes of free amine (C-N) the charged ammonium (N-H groups) as described in characterization of the resin using FTIR.



Fig. 5 SEM micrographs of untreated and treated weak base anion exchange Amberlite IRA 67 resin

CONCLUSION

Results indicate that Amberlite IRA resin treated using hydrochloric acid (HCl) has potential to be used in removing organic acids.

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