

# Synthesis and Studies on Thermal Stability, Physicochemical and Biological Activity of Melamine-Formaldehyde-Urea Ion-Exchange Resin

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## Abstract

A new, easy and cost-effective synthetic procedure for the preparation of a series of resins was synthesized and analyzed for selective ion-exchange nature for some metals. Urea was reacted with formaldehyde and melamine. These resins were characterized by elemental analysis and studied antimicrobial activities. Synthesized Resin shows ion exchange capability and moderate activity against microbial. Ion exchange resin also showed reusability and stability at an elevated temperature.

**Keywords:** Anion-exchange resin; melamine; formaldehyde; synthesis; physicochemical property; antimicrobial; antifungal.

## 1. INTRODUCTION

Melamine-Formaldehyde (MF) terpolymers/resins were great interest due to its wide applications. MF resins were modified to Ionic liquid by 1,4-butane sulfonate, which further treated with HCl shows greater reactivity compared with sulfuric acid and p-toluene sulfonic acid as a catalyst[1]. Terpolymer of resorcinol-thiourea-formaldehyde as solid support ion exchange resin and studied its chelating uptake of several metal ions for the industrial purification[2,3] at various temperatures. Selective Ion exchange[4] of Hg<sup>+</sup> ion is also seen in this type of resins. In some case, MF resins had reusability[5,6] upto 3-5 times and shows the negligible change in its properties. In current work, we have synthesized resin of Melamine-Formaldehyde-Urea, studied its thermal stabilities and reusability.

## 2. EXPERIMENTAL

For the synthesis 500 ml three-neck round bottom flask fitted with condenser and thermometer was used. 37 % formaldehyde in water was used for the synthesis. All chemicals were purchased from spectrochem (India) and used without further purification. The pH values were measured by PF 138 pH meter, which is microprocessor based, handy self-contained and portable instruments supplied by Elico limited, Hyderabad, India. C, H and N were analyzed using a GmbH Vario Micro cube Elemental Analyzer (Germany).

### 2.1 Preparation of MUF 1-5 resin

X grams of melamine (0.1 mole) and Ygrams of formaldehyde (1 mole, 90 ml of 37% formaline) were taken in a 500 ml capacity round bottom three-neck flask, fitted with a stirrer, a thermometer and condenser. The contents of the flask were warmed on a water-bath to about 70° C with stirring till all the melamine dissolved. To this was

added different gms of urea (0.1mole, 0.2 mole, 0.3 mole) and the reaction mixture was heated at 90° C under reflux conditions for about 2 hours and 20 minutes with continuous stirring. The reaction mixture gelled into a white hard mass in about 2 hours, after the addition of urea. Now, the stirring and heating was stopped and the gel was removed from the reaction vessel and cured in an electrically operated oven at 90° C for six hours and 100° C for further two hours. The white transparent hard mass was crushed to proper mesh size and the sieved resin was stored for further experimental work. Large-scale reactions were carried out under exactly similar conditions.

### 2.2 Conditioning and storage

The ion exchange resins after synthesis may contain low molecular weight polymers or unreacted monomers. In order to remove these materials Soxhlet extraction was adopted using Soxhlet apparatus with appropriate solvents. Solvents used for this purpose were ethyl alcohol and acetone. The anion-exchange resins MUF-1, MUF-2, MUF-3, MUF-4, MUF-5 were first extracted with acetone and then with ethyl alcohol.

The solvent extracted resins were conditioned by alternate treatment with 4% sodium hydroxide and 5% hydrochloric acid. After several alternate exhaustion and regeneration cycles, the resins were thoroughly washed free of acid or alkali and were dried until free flowing and stored in tightly stoppered bottles. Anion exchange resins while regenerating in "Chloride" form were washed free of acid with alcohol and stored in tightly stoppered bottles.

### 2.3 Properties Of Resins

#### 2:3.1 Determinations of moisture contents

Anion-exchange resins: About 1 gram of the air dried resin in the free base form was accurately weighed in a weighing

bottle and heated at 100° C for 24 hours in an electrically operated oven. The loss in weight was recorded and from a constant value obtained, the percentage moisture content was calculated.

### 2:3.2 Determination of exchange capacity

#### Anion-exchange capacity

About 0.5 gram of air dried ion-exchange resin in the free base form was weighed in 100ml conical flask and equilibrated with 50 ml of 0.1 N hydrochloric acid in 1.0 N sodium chloride solution. The acid consumed (neutralized) after 24 hours was determined by titrating an aliquot of the solution with standard alkali. Keeping separately 0.5 gram of the exchanger in the free base form with 50 ml of distilled water and determining the free alkalinity, if any obtained blank readings. Blank readings were considered while calculating the capacity per gram of absolute dry resin. For the determination of the salt splitting capacity, about 0.5 gram of air dried resin was weighed and equilibrated with 1.0 N sodium chloride solution and the alkali liberated after 24 hours was determined by titrating an aliquot with standard acid. Blank readings, if any, were deducted from the titration readings while calculating the salt splitting capacity per gram of absolute dry resin.

### 2:3.3 Determination of density

The wet absolute density of the free base form of the anion exchangers and amphoteric exchangers was determined by the conventional method described by Kunin.

### 2:3.4 pH titration curves

The pH titration study was carried out by the procedure described by Kunin.

#### Anion exchangers

0.5 gram of the resins MUF-1 MONAF,, MUF-2, MUF-3, MUF-4 and MUF-5 in the free base form were weighed accurately and transferred to 100 ml glass stoppered flasks. Different volumes of 1.0 N sodium chloride solution and hydrochloric acid in 1.0 N sodium chloride solution were added, keeping the total volume 50 ml. The flasks were equilibrated for 24 hours with occasional shaking. A preliminary experiment showed that 24 hours was sufficient to obtain constant pH. Blank solutions were also kept without the resins. Aliquot were withdrawn and titrated for alkalinity or acidity, as the case may be. From the difference in the titre values of blank and the supertant solution, the capacities of the resins at different pH value were calculated (moisture content was taken into account). The equilibrium pH of the supertant solution was determined using a pH meter.

### 2:3.5 Thermal stability

The following procedure was adopted for determining the thermal stability of the free base and the chloride forms of the anion-exchange resins MUF-1, MUF-2, MUF-3, MUF-4 and MUF-5. One gram of the resin (whose capacity was known) was placed in a glass empoule with 20 ml of distilled water. The empoule was sealed and placed in a constant temperature oven adjusted to the required temperature (100° C and 120° C). After 24 hours, the empoule was removed and the supertant solution was filtered and the resin was washed with distill water repeatedly. The filtrate and the washing were diluted to a known volume. Acidity or alkalinity if any was determined

by titrating an aliquot with standard alkali and acid respectively. Thus the quantity of acid or alkali liberated during heat treatment was determined. The washed resin regenerated with the proper regenerant and capacity was determined. Decrease in capacity, if any, was noted.

**Table 2.1 Properties of ion-exchange resins**

No.	Name	Moisture Content In %	Wet absolute density gm/ml	Total capacity meq/gm of absolute dry resin
SNZ : 01	MUF-1	7.3	3.021gm/ml	2.370meq/gm
SNZ : 02	MUF-2	4.0	2.915	2.412
SNZ : 03	MUF-3	10.5	3.425	2.345
SNZ : 04	MUF-4	11.3	3.840	2.802
SNZ : 05	MUF-5	1.9	2.898	2.103

**TABLE-2.2 pH titration study of SNZ : 1 (MUF-1) anion- exchange resin in the free-base form in the presence of 1.0 N sodium chloride solution.**

Quantity of resin taken = 0.5 gram (air dry)  
Moisture content = 7.3 %  
Volume of equilibrating solution = 50 ml  
Equilibrium period = 24 hours  
Equilibrium temperature = 30° C

Solutions used :

- 0.1 N hydrochloric acid in 1.0 N sodium chloride solution
- 1.0 N sodium chloride solution

Flask No.	Volume of NaCl in ml	Volume of HCl in NaCl ml	Equilibrium pH	Capacity meq/gm of absolute dry resin
1.	0.0	50.0	0.93	2.375
2.	2.5	47.5	0.96	2.160
3.	5.0	45.0	0.99	2.100
4.	7.5	42.5	1.00	2.055
5.	10.0	40.0	1.04	1.991
6.	12.5	37.5	1.09	1.902
7.	15.0	35.0	1.14	1.880
8.	17.5	32.5	1.18	1.825
9.	20.0	30.0	1.22	1.760
10.	22.5	27.5	1.30	1.700
11.	25.0	25.0	1.35	1.504
12.	27.5	22.5	1.45	1.465
13.	30.0	20.0	1.51	1.402
14.	32.5	17.5	1.60	1.402
15.	35.0	15.0	1.78	0.994
16.	37.5	12.5	1.95	0.862
17.	40.0	10.0	2.19	0.800
18.	42.5	7.5	2.70	0.760
19.	45.0	5.0	3.28	0.605
20.	47.5	2.5	3.40	0.530
21.	50.0	0.0	6.66	0.000

**TABLE-2.3 pH titration study of SNZ : 2 (MUF-2) anion- exchange resin in the free-base form in the presence of 1.0 N sodium chloride solution.**

Quantity of resin taken = 0.5 gram (air dry)  
 Moisture content = 4.0 %  
 Volume of equilibrating solution = 50 ml  
 Equilibrium period = 24 hours  
 Equilibrium temperature = 32° C

Solutions used :  
 (a) 0.1 N hydrochloric acid in 1.0 N sodium chloride solution  
 (b) 1.0 N sodium chloride solution

Flask No.	Volume of NaCl in ml	Volume of HCl in NaCl ml	Equilibrium pH	Capacity meq/gm of absolute dry resin
1.	0.0	50.0	0.94	2.475
2.	2.5	47.5	0.96	2.340
3.	5.0	45.0	0.97	2.273
4.	7.5	42.5	1.01	2.193
5.	10.0	40.0	1.05	2.166
6.	12.5	37.5	1.09	2.143
7.	15.0	35.0	1.11	2.083
8.	17.5	32.5	1.18	2.083
9.	20.0	30.0	1.24	1.856
10.	22.5	27.5	1.28	1.790
11.	25.0	25.0	1.35	1.771
12.	27.5	22.5	1.40	1.601
13.	30.0	20.0	1.54	1.458
14.	32.5	17.5	1.65	1.318
15.	35.0	15.0	1.80	1.250
16.	37.5	12.5	1.99	1.014
17.	40.0	10.0	2.07	0.937
18.	42.5	7.5	2.25	0.880
19.	45.0	5.0	2.89	0.729
20.	47.5	2.5	2.90	0.607
21.	50.0	0.0	6.61	0.000

**TABLE-2.5 pH titration study of SNZ : 4 (MUF-4) anion- exchange resin in the free-base form in the presence of 1.0 N sodium chloride solution.**

Quantity of resin taken = 0.5 gram (air dry)  
 Moisture content = 11.3%  
 Volume of equilibrating solution = 50 ml  
 Equilibrium period = 24 hours  
 Equilibrium temperature = 31° C

Solutions used :  
 (a) 0.1 N hydrochloric acid in 1.0 N sodium chloride solution  
 (b) 1.0 N sodium chloride solution

Flask No.	Volume of NaCl in ml	Volume of HCl in NaCl ml	Equilibrium pH	Capacity meq/gm of absolute dry resin
1.	0.0	50.0	0.99	2.818
2.	2.5	47.5	1.00	2.624
3.	5.0	45.0	1.01	2.440
4.	7.5	42.5	1.04	2.250
5.	10.0	40.0	1.07	2.182
6.	12.5	37.5	1.10	2.140
7.	15.0	35.0	1.13	2.004
8.	17.5	32.5	1.16	1.912
9.	20.0	30.0	1.22	1.912
10.	22.5	27.5	1.24	1.805
11.	25.0	25.0	1.29	1.660
12.	27.5	22.5	1.32	1.572
13.	30.0	20.0	1.44	1.383
14.	32.5	17.5	1.54	1.350
15.	35.0	15.0	1.63	1.310
16.	37.5	12.5	1.80	1.240
17.	40.0	10.0	1.92	1.127
18.	42.5	7.5	2.10	1.102
19.	45.0	5.0	2.52	1.010
20.	47.5	2.5	2.87	0.820
21.	50.0	0.0	6.49	0.000

**TABLE-2.4 pH titration study of SNZ : 3 (MUF-3) anion- exchange resin in the free-base form in the presence of 1.0 N sodium chloride solution.**

Quantity of resin taken = 0.5 gram (air dry)  
 Moisture content = 10.5 %  
 Volume of equilibrating solution = 50 ml  
 Equilibrium period = 24 hours  
 Equilibrium temperature = 32° C

Solutions used :  
 (a) 0.1 N hydrochloric acid in 1.0 N sodium chloride solution  
 (b) 1.0 N sodium chloride solution

Flask No.	Volume of NaCl in ml	Volume of HCl in NaCl ml	Equilibrium pH	Capacity meq/gm of absolute dry resin
1.	0.0	50.0	0.96	2.220
2.	2.5	47.5	0.99	2.131
3.	5.0	45.0	1.02	2.105
4.	7.5	42.5	1.03	2.012
5.	10.0	40.0	1.04	1.990
6.	12.5	37.5	1.09	1.870
7.	15.0	35.0	1.16	1.802
8.	17.5	32.5	1.20	1.802
9.	20.0	30.0	1.24	1.774
10.	22.5	27.5	1.31	1.670
11.	25.0	25.0	1.40	1.600
12.	27.5	22.5	1.45	1.565
13.	30.0	20.0	1.53	1.271
14.	32.5	17.5	1.66	1.115
15.	35.0	15.0	1.72	0.990
16.	37.5	12.5	1.92	0.780
17.	40.0	10.0	2.19	0.690
18.	42.5	7.5	2.66	0.612
19.	45.0	5.0	3.09	0.585
20.	47.5	2.5	3.12	0.515
21.	50.0	0.0	6.65	0.000

**TABLE-2.6 pH titration study of SNZ : 5 (MUF-5) anion- exchange resin in the free-base form in the presence of 1.0 N sodium chloride solution.**

Quantity of resin taken = 0.5 gram (air dry)  
 Moisture content = 1.9 %  
 Volume of equilibrating solution = 50 ml  
 Equilibrium period = 24 hours  
 Equilibrium temperature = 30° C

Solutions used :  
 (a) 0.1 N hydrochloric acid in 1.0 N sodium chloride solution  
 (b) 1.0 N sodium chloride solution

Flask No.	Volume of NaCl in ml	Volume of HCl in NaCl ml	Equilibrium pH	Capacity meq/gm of absolute dry resin
1.	0.0	50.0	0.98	2.025
2.	2.5	47.5	0.99	1.916
3.	5.0	45.0	1.01	1.803
4.	7.5	42.5	1.06	1.712
5.	10.0	40.0	1.11	1.660
6.	12.5	37.5	1.12	1.570
7.	15.0	35.0	1.13	1.380
8.	17.5	32.5	1.15	1.355
9.	20.0	30.0	1.19	1.310
10.	22.5	27.5	1.24	1.210
11.	25.0	25.0	1.28	1.125
12.	27.5	22.5	1.32	1.120
13.	30.0	20.0	1.42	1.100
14.	32.5	17.5	1.48	1.010
15.	35.0	15.0	1.53	0.824
16.	37.5	12.5	1.66	0.643
17.	40.0	10.0	1.74	0.562
18.	42.5	7.5	1.90	0.425
19.	45.0	5.0	2.23	0.355
20.	47.5	2.5	2.60	0.320
21.	50.0	0.0	6.51	0.000

**Table-2.7 Thermal stability of anion – exchange resins**

Temperature in °C	Name	Original capacity meq/gm of absolute dry resin	% loss in capacity of absolute dry resin as determined after heating		% loss in capacity of absolute dry resin as determined after regeneration	
			in the free base form	in the salt form	in the free base form	in the salt form
120° C	SNZ : 01	2.370	2.39	nil	2.012	nil
	SNZ : 02	2.412	2.55	nil	2.20	nil
	SNZ : 03	2.345	2.40	nil	2.18	nil
	SNZ : 04	2.802	2.97	nil	2.52	nil
	SNZ : 05	2.103	2.34	nil	2.00	nil

N. B. : All the resins found stable up to 100° C temperature only negligible loss was observed hence it. was ignored

**Table : 2.8 Anti-Bacterial Activity Of Synthesized Ion-Exchangers**

Sr. No.	Degree of inhibition of growth						
	<i>Escherichia coli</i>	<i>Pseudomonas aeruginosa</i>	<i>Salmonella typhi</i>	<i>Serratia marcescens</i>	<i>Staphylococcus aureus</i>	<i>Staphylococcus epidermidis</i>	<i>Bacillus subtilis</i>
SNZ-1	+	+	++++	++	++	++++	++++
SNZ-2	+	+	+++	+	+	++++	++
SNZ-3	+++	++	+++	+++	+++	+++++	+++
SNZ-4	+	+	+++	+	+++	++	+
SNZ-5	-	-	-	-	+	-	-
STREPTOMYCIN	++++	+++++	++++	++++	++++	++++	++++
TETRACYCLINE	+++	-	+	-	+++++	+++	++
PENICILLIN	-	-	+	-	+++++ (b)	++	++++

### 3. CONCLUSION

During the course of the investigation reported here, a series of anion-exchange resins were synthesized and only indigenously available raw material urea is used. Melamine (which is now available in the country) was used as the crosslinking agent along with formaldehyde. Five resins (all anion exchangers) were synthesized and characterized. Properties of the resins such as capacity, wet absolute density, and pH titration curves were studied by the conventional methods as adopted for various ion-exchange resins. The results showed that the anion-exchange resins were functioning as weak base anion exchangers. Thermal stability of the resins was determined and it was found that these could be used safely up to 100° C; above 100° C they were susceptible to degradation and lost part of the total exchange capacity. It was also confirmed that these resins were stable in the salt form as compared to their hydroxyl form. Antimicrobial sensitivity testing of the resins showed some interesting results. Among urea based resins, SNZ-1 and SNZ-2 showed maximum inhibitory effect on *S. typhi* and *S. epidermidis*. Resins SNZ-3 inhibited the growth of all bacterial cultures tested. SNZ-4 was more effective on *S. typhi* and *S. aureus*. SNZ-5 did not show any inhibitory effect on bacteria. *Aspergillus niger* was sensitive to resins SNZ-1 & SNZ-3. whereas rest of the resins did not show anti-fungal activity. Resins SNZ-1 showed both antibacterial as well as antifungal activity.

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