

## ION EXCHANGE EQUILIBRIUM THERMODYNAMICS IN PREDICTING THE BROMIDE ION SELECTIVITY BEHAVIOR OF AUCHLITE-ARA9366 AND AUCHLITE-A378 RESINS UNDER DIFFERENT DEGRADATION CONDITIONS

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### ABSTRACT

In the present investigation attempts were made to evaluate the  $Br^-$  ion selectivity behavior of two structurally related resins namely AuchliteARA9366 and AuchliteA-378 exposed under different degradation conditions like thermal degradation at  $120.0^\circ C$ , chemical degradation in 30%  $H_2O_2$  (9 volume) medium and under UV Radiation at 254nm for 24h towards the bromide ions solutions of different ionic concentration between temperature of  $30.0^\circ C$  to  $45.0^\circ C$  for 5 h. The degraded resins in chloride form were equilibrated separately with bromide ion solutions of concentrations 0.01, 0.025, 0.05, 0.075 and 0.1M between temperature of  $30.0^\circ C$  to  $45.0^\circ C$  for 5 h. The equilibrium constants (K) values for  $Cl^-/Br^-$  ion exchange reactions for AuchliteARA-9366 and AuchliteA378 under different degradation conditions were found to be decreases with rise in temperature. The K values calculated for  $Cl^-/Br^-$  uni-univalent ion exchange reaction using AuchliteARA-9366 resins under different degradation were higher than that obtained by using Auchlite A-378 under similar experimental conditions. The high value of equilibrium constant (K) and low enthalpy value obtained for AuchliteARA-9366 resins under different degradation indicate their greater selectivity for bromide ions in the solution as compared to that of AuchliteA-378 resins when both of them are in chloride form. The degradation of the resin surfaces were recognized and identified with sophisticated techniques like Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy.

**Keywords:** AuchliteARA-9366; Auchlite-378 UV radiation degradation., Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR)

### 1. Introduction

Ion exchange is an adsorption phenomenon in which the mechanism of adsorption is electrostatic. Electrostatic forces hold ions to charged functional groups on the surface of the ion exchange resin. The adsorbed ions replace ions that are on the resin surface on a 1:1 charge basis Deborah, L *et al* (2013) Ion exchange resins are polymers that are capable of exchanging particular ions within the polymer with ions in a solution that is passed through them. This ability is also seen in various natural systems such as soils and living cells Kumaresan, R *et al* (2006).

Ion exchange is basically a reversible chemical process are in an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. Removal of undesirable anions and cations from solution through the use of ion exchange resin Patange (2017A). Ion-exchange resins are widely used in different separation, purification, and decontamination processes. The most common examples are water softening and water purification. In many cases ion-exchange resins were introduced in such processes as a more

flexible alternative to the use of natural or artificial zeolites. Also, ion exchange resins are highly effective in the biodiesel filtration process. The principle of ion exchange process was widely used in phase transfer catalysis in various potential pharmaceutical companies as important intermediate for drug and dyes synthesis. most of research study were carried out on characterization of various nuclear and industrial grade organic as well as inorganic ion exchange resins under various stringent chemical, thermal,  $\gamma$ -rays radiation degradation condition so as to improve the performance, efficiency and selectivity behavior towards variety of cations and anions in the industrial waste effluents, purification and manufacturing process Patange (2017B) it was very difficult to choose the suitable ion exchange resins for the separations of hard ions so that there was need of some thermodynamic data or techniques which will provides the useful information about the various nuclear and industrial grade resins and helps to select which of the ion exchange resins were suitable for removal or separations of various cations and anions from industrial waste and nuclear waste. In this connections attempts were made

to evaluate the Br<sup>-</sup> ion selectivity behavior of two structurally related resins namely AuchliteARA9366 and AuchliteA-378 exposed under different degradation conditions like thermal degradation at 120.0<sup>o</sup>C, chemical degradation in 30% H<sub>2</sub>O<sub>2</sub> (9 volume) medium and under UV Radiation at 254nm for 24h towards Patange (2017C) the bromide ions solutions of different ionic concentration between temperature of 30.0<sup>o</sup>C to 45.0<sup>o</sup>C for 5h the thermodynamic data obtained from the study will helpful in predicting the selectivity behavior of the resins. The data obtained from the study will also helpful for the selection of suitable ion exchange resin under the stringent degradation. The ion exchange equilibrium studies exposed to different degradation indicates that both resins blocks the particular sites by reducing the ion exchangeable groups which will responsible for the decrease in the equilibrium constant values and the enthalpy values of for Cl<sup>-</sup>/Br<sup>-</sup> ion exchange reactions and consequently Patange (2021) affects on the performance of the resins viz AuchlieARA9366 and AuchliteA-378 which will also supported by the SEM micrographs and IR spectra of the degraded resin surfaces.

## 2. Materials and methods

### 2.1. Materials.

The anion exchange resin AuchlieARA9366 and AuchlieA-378 in hydroxide Pandey *et al* (2003) form was supplied by the Auchtel chemicals limited, Mumbai were strongly basic nuclear grade and weakly basic non-nuclear grade anion exchange resin. The resin granules of mesh size 30-40 were used for the research work. Both the resins converted into chloride ion form for the experimental study by treating the respective resin sample with 10% KCl solution for 24h in a 25cm long and 2.5cm in diameter glass column at the rate of 1ml for 60seconds. after conditioning of the resin sample in chloride form were purified with help of distill water and ethanol solvent and air dried and stored in glass bottle.

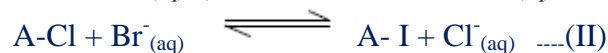
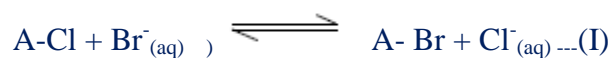
### 2.2 degradation of Resins

In order to predict the performance and selectivity nature of the resins the, degradation of resins such thermal degradation at 120.0<sup>o</sup>C, chemical degradation in 30% H<sub>2</sub>O<sub>2</sub> (9 volume)

medium and under UV Radiation at 254nm about 50g of both resin Samanta *et al* (1992) sample in chloride form placed separately placed in oven at 120.0<sup>o</sup>C, chemical degradation in 30% H<sub>2</sub>O<sub>2</sub> and in UV chamber at 254nm for 24 hours. after 24 hours both resin sample were washed with distilled water and then with ethyl alcohol and air dried and stored in glass bottle and used for further study.

### 2.2.1. Ion exchange equilibrium study

For equilibration study about 0.5g of degraded resins viz AuchliteARA9366 and AuchliteA-378 in chloride form were equilibrated Samanta *et al* (1995) separately with iodide ion solution of different ionic concentration from 0.01M, 0.025M, 0.05M, 0.075M and 0.1M on well-equipped magnetic stirrer with hot plate and automatic temperature control at the different temperatures from 30.0<sup>o</sup>C to 45.0<sup>o</sup>C for 5h as explained After 5 hours, the quantity of iodide ions transfers with the resin surface can be determined potentiometrically by using standard 0.1M AgNO<sub>3</sub> using saturated calomel electrode as reference and silver electrode as indicator



Where A=AuchliteARA-9366 = AuchliteA-378

The equilibrium constants *K* for the reaction (I) and (II) at different temperature from 30.0<sup>o</sup>C to 45.0<sup>o</sup>C

Were calculated.

## 3. Results and Discussion

The equilibrium constants (*K*) for reactions I and II were calculated by the equation

$$K = \frac{[A-Br][Cl^{-}]}{[E - A-Br][Br^{-}]} \dots\dots\dots(III)$$

Here A=AuchliteARA-9366 = AuchliteA-378Surface; *E* = ion exchange capacity of the resin .Thus by knowing[13] different ionic concentrations or amount of Br<sup>-</sup> ions in solution transfers on the respective resin surface at a given temperature, *K*- values and mean *K*-values for this batch of experiment was determined. Similar *K* values were obtained for the Cl<sup>-</sup>/Br<sup>-</sup> exchange reactions at different

temperatures. the standard  $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  in  $\text{kJ.mol}^{-1}$  of  $\text{Cl}^-/\text{Br}^-$  ion exchange reactions for degraded resin sample were determined from the slope obtained by plotting a graph of  $\log K$  against  $1/T$  ( $^\circ\text{K}$ ) Simister *et al* (2004)(figure1-4). The thermodynamic parameters calculated for  $\text{Cl}^-/\text{Br}^-$  reactions of fresh resins viz AuchliteARA-9366 and AuchliteA-378 and resins exposed to different degradation were represented in Tables 1 to 4. the equilibrium constant(K) values obtained for both resins viz AuchliteARA-9366 and AuchliteA-378 were found to be decreases under thermal degradation at  $120.0^\circ\text{C}$ , in 30%  $\text{H}_2\text{O}_2$  medium and under UV Radiation at 254nm indicating that the performance of ion exchange reaction

lowers due to loss of exchange sites or groups under different degradation conditions which was also supported by  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  as well as FTIR and SEM micrographs. The  $K$  values calculated for  $\text{Cl}^-/\text{Br}^-$  uni-univalent ion exchange reaction using AuchliteARA-9366 resins under different degradation were higher than that obtained by using AuchliteA-378 under similar experimental conditions. The high value of equilibrium constant ( $K$ ) and low enthalpy value obtained for AuchliteARA-9366 resins under different degradation indicate their greater selectivity for bromide ions in the solution as compared to that of AuchliteA-378 resins when both of them are in chloride form Singare & Patange(2014A).

AuchliteARA-9366 Resin degraded at $120.0^\circ\text{C}$						AuchliteA-378 Resin degraded at $120.0^\circ\text{C}$					
$\text{A-Cl} + \text{Br}^-_{(\text{aq})} \rightleftharpoons \text{A-Br} + \text{Cl}^-_{(\text{aq})}$ Reaction (I)						$\text{A-Cl} + \text{Br}^-_{(\text{aq})} \rightleftharpoons \text{A-Br} + \text{Cl}^-_{(\text{aq})}$ Reaction (I)					
Concentration Of $\text{I}^-$ ions taken (M)	Conc. of $\text{Br}^-$ ions (M) left after experiment [Br]	Exact Change in $\text{Br}^-$ ion conc.	Amount of $\text{Cl}^-$ ions transfer on resin surface (M) [Cl]	Amount of $\text{I}^-$ ions transfer on resin surface meq./1 g [A-Br]	Equilibrium constant in ( $K \times 10^{-2}$ )	Concentration Of $\text{Br}^-$ ions taken (M)	Conc. of $\text{Br}^-$ ions (M) left after experiment [Br]	Exact Change in $\text{Br}^-$ ion conc.	Amount of $\text{Cl}^-$ ions transfer on resin surface (M) [Cl]	Amount of $\text{I}^-$ ions transfer on resin surface meq./1 g [A-Br]	Equilibrium constant in ( $K \times 10^{-2}$ )
0.01	0.0048	0.0054	0.0054	0.27	17.47	0.01	0.0072	0.002	0.0018	0.1	4.73
0.025	0.0142	0.0066	0.0066	0.33	9.14	0.025	0.0222	0.0012	0.0012	0.06	0.57
0.05	0.0384	0.0076	0.0076	0.38	4.61	0.05	0.0472	0.0008	0.0008	0.04	0.11
0.075	0.0636	0.0064	0.0064	0.32	1.90	0.075	0.0692	0.0008	0.0008	0.04	0.08
0.1	0.0836	0.0064	0.0064	0.32	1.45	0.1	0.0904	0.0012	0.0012	0.16	0.45
<b>Mean K</b>					<b>6.91</b>	<b>Mean K</b>					<b>1.1907</b>

**Table 1:** Equilibrium constant for the ion exchange reaction using AuchliteARA-9366 and AuchliteA378 resin degraded at  $120.0^\circ\text{C}$ .

Amount of the ion exchange resin in chloride form = 0.500 g, Ion exchange capacity for AuchliteARA-9366 = 2.008 meq./0.5 g and Ion exchange capacity for AuchliteA378=0.628 meq./0.5 g, Equilibration temperature =  $30.0^\circ\text{C}$ .

**Table 2.** Thermodynamics of ion exchange reactions using AuchliteARA-9366 and AuchliteA378 resins degraded at 120.0°C.

$$\text{A-Cl} + \text{Br}^-_{(\text{aq})} \rightleftharpoons \text{A-Br} + \text{Cl}^-_{(\text{aq})}$$

Equilibration temperature (°C)	Equilibrium Constant $K \times 10^{-2}$		$\Delta H^\circ$ (kJ.mol <sup>-1</sup> )		$\Delta G^\circ$ (kJ.mol <sup>-1</sup> )		$\Delta S^\circ$ (kJ.K <sup>-1</sup> .mol <sup>-1</sup> )	
	AuchliteAR A-9366	AuchliteA 378	AuchliteA RA-9366	AuchliteA 378	AuchliteA RA-9366	AuchliteA 378	AuchliteA RA-9366	AuchliteA 378
30	6.91	1.19	-6.84	-34.59	7.04	12.16	-0.04	-0.14
35	6.70	1.15						
40	6.53	0.69						
45	6.04	0.68						

**Table 3.** Thermodynamics of ion exchange reactions using AuchliteARA-9366 and AuchliteA378 resins degraded in 30% H<sub>2</sub>O<sub>2</sub>.

$$\text{A-Cl} + \text{Br}^-_{(\text{aq})} \rightleftharpoons \text{A-Br} + \text{Cl}^-_{(\text{aq})}$$

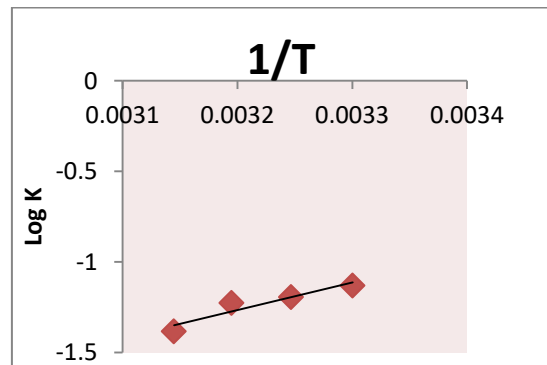
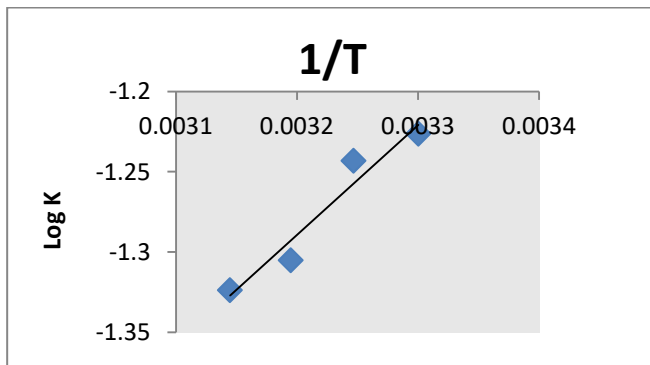
Equilibration temperature (°C)	Equilibrium Constant $K \times 10^{-2}$		$\Delta H^\circ$ (kJ.mol <sup>-1</sup> )		$\Delta G^\circ$ (kJ.mol <sup>-1</sup> )		$\Delta S^\circ$ (kJ.K <sup>-1</sup> .mol <sup>-1</sup> )	
	AuchliteAR A-9366	AuchliteA 378	AuchliteA RA-9366	AuchliteA 378	AuchliteA RA-9366	AuchliteA 378	AuchliteA RA-9366	AuchliteA 378
30	5.94	0.83	-13.05	-13.60	7.57	12.64	-0.065	-0.0838
35	5.71	0.79						
40	4.95	0.72						
45	4.74	0.64						

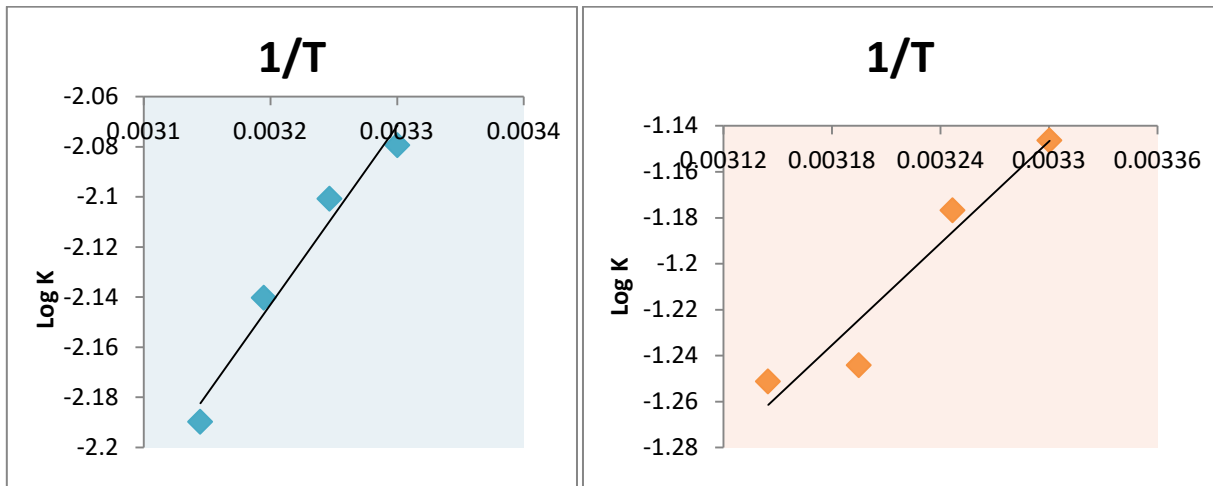
**Table 4.** Thermodynamics of ion exchange reactions using AuchliteARA-9366 and AuchliteA378 resins degraded under UV radiation at 254nm.

$$\text{A-Cl} + \text{Br}^-_{(\text{aq})} \rightleftharpoons \text{A-Br} + \text{Cl}^-_{(\text{aq})}$$

Equilibration temperature (°C)	Equilibrium Constant $K \times 10^{-2}$		$\Delta H^\circ$ (kJ.mol <sup>-1</sup> )		$\Delta G^\circ$ (kJ.mol <sup>-1</sup> )		$\Delta S^\circ$ (kJ.K <sup>-1</sup> .mol <sup>-1</sup> )	
	AuchliteAR A-9366	AuchliteA 378	AuchliteA RA-9366	AuchliteA 378	AuchliteA RA-9366	AuchliteA 378	AuchliteA RA-9366	AuchliteA 378
30	7.41	7.14	-14.81	-14.14	7.31	7.16	-0.023	-0.068
35	6.40	6.65						
40	5.94	5.70						
45	4.18	5.60						

3.1 Graphs



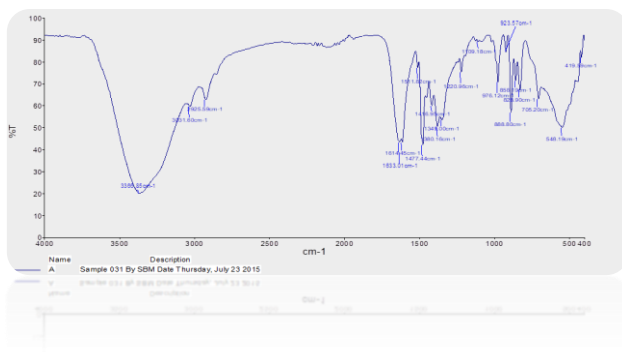


**Figure 1-4** Shows Variation of equilibrium constant for Cl<sup>-</sup>/Br<sup>-</sup>. With temperature AuchliteARA-9366 & AuchliteA-378 degraded in 30% H<sub>2</sub>O<sub>2</sub> and UV wavelength at 254nm.

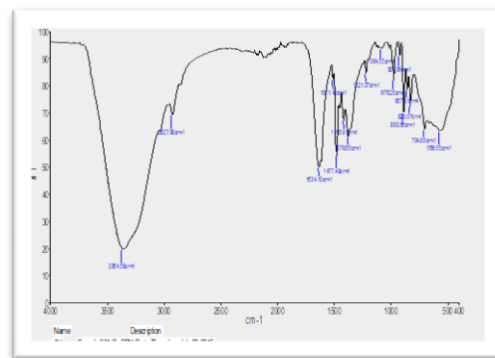
**3.2 IR Analysis of AuchliteARA-9366 and AuchliteA-378 degraded in 30% H<sub>2</sub>O<sub>2</sub> and UV Radiation at 254nm.**

IR spectra of fresh as well as degraded samples of AuchliteARA-9366 and AuchliteA378 resins Singare & Lokhande (2012).were scan on PerkinElmer 1750 FTIR spectrophotometer. Most of characteristic functional group of both fresh as well as degraded resins was found to

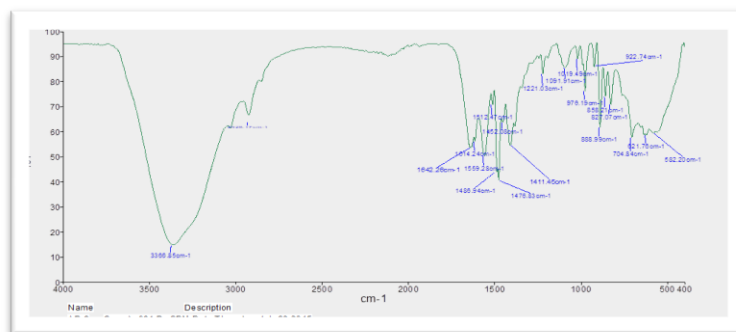
be appears at the theoretical values but some considerable changes in some characteristic Singare & Patange(2014 B) IR band were found to be broad in degraded resin sample due to the in 30% H<sub>2</sub>O<sub>2</sub> and UV Radiation at 254nm and crack the resin surface and lowers rate of ion exchange process which are also seen in SEM of both degraded resin sample Singare & Patange(2014 C).



**Figure 5**



**Figure 6**



**Figure 7**

**Figure 5-7.** FTIR Spectrum of fresh resin, AuchliteARA-9366 Resin degraded in 30% H<sub>2</sub>O<sub>2</sub> and UV radiation at 254nm.

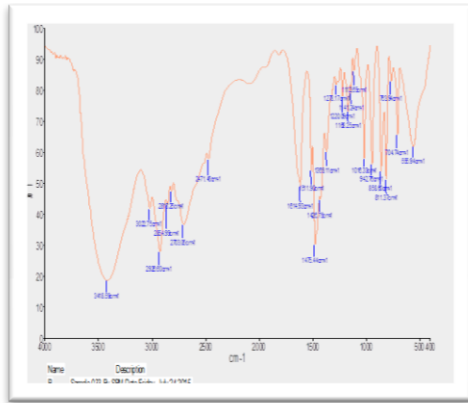


Figure 8

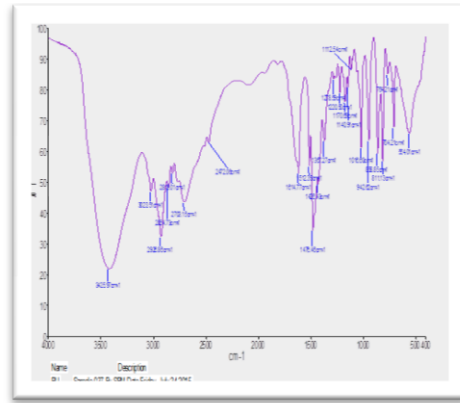


Figure 9

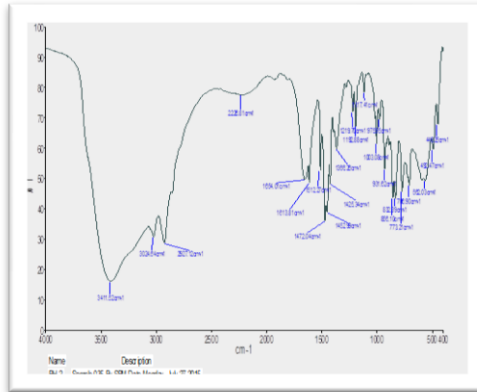
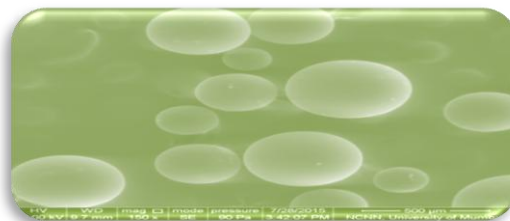


Figure 10

Figure 8-10. FTIR Spectrum of fresh resin, Auchs liteA38 Resin degraded in 30% H<sub>2</sub>O<sub>2</sub> and UV radiation at 254nm. 3.3SEM Analysis of Auchs liteARA-9366 and Auchs liteA-378Resin degraded in 30% H<sub>2</sub>O<sub>2</sub> and



UV light at 254nm:

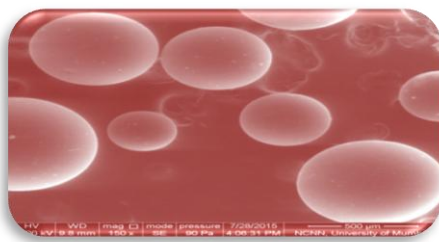


Figure 11

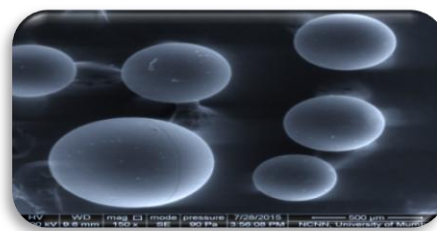
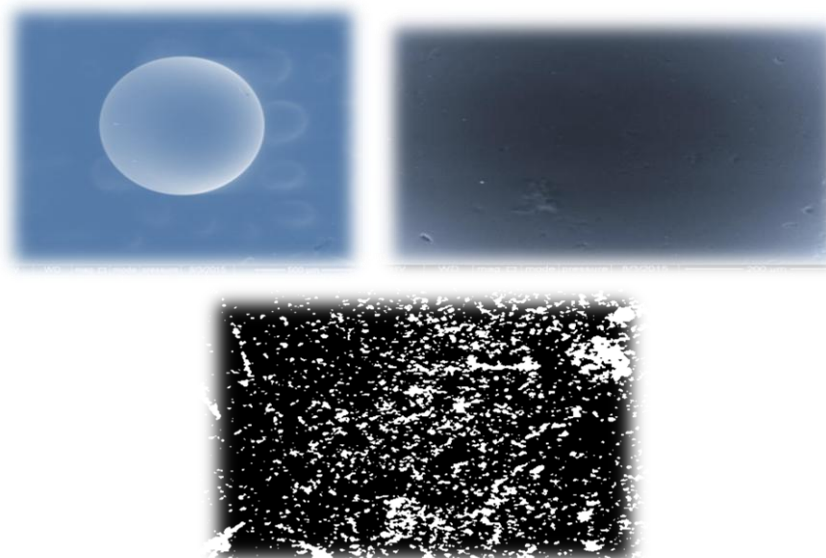


Figure 12

Figure 13

Figure 11-13 SEM micrograph of fresh resin, Auchs liteARA9366 Resin degraded in 30% H<sub>2</sub>O<sub>2</sub> and UV radiation at 254nm.

**Figure 14****Figure 15****Figure 16**

**Figure 14-16.** SEM micrograph of fresh resin AuchliteA38 Resin degraded in 30% H<sub>2</sub>O<sub>2</sub> and UV radiation at 254nm.

SEM images Singare *et al* (2010) of fresh and degraded resin surfaces were made exposed electronically in a vacuum on thin carbon layer for 60 seconds at 30 W and pictures were captured with help of JSM-6380LA model Singare & Patange(2014D). On comparing the SEM micrographs of fresh Singare *et al* (2011) as well as degraded resin surfaces, it will found that both resin were surfaces Tomoi *et al* (1997) have cracks and appears to more rough and enough to block the ion exchange site of the resin and consequently lowers down the ion exchange process as Zhu *et al* (2009) compare to fresh resin surfaces.

#### 4. Conclusion

The thermodynamic data obtained from the research study will shows that the resin AuchliteARA966 is more stable and selective towards bromide ions in external solution under different degradation conditions as compared to the resin AuchliteA378 under identical conditions. The results obtained from the work will also helpful for qualitatively assessing the efficiency, economy and performance of resins under the vigorous condition like chemical, thermal as well as under electromagnetic radiations.

#### References

1. Deborah, L., Nazila, K., Douglas, B., & James A.(2013).Evaluating ion exchange resin efficiency and oxidative Capacity for the separation of uranium (IV) and uranium (VI). *Geochemical Transactions*, 14,1-10.
2. Kumaresan, R., Sabharwal, K., Srinivasan, T., VasudevaRao, P., & Dhekane G.(2006).Evaluation of New Anion Exchange Resins for Plutonium Processing. *Solvent Extraction And Ion Exchange*, 24(4), 589 –602.
3. Patange,A,( 2017).Study on Ion Exchange behavior of Nuclear Grade Resin AuchliteARA9366 Chemically Degraded in Hydrogen Peroxide Medium. *Orient.J.Chem.* 33(1).430-438.
4. Patange, A.( 2017). Study on ion exchange behavior of auchliteara9366 and auchlitea378 resins chemically degraded in perchloric acid medium. *Global Journal of engineering science and researches*,4(8),57-71.
5. Patange, A.( 2017). Study on ion exchange behavior of auchliteara9366 and auchlitea378 resins chemically degraded in perchloric acid medium. *Global Journal of engineering science and researches*,4(8),57-71.

6. Patange, A.( 2021).Thermodynamics of ion exchange reaction in predicting the iodide ion selectivity behavior of nuclear grade and non-nuclear grade resins under different degradation conditions. Vidyabharati International Interdisciplinary Research Journal, 12(1),143-149.7.
7. Pandey, A., Goswami, A., Sen,D., & Mazumder, R.( 2003).The study of highly cross-linked AEMs synthesized from poly(vinyl benzyl chloride) quaternised using the diamines DABCO and piperazine for various applications. J.Membr. Sci., 217, 117 – 130.
8. Samanta,S., Ramaswamy, M., & Misra B. (1992).Studies on cesium uptake by phenol resins.Sep.Sci. Technol,27(2), 255–267.
9. Samanta,S., Ramaswamy, M., & Misra B. (1995).Column behavior of a resorcinol formaldehyde polycondensateresin for radio cesium removal from simulated radwaste solution. J. Nucl. Sci. Technol,32(3), 425–429.
10. Simister, C., Caronand F., & Gedye R.(2004).Determination of the thermal degradation rate of polystyrene-divinyl benzene ion exchange resins in ultra-pure water at ambient and service temperature. Journal of Radioanalytical and Nuclear Chemistry,261(3), 523-531.
11. Singare, P., & Lokhande, R. (2012).Studies on Ion-Isotopic Exchange Reactions Using Nuclear Grade Ion Exchange Resins. Ionics, 18(4), 351–357.
12. Singare, P., & Patange, A.( 2014). Thermodynamics of Ion-exchange reaction in predicting the ionic selectivity of Auchlite ARA-9366 and Auchlite A-378 anion exchange resins. International Letters of Chemistry ,Physics and Astronomy, 11, 67.
13. Singare, P., & Patange, A. ( 2014). Ion-exchange reaction thermodynamics to study the selectivity behaviour of nuclear and non-nuclear grade anion exchange resins. International Letters of Chemistry, Physics and Astronomy, 11, 44 .
14. Singare, P., & Patange, A.( 2014).Study on Halide Ions Selectivity of Industrial Grade Anion Exchange Resin AuchliteA-378. International Letters of Chemistry, Physics and Astronomy, 6, 8.
15. Singare, P., & Patange, A. ( 2014).Study on Halide Ions Selectivity of Nuclear Grade Anion Exchange Resin AuchliteARA-9366 .International Letters of Chemistry,Physics and Astronomy, ,6, 1.
16. Singare, P., Lokhande, R., & Madyal S.(2010), the thermal degradation studies of polystyrene sulfonic and polyacrylic carboxylic cationites using thermal analysis (TG) combined with Scanning Electron Microscopy (SEM).Russian Journal of General Chemistry, 80, 527.
17. Singare, P., Lokhande, R., & Madyal S. (2011). The application of non-destructive radioactive tracer technique in characterization of Dowex 550A LC and Indion-820 anion exchange resins.Open Journal of PhysicalChemistry, 1, 45.
18. Tomoi, . M., Yamaguchi, K., Ando, R., & Aosaki, H.(1997).Concerning the 18 synthesis of Thermally stable alkaline anion-exchange resins; incorporating a hexyloxy spacer group. J.Appl. Polym. Sci., 64, 1161.
19. Zhu, L., Liu, Y., & Che J.(2009). Synthesis of N-Methylimidazolium Functionalized StronglyBasic Anion Exchange Resins for Adsorption of Cr (VI).Ind. Eng. Chem. Res.,48(7), 3261–3267.