International Letters of Chemistry, Physics and Astronomy *Online: 2014-04-22*
ISSN: 2299-3843, Vol. 32, pp 112-118
doi:10.18052/www.scipress.com/ILCPA.32.112

Synthesis and Thermal Stability of Melamine-Formaldehyde-Nitro Aniline Ion-Exchange Resin

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ABSTRACT

A series of resins was synthesized and analyzed for selective ion-exchange nature for some metals. Substituted aniline was reacted with formaldehyde, melamine. For the synthesis of ion-exchange resins, sulfuric acid was used as a catalyst. 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*:** Ion-exchange; resin; melamine; formaldehyde; synthesis; thermal stability; reusability; antimicrobial

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^{+} 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-Nitroaniline, 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 MONAF resin

12.6 grams of melamine (0.1 mole) and 30 grams of formaldehyde (1 mole, 90 ml, of 37 % formalin) were taken in a 500 ml capacity round bottom three-neck flask fitted with a stirrer, a thermometer and a 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 3.25 grams of o-nitro aniline (0.025 mole) and 15 ml of concentrated sulfuric acid as a catalyst and the reaction mixture was heated at 90-95 °C under reflux conditions for about four hour and forty five minutes with stirring. The reaction mixture gelled into a dark-red soft butter like mass in about three hour and five minutes after the addition of sulfuric acid and o- nitro aniline. Now the stirring and heating was stopped and the gel was removed from the vessel and cured in an electrically operated oven at 100 °C for twenty-four hours. The mass was crushed into proper mesh size and purified and stored for further experimental work. Large-scale reactions were carried out under exactly similar conditions. C % (Found/ Calc.) = 43.97/43.96, H % (Found/ Calc.) = 3.32/3.31, N % (Found/ Calc.) = 41.01/41.00.

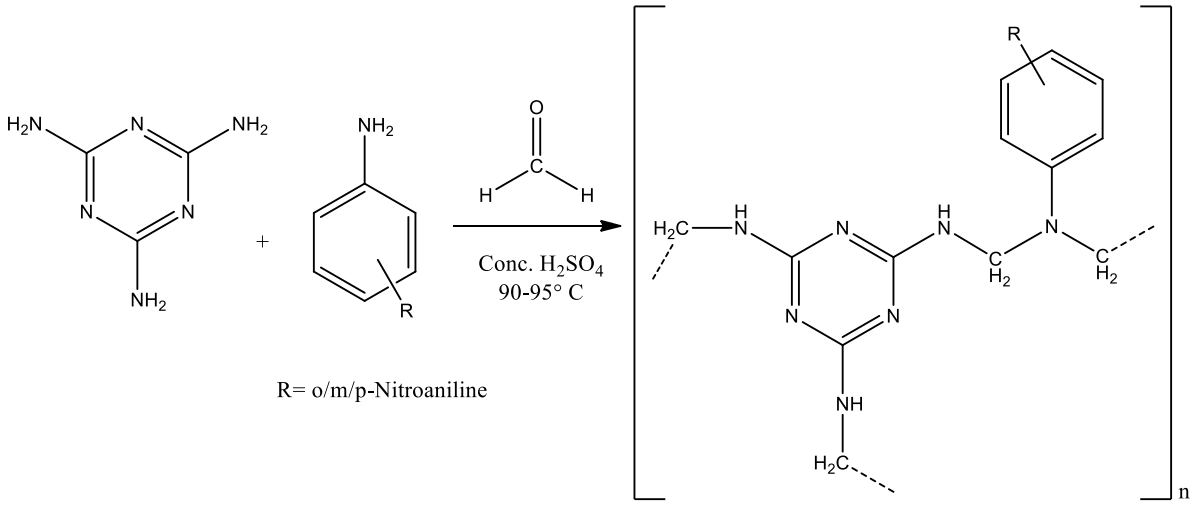

Figure 1. Common reaction scheme of resins.

2. 2. Purification, storage and moister content

The crushed solid mass was treated by soxhlet extraction method with solvents ethyl alcohol and acetone (1:1) until no resin elute with solvent. Then the pure resin was stored in air tight bottle and further sealed with Teflon tap. Moister content found in 5mg each MONAF, MMNAF and MPNAF were 21.7, 20.6 and 25.2 in percent respectively.

2. 3. pH titration of Anion exchangers

0.5 gram of the resins MONAF, MMNAF, and MPNAF 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.

Table 1. pH titration study of MONAF resin in the free-base form.

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	0.97	3.321
2.	2.5	47.5	0.99	3.300
3.	5.0	45.0	1.00	3.265
4.	7.5	42.5	1.04	2.937
5.	10.0	40.0	1.08	2.937
6.	12.5	37.5	1.12	2.899
7.	15.0	35.0	1.14	2.809
8.	17.5	32.5	1.20	2.672
9.	20.0	30.0	1.27	2.554
10.	22.5	27.5	1.33	2.427
11.	25.0	25.0	1.40	2.427
12.	27.5	22.5	1.48	2.340
13.	30.0	20.0	1.57	2.300
14.	32.5	17.5	1.70	2.043
15.	35.0	15.0	1.87	2.043
16.	37.5	12.5	1.98	1.725
17.	40.0	10.0	2.27	1.405
18.	42.5	7.5	2.35	0.926
19.	45.0	5.0	3.01	0.767
20.	47.5	2.5	3.14	0.672
21.	50.0	0.0	5.35	0.000

Table 2. pH titration study of MMNAF resin in the free-base form.

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	0.84	2.394
2.	2.5	47.5	0.88	2.290
3.	5.0	45.0	0.92	2.268
4.	7.5	42.5	0.94	2.142
5.	10.0	40.0	0.99	2.142
6.	12.5	37.5	1.01	2.120
7.	15.0	35.0	1.07	2.100
8.	17.5	32.5	1.09	2.016
9.	20.0	30.0	1.11	2.016
10.	22.5	27.5	1.17	1.925
11.	25.0	25.0	1.27	1.890
12.	27.5	22.5	1.34	1.764
13.	30.0	20.0	1.43	1.764
14.	32.5	17.5	1.54	1.669
15.	35.0	15.0	1.67	1.638
16.	37.5	12.5	1.82	1.105
17.	40.0	10.0	2.01	1.008
18.	42.5	7.5	2.25	0.780
19.	45.0	5.0	2.78	0.630
20.	47.5	2.5	2.95	0.450
21.	50.0	0.0	5.60	0.000

Table 3. pH titration study of MPNAF resin in the free-base form.

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	1.00	3.747
2.	2.5	47.5	1.03	3.613
3.	5.0	45.0	1.05	3.613
4.	7.5	42.5	1.09	3.525
5.	10.0	40.0	1.11	3.480
6.	12.5	37.5	1.19	3.402
7.	15.0	35.0	1.24	3.346
8.	17.5	32.5	1.31	3.078
9.	20.0	30.0	1.38	3.078
10.	22.5	27.5	1.42	2.924
11.	25.0	25.0	1.54	2.810
12.	27.5	22.5	1.75	2.677
13.	30.0	20.0	1.84	2.677
14.	32.5	17.5	1.99	2.513
15.	35.0	15.0	2.28	2.409
16.	37.5	12.5	2.69	1.990
17.	40.0	10.0	3.11	1.874
18.	42.5	7.5	3.76	1.250
19.	45.0	5.0	4.30	0.937
20.	47.5	2.5	4.62	0.821
21.	50.0	0.0	7.03	0.000

2. 4. Thermal stability and Reusability

The following procedure was adopted for determining the thermal stability of the free base and the chloride forms of the anion-exchange resins MONAF, MMNAF and MPNAF.

One gram of the resin (whose capacity was known) was placed in a glass ampoule with 20 ml of distilled water. The ampoule was sealed and placed in a constant temperature oven adjusted to the required temperature (100 °C and 120 °C). After 24 hours, the ampoule 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. All the resins found stable up to 100 °C temperature, only negligible loss was observed.

Table 4. Thermal stability of resins in the free base form at 120 °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
MONAF	3.321	3.34	2.98
MMNAF	2.016	2.11	1.80
MPNAF	3.881	3.99	3.45

Table 5. Loss in the capacity of the resins realized after 50 cycles.

No.	Name of the resin	% loss in capacity after 50 cycle
1	MONAF	0.85
2	MMNAF	0.78
3	MPNAF	0.81

2. 5. Antimicrobial activity

The bacterial cultures were grown overnight in Nutrient broth and 0.5 ml of actively growing culture (~106-108 cells/ml) was spread on Nutrient agar plates aseptically. Approximately, 0.5 gm of resin was spotted inoculated on each plate (four per plate). Streptomycin (10 µg), Tetracycline (30 µg) and Penicillin (10 µg) bio-discs were used as control antibiotics.

Table 6. Antibacterial activity.

Sr. No.	Degree of inhibition of growth						
	E. coli	*P. aeruginosa*	*S. typhi*	*S. marcescens*	*S. aureus*	*S. epidermidis*	*B .subtilis*
MONAF	+++	-	+++	+	++++++ (a)	+++	+++
MMNAF	+++	++	+++++	+++	+++	+++++	++++

MPNAF	+	++	+++	++	+++	+++	+++
Streptomycin	++++	+++++	++++	++++	++++	++++	++++
Tetracycline	+++	-	+	-	++++++	+++	++
Penicillin	-	-	+	-	++++++ (b)	++	++++

(a) = 40mm. (b) = 35mm. Anti. Disc. Size →5-6mm.
~10-11 mm.= + Spot size (resin)→~ 6mm.
~12-13 mm. = ++
~14-18 mm. = +++
~19-23 mm. = ++++
~24-28 mm. = +++++
~30-40 mm. = ++++++

3. CONCLUSION

Synthesized resin shows ion exchange capability and reusability with negligible change in its properties. Thermal stability at 120 °C of MMNAF resin is greater than MONAF and MPNAF (i.e. MMNAF> MONAF> MPNAF). While, all resins are thermally stable up till 100 °C, negligible loss was observed. Antibacterial study shows that resins are moderately active against various species.

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(Received 06 April 2014; accepted 14 April 2014)