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## Role of chemically modified organic resin in selective separation of $\text{Hg}^{2+}$ from other metal ions

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### Abstract

Amberlite IR-400 was chemically modified using titan yellow as a chelating agent. Adsorption studies such as effect of concentration, pH, time and temperature on the resin has been studied. Distribution coefficient studies of metal ions in varied solvent systems have been explored. On the basis of  $K_d$  values, important binary as well as ternary separations viz.  $\text{Mn}^{2+}$ - $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ - $\text{Hg}^{2+}$ ,  $\text{Mg}^{2+}$ - $\text{Bi}^{3+}$ ,  $\text{Cu}^{2+}$ - $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ - $\text{Sn}^{4+}$ ,  $\text{Pb}^{2+}$ - $\text{Bi}^{3+}$  &  $\text{Cd}^{2+}$ - $\text{Hg}^{2+}$ ,  $\text{Ca}^{2+}$ - $\text{Hg}^{2+}$ - $\text{Zr}^{4+}$ ,  $\text{Cd}^{2+}$ - $\text{Hg}^{2+}$ - $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ - $\text{Hg}^{2+}$ - $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ - $\text{Hg}^{2+}$ - $\text{Co}^{2+}$  and  $\text{Ce}^{3+}$ - $\text{Hg}^{2+}$ - $\text{Co}^{2+}$  has been achieved on columns of titan yellow modified Amberlite IR-400 resin. In order to check the selectivity and reproducibility of the method, different amounts of  $\text{Hg}^{2+}$  has been loaded in synthetic mixtures containing ( $\text{Mg}^{2+}$ =2.43mg), ( $\text{Ca}^{2+}$ =4.01mg), ( $\text{Ba}^{2+}$ =13.74 mg), ( $\text{Sr}^{2+}$  =8.76 mg), ( $\text{Pb}^{2+}$ = 20.72 mg), ( $\text{Zn}^{2+}$ = 16.54 mg), ( $\text{Cd}^{2+}$ =11.24 mg). This material can be utilized for the removal and isolation of  $\text{Hg}^{2+}$  from waste water produced from industrial units.

**Keywords:** Adsorption, anion exchange resin, separation, toxic metal ions.

### Introduction

Ion exchange method during the last decade has become increasingly important in various analyses in inorganic and organic chemistry. Nowadays, attention has been paid for the removal of heavy metals from industrial effluents and wastewater. The problem of ecosystem is increasing with developing technology. Heavy metal pollution is one of the main problems. Toxic metal compounds not only reach the surface water but also contaminate underground water in trace amounts by leaching from soil after rain and snow.

Heavy metals such as cobalt, nickel, lead, mercury etc are detected in waste streams from mining operations, tanneries, electroplating, battery and petrochemical industries. It has a harmful effect on human physiology and other biological systems when they exceed the tolerance levels. They are non biodegradable and accumulate in living organisms causing various types of ailments and disorders. The focus is mainly to solve increasing environmental problems due to excessive and indiscriminate industrialization.

A large number of methods for the analysis of various technical products and substances of biological and medicinal interest have been evolved. Determination of a particular metal ion in complex matrices like ores, minerals, biochemical samples, tissue, blood serum etc, is difficult as other components of the mixture often interfere. Thus it is important to develop a

separation method which is sensitive as well as selective.

Ion exchange resins with large surface area and macro porous structure have been successfully used for the preparation of chelating sorbents. The resin beads having different chelating agents sorbed on them show marked selectivity towards a particular metal ion. The potentiality of chelating ion exchange resins for the separation and preconcentration of metal ions have been established<sup>1-6</sup>. These materials which bear chelate forming groups and ion exchange groups are usually prepared by incorporation of complexing groups on to the ion exchange resin. The selectivity of these modified resins for metal ions depends on the nature of the functional groups of the complexing agents. Aromatic complexing agent<sup>7</sup> have shown great analytical competence and are particularly useful for metal ions on an anion exchange resin<sup>8-13</sup>. Griesbach and Lieser<sup>14</sup> described the synthesis of fifteen sorbents. Dowex 1-X-8 containing adsorbed sulfonated azo dyes<sup>15</sup> has been found to separate  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ . Azothiopyrine disulfonic acid<sup>16</sup> has been incorporated on to an anion exchange resin and the product has been used for the uptake of  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  from aqueous solution. The recovery of  $\text{Hg}^{2+}$  from wastewater utilizing a chelating strong and weak base containing imidoacetic acid and thiol groups<sup>17</sup> is also reported.

Nabi et al synthesized a variety of chelate forming resins by incorporating complexing agents such as bromophenol blue<sup>18</sup>, eriochrome black – T<sup>19</sup>, congo red<sup>20</sup>, alizarin red<sup>21</sup>, crystal violet<sup>22</sup>, neutral red<sup>23</sup>, toluidine blue<sup>24</sup>, naphthol blue black<sup>25</sup>. The successful utility of these modified resins have prompted us to start a search for other chelating agents which may exhibit for differential selectivity towards metal ions.

The present work was undertaken as an attempt to prepare modified ion exchange resins by incorporating different types of chelating agents and to explore their potentiality for the separations and isolation of metal ions. In our study titan yellow has been chosen as a chelating agent due to its great capability of forming complexes with metal ions.

## Materials and Methods

### Reagents and Chemicals

Amberlite IR –400(Cl<sup>-</sup>) from Merck (India), Disodium salts of EDTA from S.D Fine chemicals (India).Titan yellow or Clayton yellow (CDH,AR, India). 1% ethanolic solution of 1-[1-hydroxy -2-naphthol azo]-5-nitro-2-naphthol-4-sulphonic acid sodium salt ( Eriochrome Black T ),1-[2-pyridyl azo ]-2-naphthol (PAN) and 1% aqueous solution of o-cresolsulfonaphthlein 3'-3'-bis[methyl iminodiacetic acid sodium salt] (Xylenol orange ) were used as indicators and 0.01M solution of disodium salt of ethylenediaminetetraacetic acid (EDTA) was used as titrant. Ammonium chloride (Merck), Sodium acetate (S.D fine), Oxalic acid (S.D fine), Succinic acid (S.D fine). Boric acid (Merck), Borax (Merck), Sodium bicarbonate (Merck).

### Apparatus

A Genesys Spectronic -UV-Visible spectrophotometer, ELICO digital pH meter (335, India), and electronic shaker with a temperature controlled body was used.

### Solutions

0.1 M solutions of different types of solvent systems (AR Grade), 0.1M solutions of various metal ions (AR Grade) were prepared in demineralised water, 1% solution of EBT, PAN and Xylenol Orange were prepared in a 1:1 ratio mixture of ethanol and demineralised water and Buffer of pH 1-10 were also prepared.

### Adsorption Isotherms

#### Effect of Concentration

The adsorption of titan yellow was studied under static conditions at pH 6.0. 0.3 g resin was

equilibrated with solutions of titan yellow of different concentrations (10 - 180ppm) for 5h in a temperature controlled electronic shaker – incubator maintained at 25±2°C. The equilibrium concentration of titan yellow in the solution was determined spectrophotometrically at 435nm.

#### Effect of pH

To study the effect of pH on the adsorption of titan yellow, the optimum pH for maximum adsorption at 25±2°C was selected. For this, 0.3 g resin was stirred for 5 hour with 30 mL of 100 mL titan yellow solution at different pH (1-10). The pH of the solution was adjusted by adding an appropriate acid, base or buffer of the desired pH. The equilibrium concentration of the reagent was then determined spectrophotometrically at 435nm.

#### Effect of Time

The dependence of time of adsorption of titan yellow on the resin was established by performing a series of adsorption experiments at 25±2°C .A constant mass (0.3g) of Amberlite IR –400(H<sup>+</sup>) resin was stirred with an aqueous solution of titan yellow (30ml). The amount of titan yellow taken up was determined by analyzing the supernatant solution spectrophotometrically at 435 nm.

#### Effect of temperature

Effect of temperature on the adsorption of titan yellow can be studied by selecting the optimum temperature and for this, resin (0.3g) was shaken with 30mL of 100ppm solution of titan yellow for 5 h at constant pH 6.0 but at different temperatures 30, 40,50,60and 70°C in a temperature controlled electronic shaker. The amount of titan left in the solution was determined spectrophotometrically.

#### Selection of Resin

A few beads of modified ion exchange resin were placed on a spot plate .One drop of 0.1M acetic acid solution were added and thoroughly mixed with the tip of a glass rod and leave it for sometime, then washed several times with DMW in order to check whether the color is detached or not. In a similar manner, the modified resin can be tested with different solvents like 0.1M Alcohol, 0.1 M NaOH, 0.1 M HCl and 0.1 M Formic acid. The orange color of the dye was not detached even after subsequent washing with water. Thus the resin was selected for further studies.

#### Preparation of modified resin

To prepare the modified resin, 100 g Amberlite IR-400 resin in Cl<sup>-</sup> form was treated with 500 ml of aqueous solution of titan yellow (100 ppm). The

contents were left for 48 hours with intermittent shaking to ensure the optimum adsorption. The resin was separated from the solution and washed several times with demineralized water until the supernatant liquid was found free from excess reagent. Finally, the resin was dried in an oven at 60°C for 24 hour.

#### Distribution coefficient ( $k_d$ ) of the metal ions

The distribution co-efficient of the metal ions on titan yellow were determined by a batch method at

$$K_d = \frac{\text{Amount of metal ion in the resin phase/g of resin}}{\text{Amount of metal ion in the solution phase/mL of solution}} \\ = \frac{I - F / 0.3g}{I - F / F \times 100}$$

where I = Volume of EDTA used before treatment (i.e. amount of metal ion originally present in solution). F = Volume of EDTA used after treatment with the resin (i.e. amount of metal ion in the solution after treatment with the resin).

#### Quantitative separation of metal ions

For quantitative separation of metal ions elution technique was used. 2.0mL of a mixture of metal ions solution of 0.1 M in 1:1 ratio was poured into a glass column of i.d 0.8 cm with a glass wool support at the base. The solution was allowed to pass through the column containing 1.5 g modified resin with a flow rate of 0.25 mL per minute till it reaches just above the resin surface. The elution of metal ions was then started with appropriate eluting reagent keeping the flow rate 0.5 mL/minute throughout the elution time. The eluted metal ion was then determined titrimetrically using a 0.01 M solution of disodium salt of EDTA as titrant.

#### Results and Discussion

Cation and anion exchange resins were tested for the adsorption of titan yellow. It was observed that only anion exchange resin IR-400 in Cl<sup>-</sup> form adsorb titan yellow irreversibly. After adsorption of titan yellow, the color of the resin beads changes from golden yellow to bright orange. The various experimental parameters such as equilibration time, pH and concentration of the dye on the sorption behavior of resin have been studied. It was found that optimum sorption of titan yellow occurs at pH 6.0 in 5 hours. The isotherm for adsorption of titan yellow on the resin was almost linear and followed the Langmuir isotherm.

The distribution co-efficient of important metal ions were determined in various solvent systems based on polarity and dissociation constant factor (table1). Based on difference in  $K_d$  values, number of important and difficult separations has been tried and experimentally

25±2°C. For this purpose the modified resin (0.3g) was treated with 1mL of 0.1 M metal ion solution and 29mL of appropriate solvent in 100mL Erlenmeyer flask. The mixture was shaken continuously in a temperature controlled shaker at 25±2°C for 5 hours. The amount of cation in the solution before and after equilibration was determined by using 0.01M EDTA as titrant.  $K_d$  values (mL g<sup>-1</sup>) for each metal ion was calculated by the formula:

achieved on the columns of the modified resin using elution technique. It is apparent from  $K_d$  values given in the tables 2 and 3 that titan yellow has differential selectivity for metal ions. This may be due to the formation of titan yellow metal complexes with different stability constant. Quantitative binary and ternary separations of metal ions were achieved on the columns of this material using appropriate eluent. The results of binary separations of metal ions are given in the table 4.

It was found that Hg<sup>2+</sup> show exceptional behavior towards the resin as it has the highest  $K_d$  values in all the solvents studied. The highest uptake of Hg<sup>2+</sup> may be because it forms relatively more stable complex with titan yellow as compared to other metal ions. Based on the exceptional behavior of Hg<sup>2+</sup>, it was possible to separate Hg<sup>2+</sup> selectively from a mixture of metal ions on columns of titan yellow sorbed Amberlite IR-400 resin.

To demonstrate the practical utility of the material, and to check the selectivity and reproducibility of the method, separations of different amounts of Hg<sup>2+</sup> has been achieved from a synthetic mixture of metal ions containing-Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> (table 5). The selective separation of Hg<sup>2+</sup> from these metal ions can be utilized for the removal of Hg<sup>2+</sup> from industrial wastes and domestic water discharges.

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**Table: 1** Different types of solvent systems used in the determination of distribution coefficient ( $K_d$ ) of metal ions.

S. No.	Solvent systems chosen on the basis of	
	Polarity Factor	Dissociation constant
S1	Methanol	Boric acid
S2	Dimethyl sulfoxide	Succinic acid
S3	Formamide	Phenol
S4	N,N-dimethyl formamide	o-phosphoric acid
S5	Acetone	Tartaric acid
S6	Acetic acid	Trichloroacetic acid
S7	Formic acid	Nitric acid
S8	Water	Water

**Table: 2** Distribution coefficient of various metal ions in different solvent systems on Titan yellow loaded Amberlite IRA-400(Cl<sup>-</sup>) resin.

Metal ions	Distribution Co-efficient for solvent systems based on polarity factor						
	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>	S <sub>5</sub>	S <sub>6</sub>	S <sub>7</sub>
Mg <sup>2+</sup>	20.0	24.0	21.0	11.0	25.0	18.0	10.0
Ca <sup>2+</sup>	15.0	52.0	14.0	14.0	20.0	11.0	13.0
Ba <sup>2+</sup>	25.0	23.0	42.0	27.0	32.0	25.0	42.0
Sr <sup>2+</sup>	10.0	19.0	14.0	32.0	26.0	11.0	16.0
Hg <sup>2+</sup>	5350	4220	7100	5300	3500	5250	5300
Pb <sup>2+</sup>	30.0	39.0	12.0	47.0	43.0	20.0	18.0
Mn <sup>2+</sup>	10.0	20.0	9.0	16.0	18.0	14.0	16.0
Zn <sup>2+</sup>	24.0	17.0	22.0	17.0	23.0	12.0	15.0
Cd <sup>2+</sup>	25.0	41.0	41.0	30.0	28.0	21.0	15.0
Cu <sup>2+</sup>	x	x	11.0	15.0	7.0	16.0	16.0
Al <sup>3+</sup>	12.0	10.0	7.0	24.0	79.0	30.0	31.0
Fe <sup>3+</sup>	34.0	32.0	75.0	39.0	15.0	21.0	25.0
Ni <sup>2+</sup>	23.0	4.0	12.0	28.0	33.0	32.0	28.0
Co <sup>2+</sup>	25.0	533.0	270.0	278.0	241.0	212.0	350.0
Sn <sup>4+</sup>	1100	233.0	550.0	1200	300	266.0	450.0
Ag <sup>+</sup>	100	x	x	x	83.0	x	x
Zr <sup>4+</sup>	286.0	68.0	19.0	43.0	633.0	233.0	100
Th <sup>4+</sup>	223.0	290.0	238.	185.0	327.0	320.0	344.0
Ce <sup>3+</sup>	10.0	83.0	134.0	103.0	233.0	6.0	229.0
Bi <sup>3+</sup>	775	1033.0	1040	483.0	783.0	1066.0	433.0

**Table: 3** Distribution co-efficient of various metal ions in different solvent systems on Titan yellow loaded Amberlite IRA- 400(Cl<sup>-</sup>) resin.

Metal ions	Distribution co-efficient for solvent systems based on dissociation constant							
	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>	S <sub>5</sub>	S <sub>6</sub>	S <sub>7</sub>	S <sub>8</sub>
Mg <sup>2+</sup>	217.0	18.0	23.0	-	1.0	20.0	2.0	8.0
Ca <sup>2+</sup>	15.0	9.0	11.0	-	4.0	33.0	17.0	14.0
Ba <sup>2+</sup>	21.0	48.0	18.0	-	250	51.0	51.0	21.0
Sr <sup>2+</sup>	15.0	17.0	13.0	-	43.0	17.0	5.0	9.0
Hg <sup>2+</sup>	5500	5550	2450	-	5300	3466	3133	1733
Pb <sup>2+</sup>	14.0	20.0	14.0	28.0	13.0	30.0	9.0	27.0
Mn <sup>2+</sup>	15.0	10.0	7.0	6.0	21.0	14.0	88.0	13.0
Zn <sup>2+</sup>	17.0	19.0	6.0	14.0	16.0	22.0	4.0	21.0
Cd <sup>2+</sup>	31.0	12.0	11.0	85.0	18.0	24.0	16.0	22.0
Cu <sup>2+</sup>	22.0	10.0	14.0	825	9.0	10.0	5.0	3.0
Al <sup>3+</sup>	23.0	715	14.0	90.0	20.0	453	7.0	8.0
Fe <sup>3+</sup>	17.0	21.0	24.0	77.0	21.0	15.0	9.0	16.0
Ni <sup>2+</sup>	22.0	94.0	14.0	712	27.0	85.0	00.0	18.0
Co <sup>2+</sup>	21.0	82.0	47.0	757	466	290	89.0	289
Sn <sup>4+</sup>	250	75.0	125	75.0	100	122	--	166
Ag <sup>+</sup>	100	-	-	-	-	-	-	2400
Zr <sup>4+</sup>	53.0	650	-	-	-	-	191	228
Th <sup>4+</sup>	221	780	18	-	840	320	340	180
Ce <sup>3+</sup>	124	2.0	41.0	-	-	166	00.0	152
Bi <sup>3+</sup>	600	537	733	-	300	-	587	194

**Table: 4** Quantitative separations of metal ions on a column of Titan yellow loaded Amberlite IRA-400(Cl<sup>-</sup>) resin.

Binary mixture	Amount loaded (mg)	Amount recovered (mg)	Recovery of metal ions (%)	Volume of eluent (ml)	Eluent used
Mn <sup>2+</sup>	5.14	5.30	96.54	90	0.1M Methanol
Hg <sup>2+</sup>	20.06	15.05	75.02	120	0.1M Nitric acid
Zn <sup>2+</sup>	16.54	15.71	94.98	100	0.1M Succinic acid
Hg <sup>2+</sup>	20.06	12.64	63.01	120	0.1M Nitric acid
Mg <sup>2+</sup>	2.43	2.40	98.77	70	0.1M DMSO
Bi <sup>2+</sup>	20.09	17.97	85.98	80	0.1M Nitric acid
Cu <sup>2+</sup>	6.35	6.20	97.64	60	0.1M Formamide
Hg <sup>2+</sup>	20.06	19.66	98.00	100	0.1M Nitric acid
Pb <sup>2+</sup>	20.06	20.51	98.99	70	0.1M N,N DMF
Sn <sup>4+</sup>	11.87	1.37	11.54	60	0.1M Succinic acid
Pb <sup>2+</sup>	20.72	20.51	98.99	80	0.1M Acetic acid
Bi <sup>3+</sup>	20.9	19.02	91.00	120	0.1M Nitric acid
Cd <sup>2+</sup>	11.24	10.68	95.02	100	0.1M DMSO
Hg <sup>2+</sup>	20.06	19.56	97.50	120	0.1M Nitric acid

**Table 5** Selective separation of Hg<sup>2+</sup> from (Mg<sup>2+</sup>=2.43mg), (Ca<sup>2+</sup>=4.01mg), (Ba<sup>2+</sup>=13.74 mg), (Sr<sup>2+</sup> =8.76 mg), (Pb<sup>2+</sup>= 20.72 mg), (Zn<sup>2+</sup>= 16.54 mg), (Cd<sup>2+</sup>=11.24 mg).

S. No.	Metal ion	Amount loaded (mg)	Amount Found (mg)	Recovery (%)	Eluent Used (mL)	Volume of eluent used (mL)
1	Hg <sup>2+</sup>	20.05	18.02	89.9	0.1M Nitric acid	400
2	Hg <sup>2+</sup>	40.11	36.41	90.78	0.1M Nitric acid	250
3	Hg <sup>2+</sup>	60.15	52.32	85.56	0.1M Nitric acid	200
4	Hg <sup>2+</sup>	80.20	70.24	87.58	0.1M Nitric acid	150