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CHARACTERIZATION AND ION EXCHANGE PROPERTIES OF NEWLY FUNCTIONALIZED AMBERLITE XAD-2 RESIN BY 5-SULFOSALICYLIC ACID

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ABSTRACT: The functionalization of amberlite XAD-2 resin with 5-sulfosalicylic acid was carried out by using diazo-spacer (-N=N-) technique. Intermediates formed in a reaction and the final product was characterized by FTIR method. The composition of newly functionalized 5-sulfosalicylic-diazo-amberlite-XAD-2 (5-SSA-N=N-AXAD-2) has been determined by elemental analysis. Thermo-kinetic parameters of functionalized resin such as activation energy (Ea), free energy changes (ΔG), entropy change (ΔS) and order of degradation (n) were calculated by Freeman-Carroll (FC) and Sharp-Wentworth (SW) methods. The order of degradation (n) obtained by the FC method was finally confirmed by SW method. Activation energy and entropy change calculated by both of these methods were found to be in good agreement. Low values of frequency factor suggest slow degradation of functionalized resin. The ion exchange properties of 5-SSA-N=N-AXAD-2 have been studied by employing the batch equilibrium method. It was employed to study the selectivity of heavy metal ion uptake over a wide pH range and in media of various ionic strengths. The overall rate of metal ions uptake follows the order: $Hg^{+2} > Bi^{+3} > Pb^{+2} > As^{+3}$.

KEY WORDS: Amberlite XAD-2; Diazo spacer; Resin; Thermal degradation; Metal ion uptake; Ion exchange; batch equilibrium method.

1.0 INTRODUCTIONS:

Now a day, functionally modified and thermally stable polymeric material have attracted much attention of researchers, analysts, environmentalist and mordent chemist. The amberlite series resins offer novelty and versatility hence they occupy an imperative position in the field of material science. The vast applicability of functionalize resin open a new pathways in the progress of resins as they are generally useful in packaging, adhesives and coatings in electrical sensors, organometallic semiconductors and mostly in the form of ion exchanger [i-ii]. Functionalized resin also offers a good choice for separation and per-concentration as they possess superior selectivity [iii-iv].

Amberlite XAD series resin has uniform pore size distribution, high surface area, good porosity, and excellent physical and chemical properties which provide efficient support for anchoring chelating ligands. Amberlite XAD-2 and XAD-4 have been ideal for functionalization based on their porosity and surface area [v-vi]. The literature survey tells that the two methods have been often used to design good functionalized chelating resin. The first method involve the sorption of chelating ligands onto the polymeric matrix and another method is based on the covalent coupling of a ligand with polymer backbone via several spacer arm, generally azo (-N=N-), methylene (-CH_2-) and SO_2 linkage [vii-ix].

2.0 MATERIALS AND METHODS

2.1 Chemicals

The entire chemicals used in the synthesis were pure AR grade. Amberlite XAD-2 resin (surface area, 330 m^2 g^{-1}; pore diameter 9 nm; bead size, 20-60 mesh was procured from Sigma-Aldrich (USA), 5-sulfosalicylic acid (Sigma Aldrich), conc. HCl, conc. HNO_3 and conc. H_2SO_4 were procured from SD Fine Chemicals, India Ltd.

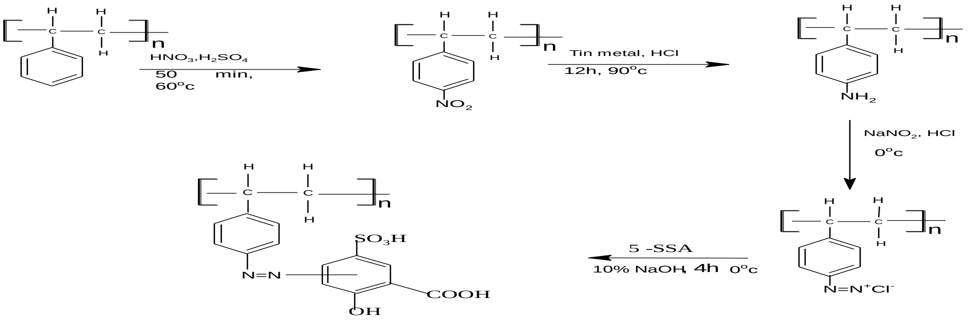
2.2 Instrumentation

Digital oil bath (Bio Techniques India, Model BTI-38) with silicone oil was used to regulate the temperature while performing the synthesis of newly functionalized resin. Infrared spectra (4000-400 cm^{-1}) were recorded on FTIR spectrometer (Bruker Alpha- 12228734). Thermo-gravimetric analysis (TGA) was carried out on a Perkin Elmer Diamond TGA thermal analyzer.

2.3 Synthesis

Functionalization of amberlite XAD-2 resin with 5-sulfosalicilyc acid (5-SSA-N=N-AXAD-2)

Amberlite XAD-2 beads (5 gm) was crushed and nitrated with 10 ml of concentrated HNO_3 and 25 ml of concentrated H_2SO_4 (nitrating mixture) for 50 min. at 60^0C. The reaction mixture was poured in ice cold water and nitrated resin (NO_2-AXAD-2) was collected by filtration. The intermediate product was repeatedly washed with distilled water until free from acid and dried. In second step nitrated resin was reduced by refluxing it for 12 hrs. with tin metal in conc. HCl (45ml) and ethanol (50ml). The modified aminated resin (NH_2-AXAD-2) was filtered and repeatedly washed with distilled water until free from acid. Aminated resin was treated with 100 ml of 2 M HCl for 30 min. filter and wash with distilled water. It was then suspended in 200 ml of ice-cold water and then diazotized with 1M $NaNO_2$ and 1M HCl at 0 to -5^0C until the reaction mixture started to change the color of iodide paper to violet. The diazotized resin was filtered, washed with ice cold water and reacted with 5-sulfosalicilyc acid (15 gm taken in 200 ml of 10% NaOH solution) the resulting product was filtered and wash with distilled water followed by dil. NaOH to remove unreacted 5-Sulfosalicylic acid then it washed with dil. HCl and finally again wash with distilled water [x-xv]. Final product was dried and stored in vacuum desiccator. The complete reaction scheme is shown below. This experimental synthesis with the reaction scheme is already published. [xvi]



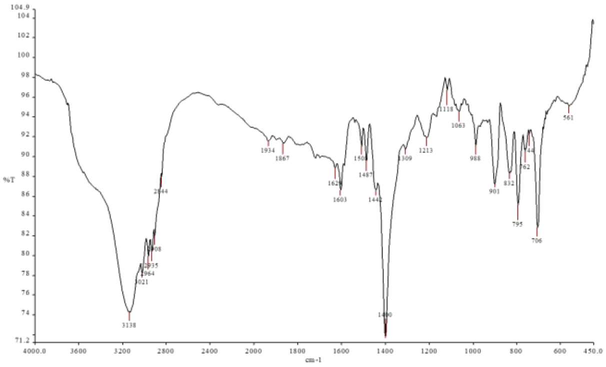
Scheme 1: Synthesis of 5-SSA-N=N-AXAD-2

3.0 RESULTS AND DISCUSSION

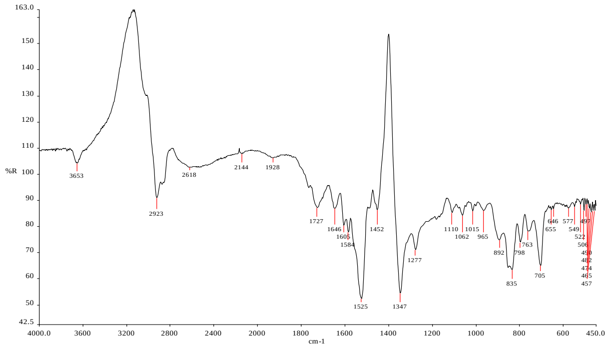
3.1 FTIR spectra

An infrared spectrum is extensively useful in obtaining structural information of the polymeric structure. The IR data of 5-SSA-N=N-AXAD-2 is given in table 1. Infrared spectra of pure AXAD-2 polymer and intermediate products obtained in each step of synthesis was characterized by FTIR spectrum. The assignment of vibrational frequencies was mainly based on the data available in the literature.

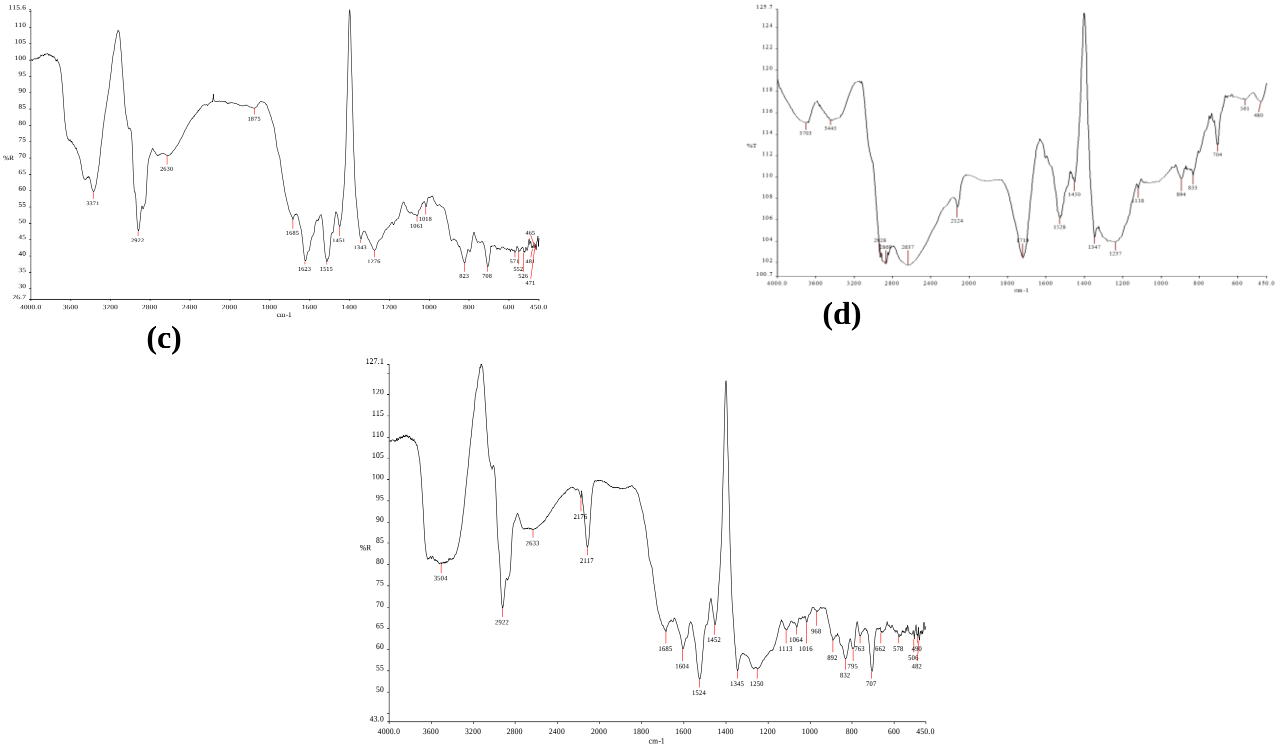
FTIR of pure AXAD-2 polymer is shown in figure 1(a). NO_2-AXAD-2 was confirmed by the prominent two peaks at 1525 and 1347 cm^{-1} which were attributed to N-O asymmetric and symmetric stretching vibration figure 1(b) [xvii]. The NH_2-AXAD-2 was confirmed by IR absorption peak at 3371 cm^{-1} for N-H stretching of primary amine figure 1(c). Peak appeared at 2124 cm^{-1} is due to –N=N- stretching figure 1(d) [xviii-xxi]. A very broad band seen in the region 3504 cm^{-1} is assigned to the stretching vibration of the hydroxyl group exhibiting intermolecular hydrogen bonding [xxii]. Peak at 832 cm^{-1} shows tetra-substituted aromatic ring, peak at 795 and 763 cm^{-1} is due to –CH_2- bending [xxiii], peak observed at 2922 cm^{-1} is due to C-H stretching of aromatics [xxiv-xxvi] absorption band at 1452 cm^{-1} suggest the carboxylic -OH bending. A peak appeared at 1604 cm^{-1} is due to aromatic ring which shows C=C stretch in benzene ring of 5-SSA-N=N-AXAD-2, absorption at 892 cm^{-1} suggest –CH_2- wagging. Peak appaired at 1016 and 1064 cm^{-1} is due to -SO_2 symmetric and asymmetric stretching of sulfonyl group present compound [xvi and xxvii-xxviii] figure 1(e).



(a)



(b)



(c)

(d)

(e)

Figure. 1 (a) FTIR Spectrum of pure-AXAD-2 resin, **(b)** FTIR Spectrum of NO_2-AXAD-2, **(c)**FTIR Spectrum of NH_2-AXAD-2, **(d)** FTIR Spectrum of Cl-N=N-AXAD-2, **(e)** FTIR Spectrum of 5SSA-N=N-AXAD-2

Table 1 : Characteristics IR data of 5-SSA-N_2-AXAD-2 and its intermediates

Resin	IR (frequency in cm-1)	Nature of fragment assigned	Figure
5-SSA-N=N-AXAD-2	1525	N-O stretching	3.1.3
	1347		
	3371	N-H stretching of primary amine	3.1.4
	2124	-N=N- stretching	3.1.5
	3504	phenolic -OH	3.1.6
	2922	C-H stretching in aromatics	
	1604	presence of aromatic ring	
	1452	carboxylic -OH bending	
	1345	phenolic -OH bending	
	1064	S=O stretching	
	1016		
	892	- CH2 - wagging	
	795	-CH2- bending	
	763		

3.2 Elemental analysis

Elemental analysis of functionalized **5-SSA-N=N-AXAD-2** has been carried out for the determination of the percentage of carbon, hydrogen, nitrogen and oxygen content. The elemental analysis was carried out at the Central Institute of Mining and Fuel Research Nagpur, India. The details of elemental analysis and molecular weight of repeated units are given in table 2.

Table-2 Elemental analysis of functionalized 5-SSA-N=N-AXAD-2

Resin	% of Carbon found **(Calc.)**	% of Hydrogen found **(Calc.)**	% of Nitrogen found **(Calc.)**	% of Sulpher found **(Calc.)**	Empirical formula of repeating unit	Molecular weight of repeating unit
A-N=N-AXAD-2	51.00 **(51.73)**	3.39 **(3.44)**	7.92 **(8.04)**	9.07 **(9.20)**	$C_{15}H_{12}O_6N_2S$	353

3.3 Thermogravimetric Analysis (TGA)

TGA analysis of 5-SSA-N=N-AXAD-2 was carried out at department of material science, Vishvesharaya National Institute Nagpur (M.S.) India. The sample was allowed to heat up to 1000^0C by Perkin Elmer Diamond TGA/DTA analyzer in an argon environment at a linear heating rate 20^0C min^{-1}. The resultant thermogram reveals that initial weight loss up to 120^0C due to loss of water (Figure 2). The thermal stability at the half decomposition temperature of resin is more and decomposition of resin between temperature range 405 to 474 ^{0}C was studied. FC and SW plots of 5-SSA-N=N-AXAD-2 are shown in figure 3(a) and figure 3(b) respectively. In 5-SSA-N=N-AXAD-2 resin, the order of decomposition was found to be 0.5 order as determined by the FC method which was further confirmed by SW method [xxix]

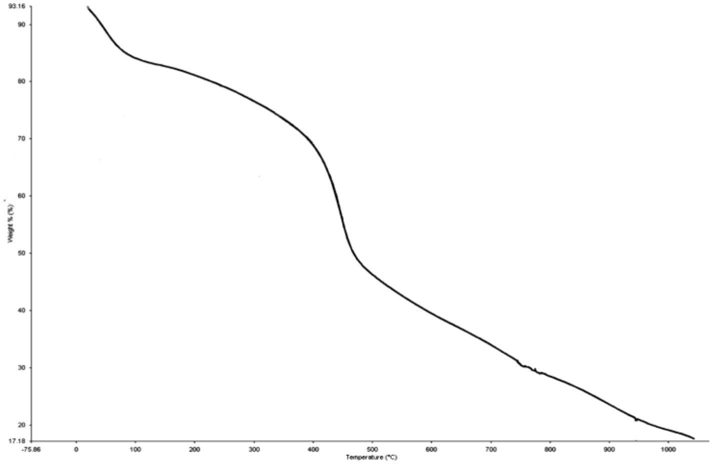
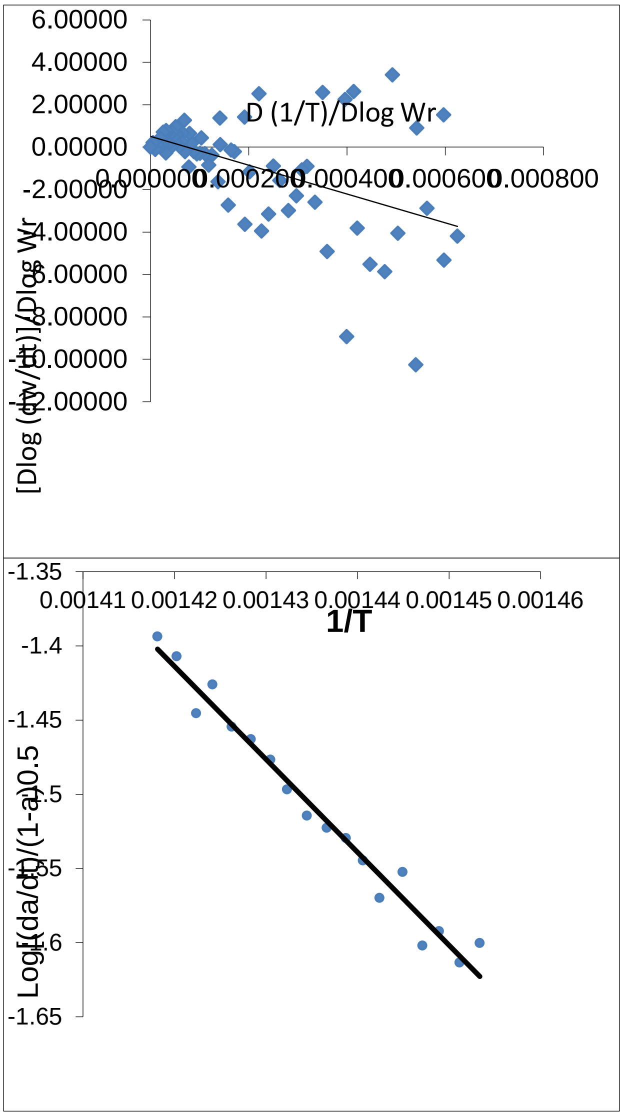


Figure 2 - TG Curve of 5-SSA-N=N-AXAD-2

The various thermokinetic properties of 5-SSA-N=N-AXAD-2 like activation energy (Ea), free energy changes (ΔG) and entropy change (ΔS), order of degradation (*n*) has been determined by using the following FC and SW methods [xxx-xxxi]. Calculated values of the thermokinetic parameters has been shown in **table 3.**



(a) **(b)**

Figure 3: (a)Freeman-Carroll plot of 5-SSA-N=N-AXAD-2, (b) Sharp-Wentworth plot of 5-SSA-N=N-AXAD-2

Table-3 : Thermokinetic parameters of 5-SSA-N=N-AXAD-2

Resin	Parameter	Freeman-Carroll	Sharp-Wentworth
5-SSA-N=N-AXAD-2	Temperature range (^{0}C)	405-480	405-480
	Activation energy Ea (kJ)	124.32	119.94
	Frequency factor A (min^{-1})	4 x 10^8	3.034 x 10^8
	Entropy ΔS (JK-1)	-87.07	-89.83
	Free Energy ΔG (kJ)	1860.68	184.27
	Order of degradation *n*	0.5	0.5

4.0 ION EXCHANGE PROPERTIES

Toxicity of heavy metal ion has been increasing substantially because of the use of metal ion as a catalyst in many industries. Many methods also have been developed for the preconcentration and removal of toxic metal ions. However, the metal on removal by chelating ion exchange resin using the batch calibration method has gained rapid acceptance because of its wide variety of sorbent phases [xxxii-xxxiii]. The ion-exchange study was carried out using three experimental variables

1. Nature of electrolyte
2. Rate of metal ion uptake
3. pH of the aqueous medium

4.1 Effect of different electrolytes on metal ions uptake

The influences of different electrolyte such as NaCl, $NaNO_3$, Na_2SO_4 and Na_2SO_3 at various concentrations in an equilibrium state of metal resin interaction was studied. Effect of electrolyte on metal uptake is summarized in table 4. Careful inspection of data revealed that most suitable electrolyte for the exchange of Bi^{+3}, Pb^{+2}, Hg^{+2} and As^{+3} ions on the polymer matrix of 5-SSA-N=N-AXAD-2 was NaCl (2.0 M) and Na_2SO_4 (2.0 M).

For NaCl, and Na_2SO_4, as the concentration increases the amount of metal ion uptake increases for Bi^{+3}, Pb^{+2}, Hg^{+2} except As^{+3}. In presence electrolyte of NaCl and Na_2SO_4 for the exchange of Pb^{+3} ion the amount of metal ion increases with increase in the concentration of electrolyte. Similarly, for Bi^{+3}, $NaNO_3$ and Na_2SO_3 at 2.0 M concentration found to increases the ion exchange activity of resin. Thus, the choice of electrolyte for the exchange of Bi^{+3}, Pb^{+2}, Hg^{+2} and As^{+3} decrease in the order NaCl> Na_2SO_3> $NaNO_3$> Na_2SO_3

Table 4: Evaluation of effect of the electrolyte on amount of metal ion uptake on 5-SSA-N=N-AXAD-2 (mg of metal exchange per g of resin)

Metal ion	**Conc.**	**Electrolytes**			
		NaCl	**$NaNO_3$**	**Na_2SO_4**	**Na_2SO_3**
Bi^{+3}	**0.5**	124.36	121.87	135.65	107.03
	1.0	103.01	128.28	122.83	162.02
	1.5	125.31	159.02	106.50	156.37
	2	134.33	167.09	153.96	153.43
Pb^{+2}	**0.5**	56.25	50.55	18.38	7.24
	1.0	66.30	96.12	36.62	107.08
	1.5	46.14	5.03	136.67	38.28
	2	182.30	27.28	231.90	95.17
Hg^{+2}	**0.5**	168.72	82.24	106.96	14.78
	1.0	105.71	46.91	112.79	79.49
	1.5	147.68	58.15	71.80	46.82
	2	89.31	68.73	92.68	56.86
As^{+3}	**0.5**	13.52	15.49	9.62	10.73
	1.0	9.93	14.75	6.04	9.04
	1.5	13.27	9.96	6.09	10.30
	2	14.57	10.34	2.75	6.62

Metal ion solution = 5 ml; Electrolyte= 20 ml; Equilibrium state= 24hrs; Wt. of resin=25 mg; Temperature = Room Temperature; Metal ions were estimated spectrophotometrically.

The plots of mg of metal exchange per gram of 5-SSA-N=N-AXAD-2 resin verses concentration of electrolyte is shown below in figure 4:

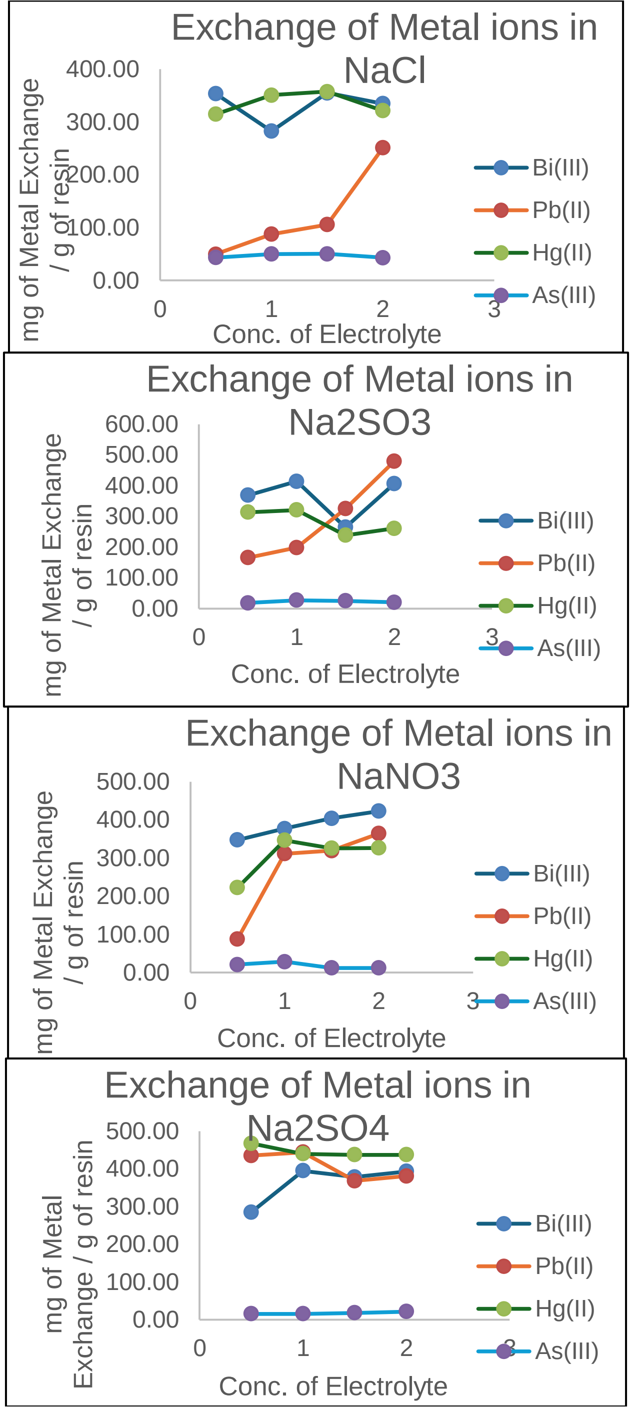


Figure 4: Graphical representation of the effect of different electrolytes on metal ions uptake

4.2 Rate of metal ion uptake for 5-SSA-N=N-AXAD-2

The percent rate of metal ion uptake for the metal ions Bi^{+3}, Pb^{+2}, Hg^{+2} and As^{+3} (Figure 5) were calculated by assuming that the equilibrium reached in 24 hours i.e. the 100% rate of metal ion uptake was assume to occur in 24 hours. However, the minimum time required to reach nearer to equilibrium was found to be 5 hours. The data showed that, the amount of metal ion uptake increases with increase in the contact time. Rates of metal ion uptake for

Hg^{+2} was higher which was followed by Bi^{+3} and Pb^{+2}. Rates of metal ion uptake for As^{+3} was found to lower compared to all the metal under study.

It can be observed that, the rate of metal ion uptake decreases in order $Hg^{+2} > Bi^{+3} > Pb^{+2} > As^{+3}$.

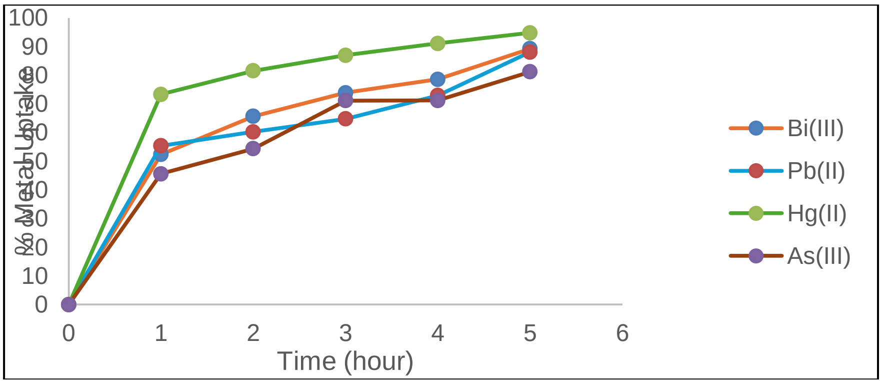


Figure 5: Rate of metal ion uptake for 5-SSA-N=N-AXAD-2

4.3 Distribution coefficient (K_D)

The effect of pH on ion exchange properties of resins for metal ion under study provides the information about the ion exchange selectivity of resins on the basis of distribution coefficient between resin phase and solution phase. Distribution coefficient values between resin phase and solution phase were reported in table 5. Distribution coefficient was studied as a function of pH varying from 4 to 8.

The resin 5-SSA-N=N-AXAD-2 was found to be more selective for Pb^{+2} from pH 4 to 6. However, it is comparatively more selective for Bi^{+3} at pH = 8, thus this resin can be used for the separation of As^{+3} from the mixture containing As^{+3} and Pb^{+2}. Similarly, the resin was found to be very less selective for Hg^{+2} from pH 5 to 6, therefore this resin can be conveniently used to separate Pb^{+2} from mixture containing Pb^{+2} and Hg^{+2}.

Table 5: Distribution coefficient (K_D) of different metal ions as a function of pH for 5-SSA-N=N-AXAD-2

pH	**K_D x 10^{-2}**			
	Bi^{+3}	**Pb^{+2}**	**Hg^{+2}**	**As^{+3}**
4	1.75	5.03	3.65	4.13
5	4.06	5.75	1.80	4.17
6	4.46.	5.91	2.33	5.28
7	7.08	0.38	2.88	5.35
8	17.86	0.25	4.09	6.15

Metal ion solution = 5 ml; Electrolyte= NaNO3, 2 M, 20 ml; Equilibrium state= 24hrs; Wt. of resin=25 mg; Temperature = Room Temperature; Metal ions were estimated spectrophotometrically.

5.0 CONCLUSION

Modified 5-SSA-N=N-AXAD-2 resin was synthesized using azo spacer technique, the intermediate product and the reaction were monitored with the help of FTIR data. The structure of resin was confirmed by elemental analysis, FTIR, TGA data. Order of decomposition (n) was found to be 0.5 order as determined by the FC method which was further confirmed by SW method found to be in good agreement. Further, the low value of frequency factor suggest slow degradation of resin. The characteristic data obtained in present work support to the tentative structure of resin. The value of Ion exchange study revealed that the 5-SSA-N=N-AXAD-2 resin is more selective for Pb^{+2} from pH 4 to 6. However, it is comparatively more selective for Bi^{+3} at pH = 8, thus this resin can be used for the separation of As^{+3} from the mixture containing As^{+3} and Pb^{+2}. Similarly, the resin was found to be very less selective for Hg^{+2} from pH 5 to 6, therefore this resin can be conveniently used to separate Pb^{+2} from mixture containing Pb^{+2} and Hg^{+2}.

6.0 ACKNOWLEDGMENT

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