



TO STUDY THE EFFECT OF TEMPERATURE ON THE ION EXCHANGE BEHAVIOUR OF INDUSTRIAL GRADE RESIN DUOLITE A378

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ABSTRACT

The thermal degradation of DuoliteA-378 70.0°C, 100.0°C and 120.0°C was carried out to predict the effect of temperature on the selectivity behaviour of DuoliteA378 towards anions like iodide and bromide. The equilibrium constant *K* values for the ion exchange reactions at different degradation temperatures of 70.0°C, 100.0°C and 120.0°C were calculated at different temperatures from which the standard enthalpy, standard entropy and standard free energy values were obtained. The standard enthalpy values of the above ion exchange reaction performed by using fresh and degraded resins Duolite A378 at 70.0°C, 100.0°C and 120.0°C were calculated as -40.15, -27.28, -44.89, -76.71 kJ/mole for Cl⁻/I⁻ and for Cl⁻/Br⁻ were -31.23, -53.72, -82.14, -34.59 kJ/mole respectively. The results obtained from the study shows that iodide ions were easily exchange towards the resin surface compared to bromide ions. The degradation of resin surfaces characterised and identified with help of SEM and IR.

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INTRODUCTION

The selection of appropriate ion exchangers depends on the needs of the system [1] and the process of selection becomes more difficult at high concentrations for chemically similar ions in the waste water. In the past decade inorganic ion exchange materials have a good alternative for replacement or complement for conventional organic ion exchange resins. Because of specific physical and chemical reasons the use of organic ion exchange resins is continued globally for various technical applications [2-3] and cannot be replaced by inorganic ion exchangers. The synthetic organic ion exchange resins having many industrial applications like purification and separations [3-5] and are mainly used for water treatment and in the preparation of demineralized water. The resins remove both radiological and non-radiological impurities [6-8]. Generally the synthesis, characterization and development of selected ion exchange materials must be compatible with the chemical nature of the liquid itself such as, type of ionic species present, pH as well as the operating parameters, in particular temperature [9-10]. Also the resins used must be resistant to degradation effect and should exhibit consistent performance under various degradation conditions. In view of this, the present research work was carried out to understand the performance of the anion exchange resins namely DuoliteA378 (nuclear grade) exposed to thermal degradation

at different degradation temperatures of 70.0°C, 100.0°C and 120.0°C [11]. The performance behaviour of the thermally degraded resins is evaluated by studying their selectivity behaviour towards bromide and iodide ions in the solution and also by studying the thermodynamic feasibility of the ion exchange reactions. Therefore, in the present investigation thermal degradation of resin [12-16] was performed to understand the degradation steps and to compare the relative thermal stability.

Experimental

Thermal degradation of resins

In order to understand the performance of thermally degraded resins, in the present study 25g of DuoliteA378 resin in chloride form are taken in watch glass and heated in oven separately at 70.0°C, 100.0°C and 120.0°C temperature for 24 h. After 24h, the thermally degraded resin is cooled over P₂O₅ in desiccators.

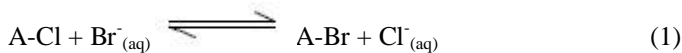
Conditioning and equilibration of thermally degraded resins

The conversion of the Resins in chloride form was done by using 20% potassium chloride solution in a conditioning Column by routine Methods [19-20]. The thermally degraded resins in chloride form were equilibrated separately for 3h with bromide ion solutions of different concentration from 0.01M, 0.02M, 0.05M, 0.08M and 0.10M in the equilibration temperatures ranging from 30.0°C to 45.0°C as explained [17-18]. After 3h the resins were filtered and the bromide ion solutions in equilibrium with resins in chloride form are

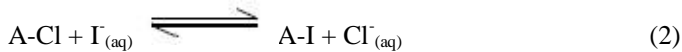
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analyzed for their chloride and bromide ion concentrations potentiometrically by using standard 0.01M silver nitrate solution.



From the results the equilibrium constants *K* for the reaction (1) is calculated for different equilibration temperatures ranging from 30.0°C to 45.0°C.



Similar studies are performed to study the equilibrium constants *K* for the reaction (2) by equilibrating thermally degraded resins in chloride form with iodide ion solution of different concentrations for 3h in the different equilibration temperature ranging from 30.0°C to 45.0°C.

RESULTS AND DISCUSSION

The equilibrium constants (*K*) for reactions 1 and 2 are calculated by the equation

$$K = \frac{C_{A-X} \cdot C_{Cl^-}}{(B - C_{A-X}) \cdot C_X^-} \quad (3)$$

experiment is obtained. Similar *K* values are calculated for the reactions 1 and 2 performed at different temperatures. From the slope of the graph of log *K* against 1/*T* (in Kelvin) the enthalpies of the ion exchange reactions 1 and 2 were calculated. From the values of *K* at different temperatures, the standard enthalpy change ΔH° (kJ.mol⁻¹), standard free energy change ΔG° (kJ.mol⁻¹) and standard entropy change ΔS° (kJ.K⁻¹.mol⁻¹) values were calculated of the above ion exchange reactions for thermally degraded DuoliteA378 at 70.0°C, 100.0°C and 120.0°C. The thermodynamic parameters calculated for the ion exchange reactions 1 and 2 using the fresh resins and resins exposed to different degradation temperatures 70.0°C, 100.0°C and 120.0°C. were presented in Tables 1-2.

The equilibrium constant (*K*) values for Cl⁻/I⁻ and Cl⁻/Br⁻ ion exchange reactions using DuoliteA-378 resins degraded at 70°C decreases from 5.67x10⁻² to 3.40 x 10⁻² and from 1.98 x10⁻² to 0.70x10⁻² respectively with rise in equilibration temperature from 30.0 °C to 45.0 °C. The standard enthalpy change (ΔH°) and standard entropy change (ΔS°) calculated for Cl⁻/I⁻ ion exchange reactions are -27.29 kJ.mol⁻¹ and -0.11 kJ.K⁻¹.mol⁻¹ respectively which are higher than the respective values

Table 1 Equilibrium constant for the ion exchange Reaction (1) and Reaction (2) using DuoliteA378 resin degraded at 70.0°C Amount of the ion exchange resin in chloride form = 0.500 g, Ion exchange capacity = 1.80meq./0.5 g, Equilibration temperature = 30.0 °C.

DuoliteA378 resin degraded at 70.0°C. Reaction (1)						DuoliteA378 resin degraded at 70.0°C. Reaction (2)						
Initial conc. Of bromide ions (M)	Final Conc. of bromide ions (M) C _{Br-}	Change in bromide ion conc.	Conc. of Cl ions exchanged (M) C _{Cl-}	Amount of bromide ions Exchange on the resin meq./0.5 g C _{RBr}	Equilibrium constant K x10 ⁻²	Initial conc. Of iodide ion(M)	Final Conc. Of iodide ions (M) C _{I-}	Change in iodide ion Conc.	Conc. Of Cl ions exchanged (M) C _{Cl-}	Amount of iodide ions exchanged on the resin meq./0.5 g C _{RI}	Equilibrium constant K x10 ⁻²	
0.01	0.0078	0.0028	0.0028	0.14	8.54	0.01	0.0064	0.0036	0.0036	0.18	19.70	
0.02	0.0184	0.0016	0.0016	0.08	0.88	0.02	0.0164	0.0036	0.0036	0.18	5.79	
0.05	0.0462	0.0006	0.0006	0.03	0.05	0.05	0.0456	0.0024	0.0024	0.12	1.03	
0.08	0.0796	0.0004	0.0004	0.02	0.01	0.08	0.0776	0.0024	0.0024	0.12	0.71	
0.1	0.0804	0.0012	0.0012	0.16	0.42	0.1	0.092	0.0036	0.0036	0.16	1.10	
					Average <i>K</i>						Average <i>K</i>	5.67

Table 2 Thermodynamics of Cl⁻/Br⁻ and Cl⁻/I⁻ reactions using fresh DuoliteA378 and resin degraded at 70.0°C, 100.0°C and 120.0°C.

Resin.	A-Cl + Br ⁻ _(aq) ⇌ A-Br + Cl ⁻ _(aq) (I)		30	35	40	45	ΔH ^o (KJ/mol)	ΔG ^o (KJ/mol)	ΔS ^o (KJ/mol)
	A-Cl + I ⁻ _(aq) ⇌ A-I + Cl ⁻ _(aq) (II)								
	Equilibrium Temperature (°C)								
Fresh DuoliteA378	Equilibrium Constant	Reaction (I)	1.86	1.68	1.17	1.10	-31.23	10.99	-0.13
	In K x10 ⁻²	Reaction (II)	9.13	5.00	4.73	4.05	-40.15	7.53	-0.15
DuoliteA378. Degraded at 70.0°C.	Equilibrium Constant	Reaction (I)	1.98	1.55	1.25	0.69	-53.72	11.26	-0.20
	In K x10 ⁻²	Reaction (II)	5.67	3.97	3.40	3.39	-27.28	8.30	-0.11
DuoliteA378. Degraded at 100.0°C	Equilibrium Constant	Reaction (I)	1.12	0.70	0.42	0.24	-82.14	13.53	-0.30
	In K x10 ⁻²	Reaction (II)	5.32	3.42	2.74	2.15	-44.89	8.90	-0.17
DuoliteA378. Degraded at 120.0°C	Equilibrium Constant	Reaction (I)	1.19	1.15	0.69	0.68	-34.59	12.16	-0.14
	In K x10 ⁻²	Reaction (II)	2.47	2.48	2.37	1.80	-76.71	10.6	-0.27

Here, A represent the resin phase; B is the ion exchange capacity of the resin; X represents I and Br⁻ ions. For different concentrations of X⁻ ions in solution at a given temperature, *K* values are calculated and an average of *K* for this set of

of -53.72 kJ.mol⁻¹, -0.21 kJ.K⁻¹.mol⁻¹ as that obtained for Cl⁻/Br⁻ ion exchange reactions. However, lower value of free energy change (ΔG°) 8.31kJ.mol⁻¹ is obtained for Cl⁻/I⁻ ion exchange reactions as compared to 11.26kJ.mol⁻¹ obtained for Cl⁻/Br⁻ ion

exchange reactions (Table 1). The equilibrium constant (K) values for Cl^-/I^- and Cl^-/Br^- ion exchange reactions using DuoliteA-378 resins degraded at 100°C decreases from 5.32×10^{-2} to 2.15×10^{-2} and from 1.12×10^{-2} to 0.24×10^{-2} respectively with rise in equilibration temperature from 30.0°C to 45.0°C . The standard enthalpy change (ΔH°) and standard entropy change (ΔS°) calculated for Cl^-/I^- ion exchange reactions are $-44.89 \text{ kJ.mol}^{-1}$ and $-0.17 \text{ kJ.K}^{-1}\text{mol}^{-1}$ respectively which are higher than the respective values of $-82.15 \text{ kJ.mol}^{-1}$ and $-0.31 \text{ kJ.K}^{-1}\text{mol}^{-1}$ as that obtained for Cl^-/Br^- ion exchange reactions. However, lower value of standard free energy change (ΔG°) 8.91 kJ.mol^{-1} is calculated for Cl^-/I^- ion exchange reactions as compared to $13.54 \text{ kJ.mol}^{-1}$ obtained for Cl^-/Br^- ion exchange reactions (Table 2).

The equilibrium constant (K) values for Cl^-/I^- and Cl^-/Br^- ion exchange reactions using DuoliteA-378 resins degraded at 120°C decreases from 2.47×10^{-2} to 1.80×10^{-2} and from 1.19×10^{-2} to 0.68×10^{-2} respectively with rise in equilibration temperature from 30.0°C to 45.0°C . The standard enthalpy change (ΔH°), standard free energy change (ΔG°) and standard entropy change (ΔS°) calculated for Cl^-/I^- ion exchange reactions are $-76.71 \text{ kJ.mol}^{-1}$, $10.66 \text{ kJ.mol}^{-1}$ and $-0.28 \text{ kJ.K}^{-1}\text{mol}^{-1}$ respectively which are lower than the respective values of $-34.59 \text{ kJ.mol}^{-1}$, $12.17 \text{ kJ.mol}^{-1}$ and $-0.15 \text{ kJ.K}^{-1}\text{mol}^{-1}$ as that obtained for Cl^-/Br^- ion exchange reactions (Table 2). The high K values and standard enthalpy change (ΔH°), standard free energy change (ΔG°) and standard entropy change (ΔS°) values [as given in Tables 1 & Table 2] obtained for Cl^-/I^- ion exchange reactions as compared to the Cl^-/Br^- ion exchange reaction for fresh and thermally degraded DuoliteA-378 at 70°C , 100°C and 120°C indicate their greater selectivity for iodide ions in the solution as compared to that of bromide ions. Similarly the decrease in K values obtained for both Cl^-/I^- and Cl^-/Br^- ion exchange reactions with rise in the degradation temperatures from 70°C to 120°C for the resin DuoliteA-378 indicates that the resin DuoliteA-378 was thermally less stable and degraded easily with rise in degradation temperatures under similar conditions.

Graphs

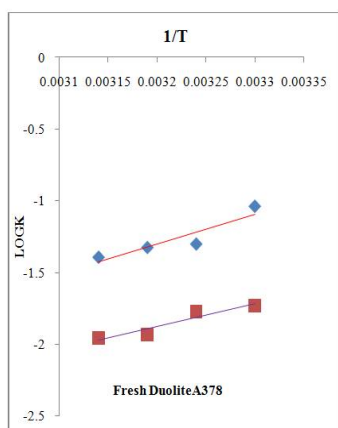


Figure 1 Shows Variation of equilibrium constant with temperature for fresh DuoliteA378 for Cl^-/I^- & Cl^-/Br^- ion exchange reaction.

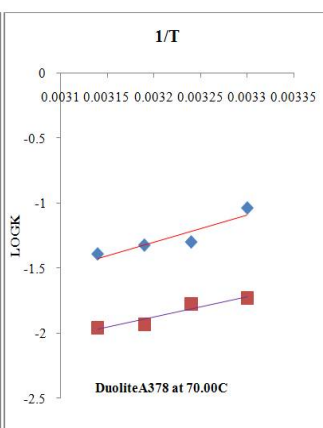


Figure 2 Shows Variation of equilibrium constant with temperature for fresh DuoliteA378 for Cl^-/I^- & Cl^-/Br^- ion exchange reaction degraded at 70°C .

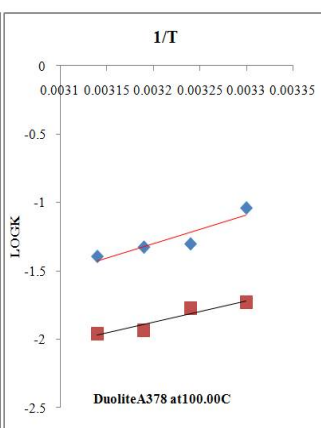


Figure 3 Shows Variation of equilibrium constant with temperature for DuoliteA378 Cl^-/I^- & Cl^-/Br^- ion exchange reaction degraded at 100°C .

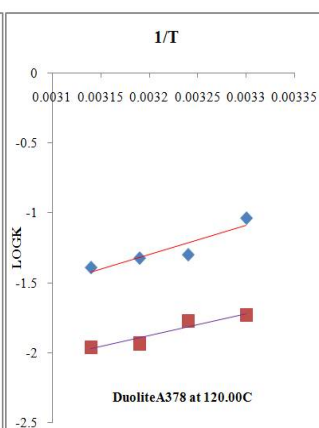


Figure 4 Shows Variation of equilibrium constant with temperature for DuoliteA378 for Cl^-/I^- & Cl^-/Br^- ion exchange reaction degraded at 120°C .

FTIR spectrum of fresh (at room temperature) and thermally (at 70.0°C , 100.0°C and 120.0°C) degraded DuoliteA378 resin

FTIR spectra of fresh and thermally degraded samples of DuoliteA378 were recorded in KBr pellets using a FTIR

PerkinElmer 1750 spectrophotometer. The degradation effect on the resins was studied by comparing the FTIR spectra of fresh resin with that of degraded resins.

In the IR spectrum (Figure 5) of fresh DuoliteA-378 resin the broad band appears at 3418 cm^{-1} is for the amine salts group and the band at $2854\text{--}2703 \text{ cm}^{-1}$ for --N--H stretching in amine. The strong band at 1168 cm^{-1} and the weak band at 1369 cm^{-1} for --C--N stretching in aliphatic and aromatic amine [21-22]s. A variable absorption band at 1614 cm^{-1} is for --C=C-- stretching for alkenes group. The weak band at 3022 cm^{-1} is the characteristic stretching band for aromatic ring. A strong band at 2926 cm^{-1} and weak band at 2854 cm^{-1} is the C--H stretching band for --CH_2 group. The moderate band at 1511 cm^{-1} is due to the --C=C-- stretching in aromatic ring. The strong band at 704 cm^{-1} is the characteristic band of mono substituted aromatic rings.

Similarly in IR spectrum of DuoliteA-378 resin thermally degraded at 70.0°C , 100.0°C and 120.0°C (figures 6 to 8), it was observed that there is no significant changes in absorption frequencies of various characteristic absorption bands such as ammonium group, and bands of --N--H stretching in amine salts ($\text{R}_3\text{--N}^+\text{--H}$), --C--N stretching, --C=C-- stretching in alkenes, C--H stretching and --C--H bending for --CH_2 groups, --C=C-- stretching in aromatic ring and the characteristic bands of mono-substituted aromatic rings. After the careful observation of IR spectrum of degraded resin it can be concluded that the resin is thermally stable and there is no significant change in structure of the resin and but only some of the resin sites are blocked or cracked with rise in the temperature which is also confirmed by comparing the SEM images of fresh resin (figure 9) and thermally degraded resin (figure 10 to 12).

Scanning electron microscopy (SEM) studies of fresh (at room temperature) and thermally (at 70.0°C , 100.0°C and 120.0°C) degraded DuoliteA 378 resin.

Scanning electron micrographs of both fresh and degraded resin surfaces were obtained with the help of SEM technique

using JSM-6380LA Scanning Electron Microscope (Jeol Ltd., Japan). The pictures were taken at an excitation voltage of 15 kV under a 90 Pascal pressure and a magnification of $\times 150$, $\times 500$, $\times 1000$, $\times 2500$ and $\times 5000$.

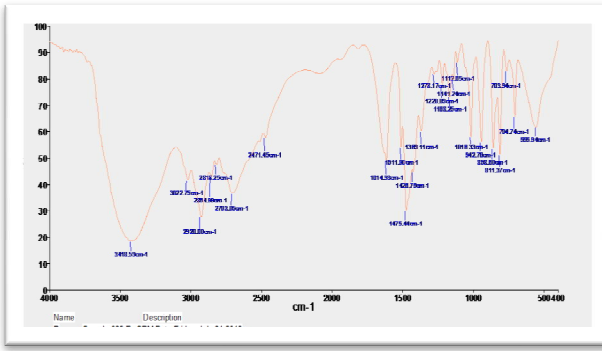


Figure 5 FTIR Spectrum of fresh resin DuoliteA378

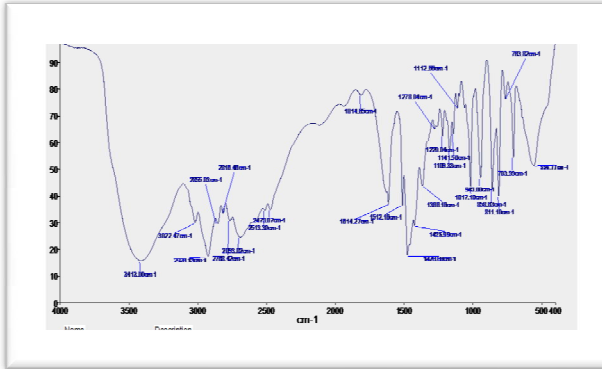


Figure 6 FTIR Spectrum of degraded resin DuoliteA378 at 70.0°C

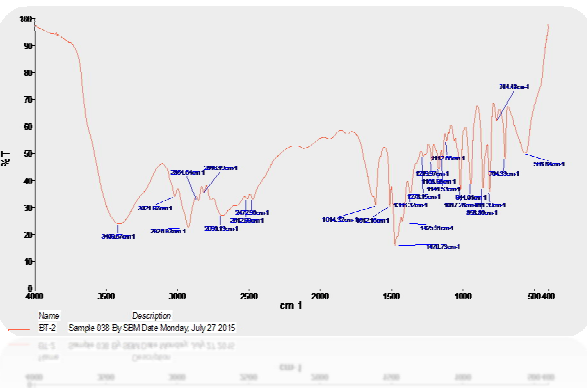


Figure 7 FTIR spectrum of degraded resin DuoliteA-378 at 100.0°C

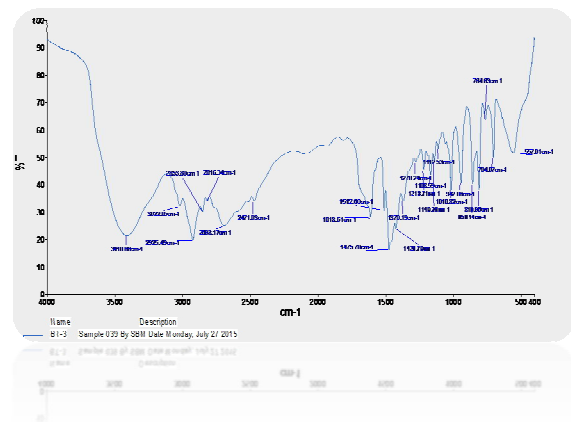


Figure 8 FTIR Spectrum of degraded resin in Duolite A378 at 120.0°C

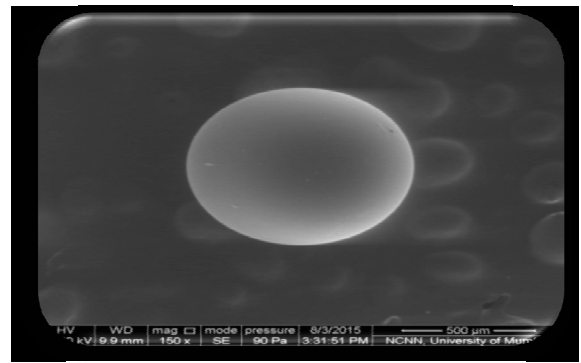


Figure 9 SEM image of fresh DuoliteA378

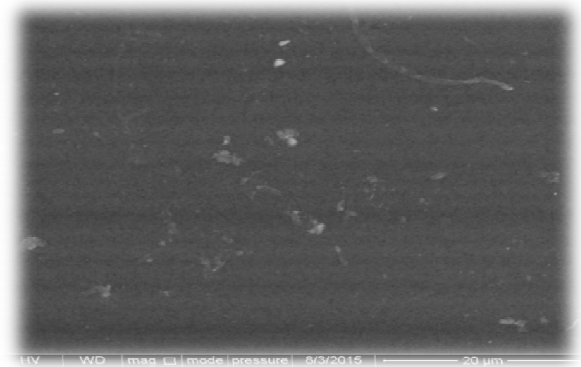


Figure 10 SEM image of DuoliteA378 resin degraded at 70.0°C

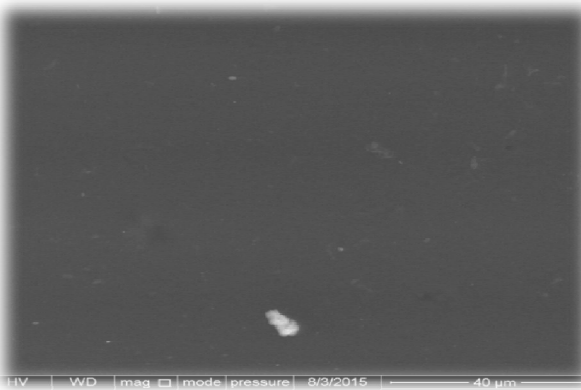


Figure 11 SEM of DuoliteA378 degraded at 100.0°C

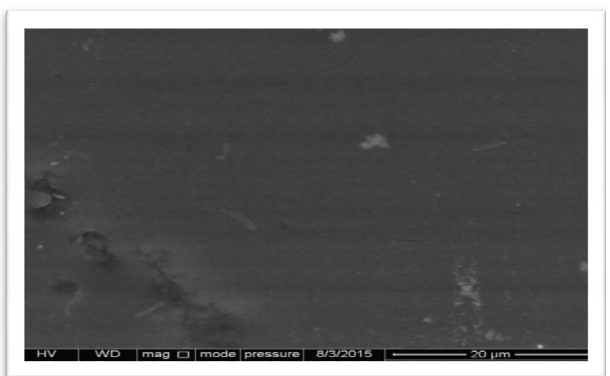


Figure 12 SEM of DuoliteA378 degraded at 120.0°C.

Figure 9 shows the surface morphology [23] of fresh DuoliteA 378 resins indicating plane spherical structure and smooth surface. The SEM image of thermally degraded resin DuoliteA 378 at 70°C shows little cracks and thread like appearance on the surface. The SEM image of DuoliteA378 at 100°C shows small cracks and thread like appearance and surface of the

resin is appearing too rougher with rise in the degradation temperature as compare to the surface of fresh resin (Figure 11). whereas SEM of the resin at 120°C (Figures12) indicate hair line cracks and deformation on the plane spherical surface.

CONCLUSION

Ion exchange technology is widely being used for separation of particular ionic species in presence of other. The selection of suitable ion exchange material is still more difficult when the process involves separation of two or more chemically same ionic species in the solution. In most of the cases the resins are subjected to stringent operational conditions during which the stability of the resins is a crucial issue. Under such critical conditions the present experimental work will be useful in deciding about the selection of suitable ion exchange material. The results of such studies will help in selection of suitable ion exchange resins for efficient industrial applications.

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