



Research Article

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Synthesis, physicochemical and biological activity studies of ion-exchange resin derived from melamine and phenylenediamine with formaldehyde

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ABSTRACT

A number of resins have been synthesized by reacting melamine with diamine and formaldehyde in presence of HCl as catalyst, proved to be selective anion-exchange resins for certain metals. The present paper reports the synthesis and ion exchange properties of a resin derived from melamine and phenylenediamine with formaldehyde. The resin **MOPDAF**, **MMPDAF** and **MPPDAF** were synthesized by the condensation of ortho-, meta-, and para-phenylenediamine, respectively with formaldehyde and melamine in the presence of a hydrochloric acid catalyst. These resins were characterized by elemental analysis and antimicrobial activity against several bacterial strains as (*Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella typhi*, *Serratia marcescens*, *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Bacillus subtilis*) and fungal strains as (*Aspergillus niger*, *Neurospora crassa*).

Keywords: Anion-Exchange Resins; Physicochemical properties; Antimicrobial activity

INTRODUCTION

The wide spread use of ion-exchange resins has resulted in the development of many unique procedures and processes, for both laboratory and industry. Ion exchangers are broadly used in hydrometallurgy, antibiotic purification, analytical chemistry, separation of radioisotopes and also discover large scale application in water treatment and pollution [1-4]. To-day, ion-exchange is firmly established as a unit operation. Numerous plants are in operation all over the world using these materials for applications ranging from the recovery of metals from industrial wastes to the separation of rare earths. In the laboratory, ion-exchangers are used in analytical and preparative chemistry. Ion-exchange membranes have extended further, the application of these materials. The most important use of the membranes is in the demineralizations of water besides other applications [5]. Anion-exchange resins were prepared from aromatic amines such as m-phenylene diamine by condensation with formaldehyde [6-8]. Anion exchange resins were also synthesized from aliphatic polyamines, which have the advantage of being not quite so weakly basic as the aromatic amines and can be condensed with aldehydes and phenol or an aromatic amine is added to facilitate the condensation [9-13]. Condensation of urea and urea derivatives with aldehyde [14-18] and condensation of phenols, aldehydes and nitroparaffins followed by reduction of nitro groups [19] yield anion-exchange resins. Dasare [20] reported preparation of anion-exchange resins from melamine, formaldehyde and hexamine and from commercial cashnut shell liquid, tetraethylenephentamine and formaldehyde. Anion-exchange resins have also been prepared using polyvinylchloride, pyridine and tetraethylenephentamine [21]. Mostly the resins prepared from condensation polymerization are granular in shape. However, recent attempts at preparing them in bead form have been successful [22]. However, the literature studies have revealed that no resin has been synthesized using the monomers melamine, phenylenediamine and formaldehyde. Therefore, in the present communication we report synthesis, characterization and Physicochemical properties of **MOPDAF**, **MMPDAF** and **MPPDAF** anion exchange resins.

EXPERIMENTAL SECTION

All the chemicals and reagents were used of analytical grade or chemically pure grade of Sdfine, Sigma- Aldrich and Merck unless and otherwise specified. Unless otherwise mentioned, double distilled water was used for preparation of the solutions and washing of the ion-exchange resins. HPLC grade DMF (dimethylformamide) and DMSO (dimethoxysulfoxide) were used. 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 Elementar Analyzer (Germany).

Storage and Conditioning

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 MOPDAF, MMPDAF and MPPDAF 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.

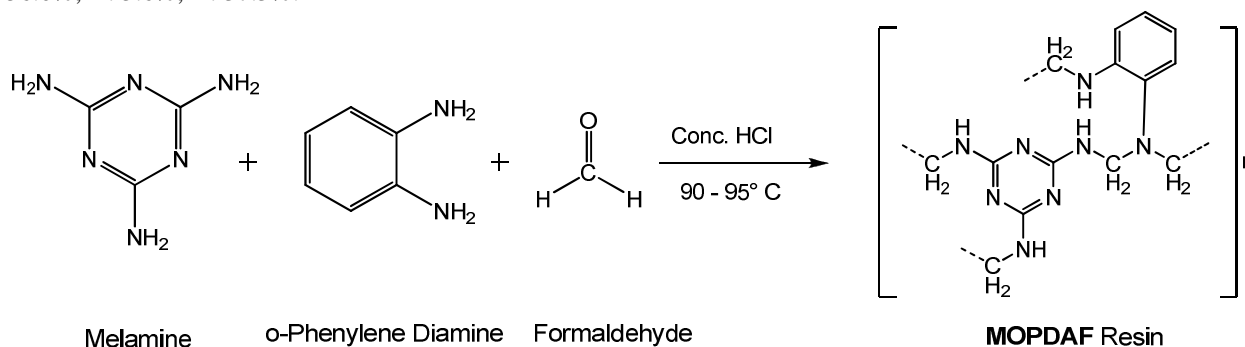
Synthesis of Anion-exchange resins

Melamine was used as cross linking agent for the synthesis of the resins.

Preparation of MOPDAF resin

12.6 grams of melamine (0.1mole) and 30 grams of formaldehyde (1mole, 90ml, of 37% formaline) were taken in a 500ml 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 10.8 grams of o-phenylene diamine (0.1mole) and 22 ml of concentrated hydrochloric acid as catalyst and the reaction mixture was heated at 90° C-95°C under reflux conditions for about one hour and five minutes with stirring. The reaction mixture gelled into a brown mass in about thirty-five minutes after the addition of hydrochloric acid and o-phenylene diamine. 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 the sieved resin was stored for further experimental work. Large scale reactions were carried out under exactly similar conditions. Analytical data for C₁₄H₁₈N₈ as per numerical calculations and experimental evidences are mentioned below respectively.

Elemental analysis data: Theoretically calculated C: 56.3%, H: 6.0%, H: 37.5% and experimentally found C: 56.0%, H: 5.6%, H: 37.3%.



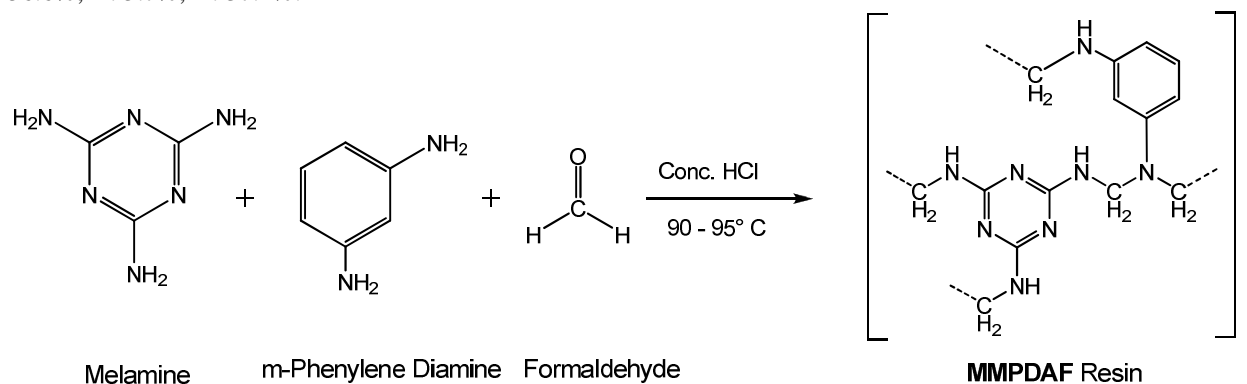
Scheme 1. Synthetic pathway of MOPDAF resin

Preparation of MMPDAF resin

12.6 grams of melamine (0.1 mole) and 30 grams of formaldehyde (1mole, 90ml, of 37% formaline) were taken in a 500ml 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 10.8 grams of m-phenylene diamine (0.1mole) and 20ml of concentrated hydrochloric acid as catalyst and the reaction mixture was heated at 90° C-95° C under reflux conditions for about forty five minutes with stirring. The reaction mixture gelled into a black mass in about ten minutes after the addition of hydrochloric acid and m-phenylene diamine. 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 the

sieved resin was stored for further experimental work. Large-scale reactions were carried out under exactly similar conditions. Analytical data for $C_{14}H_{18}N_8$ as per numerical calculations and experimental evidences are mentioned below respectively.

Elemental analysis data: Theoretically calculated C: 56.3%, H: 6.0%, H: 37.5% and experimentally found C: 56.6%, H: 5.7%, H: 37.2%.

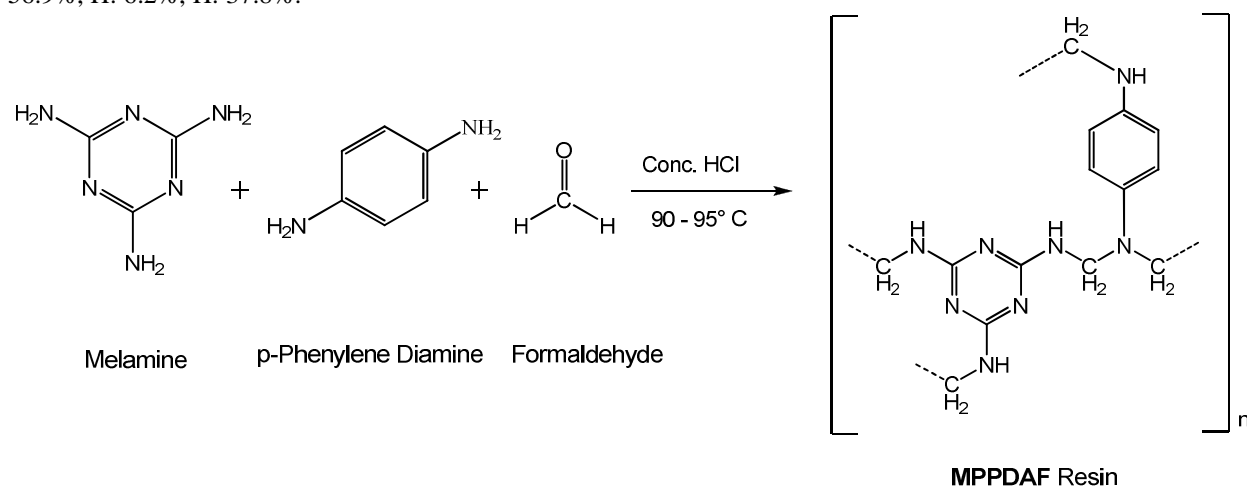


Scheme 2. Synthetic pathway of MMPDAF resin

Preparation of MMPDAF resin

12.6 grams of melamine (0.1 mole) and 30 grams of formaldehyde (1 mole, 90ml, 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 10.8grams of p-phenylene diamine (0.1mole) and 20ml of concentrated hydrochloric acid as catalyst and the reaction mixture was heated at 90°C - 95°C under reflux conditions for about one hour and forty five minutes with stirring. The reaction mixture gelled into a greenish black mass in about one hour and five minutes after the addition of hydrochloric acid and p-phenylene diamine. 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 greenish black mass was crushed into proper mesh size and the sieved resin was stored for further experimental work. Large-scale reactions were carried out under exactly similar conditions. Analytical data for $C_{14}H_{18}N_8$ as per numerical calculations and experimental evidences are mentioned below respectively.

Elemental analysis data: Theoretically calculated C: 56.3%, H: 6.0%, H: 37.5% and experimentally found C: 56.9%, H: 6.2%, H: 37.8%.



Scheme 3. Synthetic pathway of MMPDAF resin

Physicochemical Properties of Resins

Results of physicochemical properties are reported in **Table 1-3**.

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. Results are reported in **Table 1**.

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 [23]. Results are reported in **Table 1**.

Determination of 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 0.1N hydrochloric acid in 1.0N 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. Results are reported in **Table 1**.

pH titration study

The pH titration was carried out by the procedure described by Kunin [23]. The pH titration study of anion-exchange resins are depicted in **Table 2.1 – 2.3**.

Anion exchangers

0.5 gram of the resins MOPDAF, MMPDAF and MPPDAF 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. Results are portrayed in **Table 3**.

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 MOPDAF, MMPDAF and MPPDAF.

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. Results are reported in **Table 3**.

Rate of exchange

0.5 gram lots of the free base form of the resins were equilibrated separately with 50 ml of 0.1 N hydrochloric acid solution for different time intervals with intermittent shaking. At the end of definite predetermined intervals, the solutions were decanted and a known volume was titrated against standard alkali to determine the quantity of acid consumed. From this, the percentage of capacity realized at different time intervals was calculated. Results are reported in **Table 3**.

In vitro antimicrobial activity

The bacterial cultures were grown overnight in Nutrient broth and 0.5 ml of actively growing culture ($\sim 10^6$ - 10^8 cells/ml) was spread on Nutrient agar plates aseptically. Approximately 0.5 gm of resin was spot inoculated on each plate (four per plate). Streptomycin (10 μ g), Tetracycline (30 μ g) and Penicillin (10 U) bio discs were used as control antibiotics. The plates were incubated at 37° C overnight and size of zone of inhibition was measured. The fungal cultures were cultivated on MRB agar medium and spore suspension was prepared (10^6 - 10^7 spores/ml). 0.3 ml was spread and resins were applied as described above. The sizes of zone of inhibition were measured after incubation at room temperature ($\sim 25^\circ - 30^\circ$ C) for 3-4 days. The degree of inhibition was determined based on the size of zone of inhibition measured in millimeters (mm). The antimicrobial activity of the resins on bacteria and fungi are given in **Table 4**.

RESULTS AND DISCUSSION

Three ion exchange resins were prepared and only indigenously available raw materials such as o-phenylene diamine, m-phenylene diamine, p-phenylene diamine, and melamine were used. The nature of the raw materials leaves no choice but to adopt condensation polymerization for the synthesis of the resins. In the preparation of anion-exchange resin, the temperature and viscosity of the melamine and formaldehyde condensate at the time of addition of phenylene diamine was observed to be critical. Concentrated hydrochloric acid were used as catalyst in the synthesis of anion exchange resins. The reaction between melamine, m-phenylene diamine and formaldehyde **MMPDAF** took very shorter time for gelling than in the reaction between melamine, o-phenylene diamine and formaldehyde **MOPDAF** and the reaction between melamine, p-phenylene diamine and formaldehyde **MPPDAF**.

Table 1. Properties of ion-exchange resins

Resin	Moisture Content in %	Wet absolute density gm/ml	Total capacity meq/gm of absolute dry resin
MOPDAF	13.9	2.835	3.833
MMPDAF	16.4	3.150	2.870
MPPDAF	18.5	4.022	3.721

Table 2.1 pH titration study of MOPDAF 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 = 13.9 %
 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	3.832
2.	2.5	47.5	0.96	3.770
3.	5.0	45.0	0.97	3.717
4.	7.5	42.5	0.99	3.650
5.	10.0	40.0	1.10	3.600
6.	12.5	37.5	1.19	3.484
7.	15.0	35.0	1.28	3.484
8.	17.5	32.5	1.33	3.367
9.	20.0	30.0	1.36	3.367
10.	22.5	27.5	1.42	3.290
11.	25.0	25.0	1.55	3.252
12.	27.5	22.5	1.62	2.925
13.	30.0	20.0	1.71	2.671
14.	32.5	17.5	1.90	2.207
15.	35.0	15.0	2.15	2.207
16.	37.5	12.5	2.47	1.805
17.	40.0	10.0	2.95	1.509
18.	42.5	7.5	3.30	0.924
19.	45.0	5.0	3.86	0.813
20.	47.5	2.5	3.97	0.750
21.	50.0	0.0	6.94	0.000

All the anion-exchange resins had excellent physical stability and were insoluble in all the solvents. The data about the moisture content, density and capacity of the synthesized anion-exchangers **MOPDAF**, **MMPDAF** and **MPPDAF** are presented in **Table 1-3**.

Table 2.2 pH titration study of MMPDAF 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 = 16.4 %
 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	2.751
2.	2.5	47.5	0.98	2.631
3.	5.0	45.0	1.00	2.631
4.	7.5	42.5	1.03	2.512
5.	10.0	40.0	1.05	2.512
6.	12.5	37.5	1.08	2.405
7.	15.0	35.0	1.15	2.392
8.	17.5	32.5	1.20	2.290
9.	20.0	30.0	1.22	2.272
10.	22.5	27.5	1.30	2.190
11.	25.0	25.0	1.36	2.153
12.	27.5	22.5	1.40	1.794
13.	30.0	20.0	1.52	1.794
14.	32.5	17.5	1.62	1.674
15.	35.0	15.0	1.76	1.320
16.	37.5	12.5	1.92	0.990
17.	40.0	10.0	2.05	0.957
18.	42.5	7.5	2.15	0.718
19.	45.0	5.0	2.70	0.718
20.	47.5	2.5	2.78	0.620
21.	50.0	0.0	6.40	0.000

Table 2.3 pH titration study of MPPDAF 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 = 18.5 %
 Volume of equilibrating solution = 50 ml
 Equilibrium period = 24 hours
 Equilibrium temperature = 34° 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	1.14	3.802
2.	2.5	47.5	1.14	3.802
3.	5.0	45.0	1.15	3.679
4.	7.5	42.5	1.20	3.598
5.	10.0	40.0	1.24	3.556
6.	12.5	37.5	1.29	3.556
7.	15.0	35.0	1.37	3.530
8.	17.5	32.5	1.40	3.490
9.	20.0	30.0	1.53	3.434
10.	22.5	27.5	1.66	3.311
11.	25.0	25.0	1.77	3.311
12.	27.5	22.5	1.96	3.205
13.	30.0	20.0	2.20	3.066
14.	32.5	17.5	2.42	2.662
15.	35.0	15.0	2.68	2.330
16.	37.5	12.5	2.97	1.594
17.	40.0	10.0	3.26	1.594
18.	42.5	7.5	3.40	0.806
19.	45.0	5.0	3.96	0.736
20.	47.5	2.5	4.02	0.603
21.	50.0	0.0	6.69	0.000

From the results summarized in the tables, it was clear that the capacities of the synthesized resins were comparable to those of similar type of conventional commercial ion-exchange resins. Hojo, Kido and Takizawa[24] reported a chelating resin based on gallic acid, phenol and formaldehyde. Gregor, Taifor, Citaral and Becker [25] have reported a chelating resin based on anthranilic acid, resorcinol and formaldehyde. Matsumura and Komiya [26], Rabeck and Zielinaki [27], Devies, Kennedy, Lane and Willians [28] have reported salicylic acid and formaldehyde polymers. But in all the cases only cation-exchange capacities have been determined.

Figure 1. The pH titration curve of MOPDAF resin

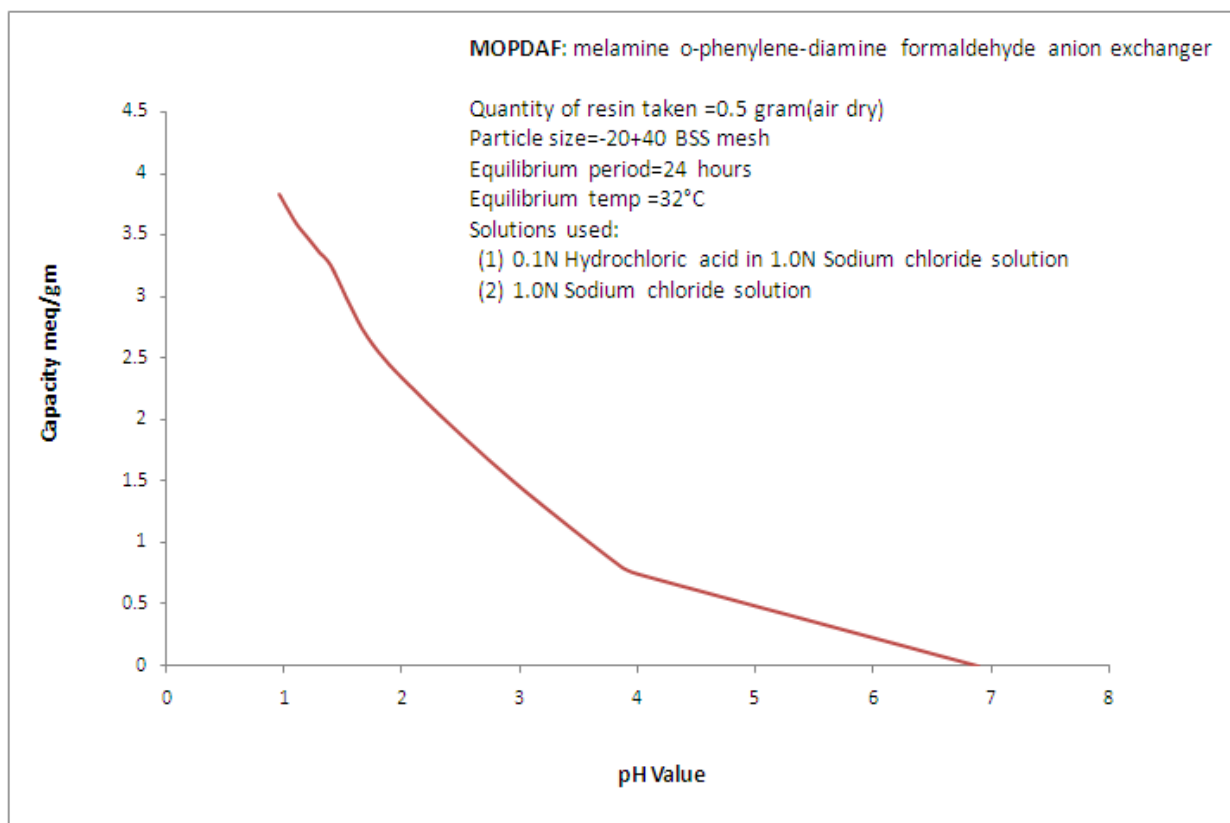


Figure 2. The pH titration curve of MMPDAF resin

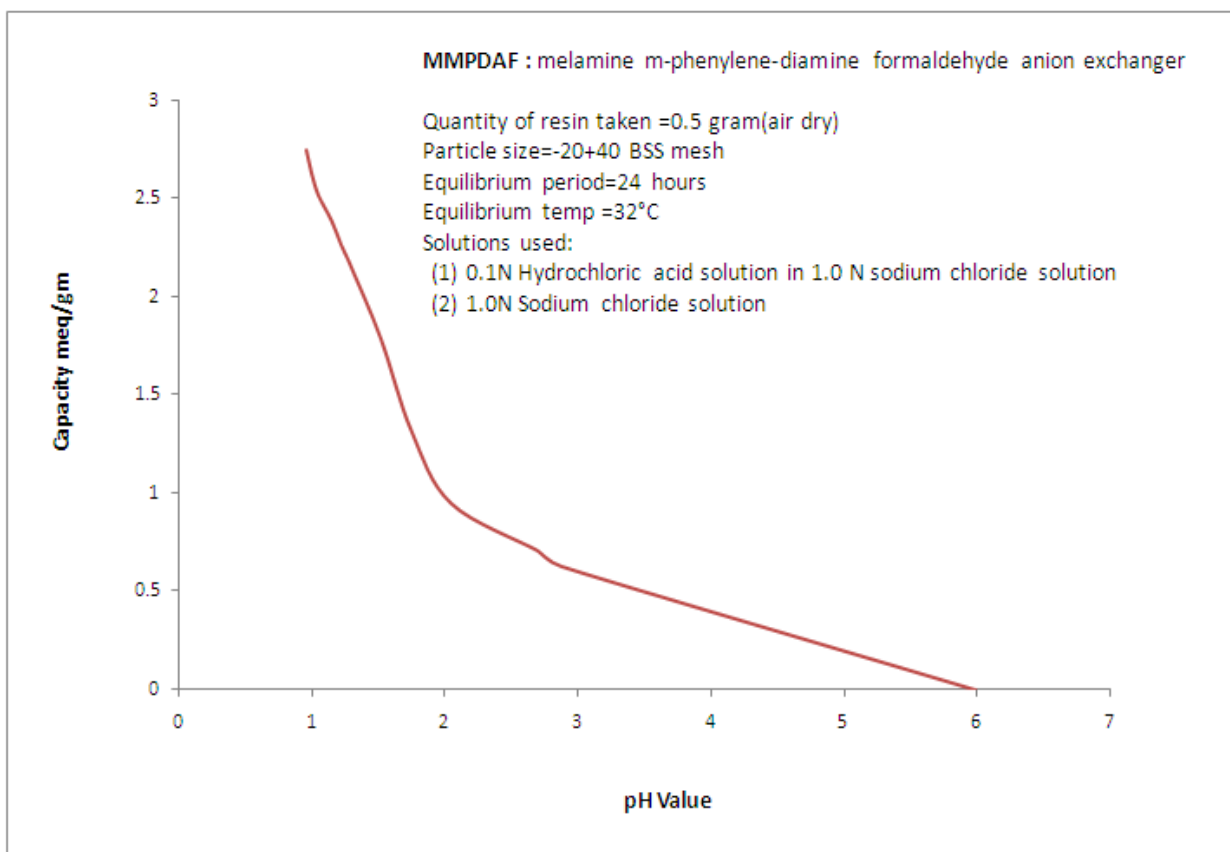
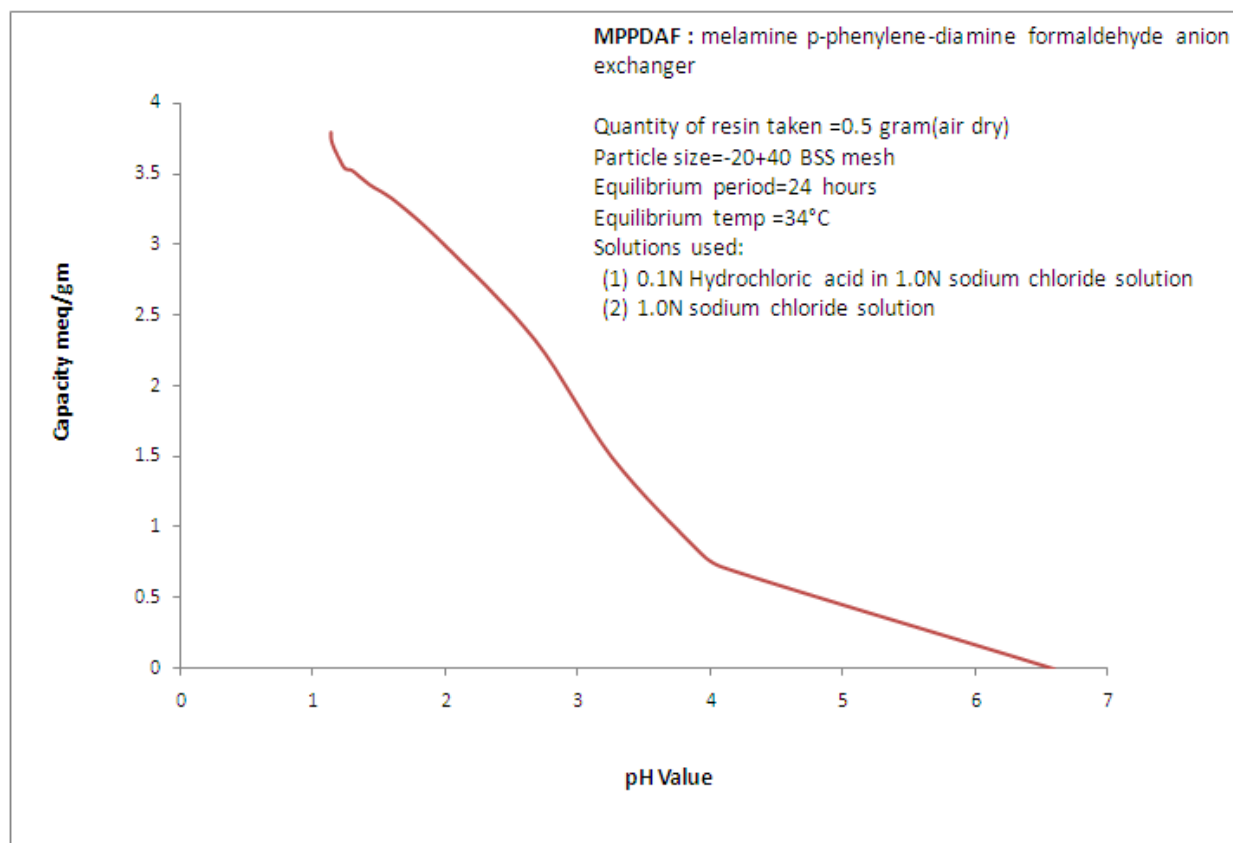


Figure 3. The pH titration curve of MPPDAF resin



However, in the investigation melamine was used as the crosslinking agent instead of phenol. Hence, anion-exchange properties were introduced. Thus, by replacing a crosslinking agent like phenol and using melamine (with primary amino groups) it was possible to obtain crosslinked products having the anionic group present on the polymer matrix yielding resins.

Table 3. Thermal stability of anion – exchange resins

Temp. 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	MOPDAF	3.833	3.98	nil	3.04	nil
	MMPDAF	2.870	2.92	nil	2.63	nil
	MPPDAF	3.721	3.75	nil	3.45	nil

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

Table 4. Antimicrobial Activity of Synthesized Ion-Exchangers

Name	Degree of inhibition of growth								
	Antibacterial						Antifungal		
	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>S. typhi</i>	<i>S. marcescens</i>	<i>S. aureus</i>	<i>S. epidermidis</i>	<i>B. subtilis</i>	<i>A. niger</i>	<i>N. crassa</i>
MOPDAF	-	-	++	-	+++	+++	+++	-	-
MMPDAF	+++	+++	+++	++	+++++ (a)	++++	+++	+	+++
MPPDAF	-	-	+++	-	++++	+	+	-	-
STREPTOMYCIN	++++	+++++	++++	++++	++++	++++	++++	-	-
TETRACYCLINE	+++	-	+	-	+++++	+++	++	-	-
PENICILLIN	-	-	+	-	+++++ (b)	++	++++	-	-

~10-11 mm. = +
 ~12-13 mm. = ++
 ~14-18 mm. = +++
 ~19-23 mm. = ++++
 ~24-28 mm. = ++++
 ~30-40 mm. = +++++

(a) = 40mm.

(b) = 35mm.

Anti. Disc. Size → 5-6mm.
 Spot size (resin) → ~ 6mm.

Figure 1 to 3 are the pH titration curves of the anion-exchange resins **MOPDAF**, **MMPDAF** & **MPPDAF** and were characteristic curves for weakly basic anion-exchange resins. These were compared with the pH titration curves of the weakly basic commercially available resin, Tulsion-WB [29, 30].

CONCLUSION

During the course of the investigation reported here, anion-exchange resins were synthesized and only cheaply available raw materials o-phenylene diamine, m-phenylene diamine, p-phenylene diamine were used. Melamine (which is now available in the country) was used as the cross linking agent along with formaldehyde. Three anion exchanger resins were synthesized and characterized.

An attempt was made to elucidate the structure of the resins by determining their elemental analysis. Theoretical elemental contents of the resins were calculated from the moles of the reactants taken for the synthesis and the observed capacity of the resins. These values were compared with the elemental content experimentally determined and were found to be almost similar.

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 o-, m-, and p-phenylene diamine based resins **MMPDAF** was more effective, especially on gram-positive bacteria namely, *S. aureus*. All were more effective in inhibiting the growth of gram-positive bacteria. Resins **MMPDAF** showed both antibacterial as well as antifungal activity.

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