



Synthesis, characterization and analytical application of hybrid; *Acrylamide zirconium (IV) arsenate* a cation exchanger, effect of dielectric constant on distribution coefficient of metal ions

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ARTICLE INFO

Article history:

Received 21 March 2007
Received in revised form 7 March 2008
Accepted 4 July 2008
Available online 11 July 2008

Keywords:

Hybrid ion exchanger
Synthesis
Characterization
Analytical application
Acrylamide zirconium (IV) arsenate

ABSTRACT

A new hybrid inorganic–organic cation exchanger *acrylamide zirconium (IV) arsenate* has been synthesized, characterized and its analytical application explored. The effect of experimental parameters such as mixing ratio of reagents, temperature, and pH on the properties of material has been studied. FTIR, TGA, X-ray, UV–vis spectrophotometry, SEM and elemental analysis were used to determine the physicochemical properties of this hybrid ion exchanger. The material behaves as a monofunctional acid with ion-exchange capacity of 1.65 meq/g for Na⁺ ions. The chemical stability data reveals that the exchanger is quite stable in mineral acids, bases and fairly stable in organic solvents, while as thermal analysis shows that the material retain 84% of its ion-exchange capacity up to 600 °C. Adsorption behavior of metal ions in solvents with increasing dielectric constant has also been explored. The sorption studies reveal that the material is selective for Pb²⁺ ions. The analytical utility of the material has been explored by achieving some binary separations of metal ions on its column. Pb²⁺ has been selectively removed from synthetic mixtures containing Mg²⁺, Ca²⁺, Sr²⁺, Zn²⁺ and Cu²⁺, Al³⁺, Ni²⁺, Fe³⁺. In order to demonstrate practical utility of the material quantitative separation of the Cu²⁺ and Zn²⁺ in brass sample has been achieved on its columns.

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1. Introduction

The prerequisite for more highly favorable metal recovery process in both hydrometallurgy and environmental application has lead to appealing interest in advancement of selective ion exchangers. In this reverence persistent efforts have been going to improve the mechanical, chemical and thermal stabilities of ion exchangers and to make them selective for particular metal ion. Incidentally, materials that contain both organic and inorganic moieties offer an attractive field of research due to their composite properties and appear as creative alternative for obtaining new materials. The limitations with the existing organic ion exchangers is that the mechanical strength and removal capacity tend to decrease at high temperatures and degradation of ion exchange properties under high radiation conditions where as problem with inorganic ion exchangers is their low mechanical and chemical strength and difficulty in obtaining granulated materials with suitable mechanical properties for use in column application than organic ion exchangers. To overcome these limitations hybrid ion exchangers have been introduced which conjugate mechanical properties of poly-

mer with intrinsic properties of inorganic compound. Synthesis of hybrid ion exchangers with controlled functionality and hydrophobicity open new avenues for organo-metallic chemistry and there use as sorbents [1,2], ion exchangers [3–5], catalysts [6] and in ion-selective electrodes [7–10]. In the continuing quest for these materials large number of hybrid ion exchangers based on acrylonitrile [11], nylon-6,6 [12], acrylamide [13,14], triethylammonium [15], polypyrrole/polyantimonic acid [16] and poly-*o*-toluidine [17] have been synthesized.

In the present study we report the detailed study of synthesis, characterization and analytical applications of newly synthesized hybrid cation exchanger *acrylamide zirconium (IV) arsenate*. The exchanger possesses the mechanical stability due to presence of organic polymer species and a basic characteristic of inorganic ion exchangers. The exchanger is found selective for Pb²⁺ ions, a potential pollutant in environment. It is one of the most toxic heavy metal ion, though two of its former uses as additive in gasoline or paint were discontinued due to health concerns. Pb²⁺ ions are still found in batteries, ammunition and computer circuits boards. The main target of the Pb²⁺ ions is nervous system but it also causes nephropathy, sluggishness, loss of skin color [18]. The present work explored the utility of this material in qualitative as well as quantitative separation of Pb²⁺ ions from some binary mixtures on *acrylamide zirconium (IV) arsenate* columns.

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2. Experimental

2.1. Reagents

Zirconium (IV) oxychloride, sodium arsenate and acrylamide were obtained from LOBA-CHEMIA (Bombay) and CDH (India), Brass alloy sample. All other reagents were used of analytical reagent grade.

2.2. Instruments

A digital pH-meter (Elico L1-10, India) for pH measurements, Perkin Elmer 'Spectrum One' spectrophotometer for FTIR studies, NETZSCH TG 209 F1 for thermogravimetric analysis, 'X' Pert Pro P Analytical for X-ray diffraction, Perkin Elmer Series II CHNS/O 2400 for CHN analysis and Muffle furnace (MSW-275, India) and Shaker cum incubator for shaking were used.

2.3. Synthesis of acrylamide zirconium (IV) arsenate

Acrylamide zirconium (IV) arsenate was prepared using the following procedure. Ten different samples were prepared under varied conditions of temperature, pH and mixing ratio of reagents. On the basis of higher ion exchange capacity sample S-8 was selected for detailed studies. Sample (S-8) was prepared by adding mixture of aqueous solution of sodium arsenate (0.25 M) and acrylamide (0.25 M) in a volume ratio of 1:2 at a flow rate of 1.0 mL/min into the aqueous solution of zirconium oxychloride (0.25 M) while stirring the solution continuously. The pH of the solution was adjusted by adding either the dilute solution of ammonia or nitric acid. The resulting white precipitate so formed was kept overnight (24 h) in the mother liquor to settle down and filtered under suction. The excess of acid was removed by washing with demineralized water and dried at 50 °C in an oven. The dried material was cracked into small granules, sieved and converted into H⁺ form by treating with 1.0 M nitric acid for 24 h with occasional shaking. The material was finally washed with demineralized water to remove excess of acid and dried at 50 °C in an oven and used as such.

2.4. Ion-exchange capacity

One gram of the exchanger (S-8) in H⁺ form was taken into glass column (i.d. 0.5 cm, length 25 cm) fitted with glass wool support at the bottom. The bed length was approximately 1.5 cm of column height. Alkali and alkaline earth metal nitrates (1.0 M) were used to elute H⁺ ions from the acrylamide zirconium (IV) arsenate column, maintaining a flow of 0.5 mL/min. The effluent was titrated against a standard 0.1 M sodium hydroxide solution. The ion-exchange capacity in meq/g for various metals ions was determined by usual column process.

2.5. pH titration

0.50 g of the exchanger in H⁺ form were placed in each of several 250 mL conical flasks followed by the addition of equimolar solution of alkali metal chlorides and their hydroxides in different volume ratio, the final volume is adjusted to 50 mL to maintain the ionic strength constant.

2.6. Chemical stability

The 0.25 g of the exchanger in H⁺ form was kept in 25 mL solvent of analytical interest for 12 h at room temperature 25 ± 2 °C with intermittent shaking. The supernatant liquid was analyzed for zir-

conium [19] and arsenate [20] by the standard spectrophotometric methods.

2.7. Chemical composition

0.50 g of the sample was dissolved in 10 mL hot concentrated H₂SO₄. The dissolved sample was diluted to 50 mL. The amount of zirconium and arsenate were determined by standard spectrophotometric methods [19,20]. Carbon, hydrogen and nitrogen contents of the material were determined by elemental analysis.

2.8. Effect of eluent concentration

A fixed volume (250 mL) of varying concentration of sodium nitrate solution was used for complete elution of H⁺ ions from the column containing 1.0 g of the exchanger in H⁺ form. The effluent was titrated against the standard 0.1 M sodium hydroxide solution.

2.9. Elution behavior

A column containing 1.0 g of exchanger in H⁺ form was eluted with 1.0 M NaNO₃ solution. The effluent was collected in 10.0 mL fraction at a flow rate (0.5 mL/mL). Each fraction of 10.0 mL was titrated against a standard 0.1 M sodium hydroxide solution.

2.10. FTIR studies

The FTIR study of acrylamide zirconium (IV) arsenate sample was performed by KBr disc method. For this 10 mg of the exchanger in H⁺ form was taken and thoroughly mixed with 100 mg of KBr to a fine powder. A transparent film was formed by applying a pressure of 80,000 psi in a moisture free atmosphere. The disc formed contained 50–100 mg of ion exchanger. IR absorption spectrum was recorded in the region 400–4000 cm⁻¹.

2.11. X-ray studies

The X-ray diffraction pattern of the material acrylamide zirconium (IV) arsenate was recorded by 'X' Pert Pro P Analytical.

2.12. Thermal stability

The effect of drying temperature of the material on the ion-exchange capacity was studied by heating the acrylamide zirconium (IV) arsenate from 50 to 800 °C for 1 h. The ion-exchange capacity for each heated sample was determined as described earlier.

2.13. Thermal analysis

A thermogravimetric analysis was carried out by heating the sample up to 800 °C at a constant rate of 10 °C per minute in nitrogen atmosphere.

2.14. Scanning electron microscopy

Electron micrographs were recorded for acrylamide zirconium (IV) arsenate using Scanning Electron Microscope operating at 15.0 kV at different magnifications.

2.15. Distribution (sorption) studies

The distribution coefficient (K_d) of metal ions Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Pb²⁺, Hg²⁺, Cd²⁺, Zn²⁺, Mn²⁺, Cu²⁺, Fe³⁺, Ni²⁺, Al³⁺, Bi³⁺, Ce⁴⁺, Th⁴⁺, La³⁺ were determined by batch method in different solvents of analytical interest. Distribution coefficient is actually used to access

Table 1
Synthesis and properties of different samples of *acrylamide zirconium (IV) arsenate*

Sample No.	Condition of synthesis						Appearance of beads	Ion-exchange capacity (meq/g exchanger) for Na ⁺ ions
	A (mol L ⁻¹)	B (mol L ⁻¹)	C (mol L ⁻¹)	Mixing ratio (v/v/v)	pH	Temperature (°C)		
S-1	0.1	0.1	0.1	1.0/1.0/1.0	1.0	25 ± 2	White	0.42
S-2	0.1	0.25	0.1	1.0/1.0/1.0	1.0	25 ± 2	White	0.64
S-3	0.25	0.25	0.25	1.0/1.0/1.0	1.0	25 ± 2	white	0.62
S-4	0.25	0.25	0.25	1.0/1.0/1.0	0.75	25 ± 2	No precipitate	–
S-5	0.25	0.25	0.25	1.0/1.0/1.0	1.5	25 ± 2	Glassy	0.52
S6	0.25	0.25	0.25	1.0/1.0/1.0	2.0	25 ± 2	Glassy	0.43
S7	0.25	0.25	0.25	1.0/2.0/1.0	1.0	25 ± 2	White	1.14
S8	0.25	0.25	0.25	1.0/2.0/1.0	1.0	70 ± 2	White	1.53
S9	0.25	0.25	0.25	1.0/2.0/2.0	1.0	70 ± 2	Dirty white	1.13
S10	0.25	0.25	0.25	1.0/2.0/1.0	1.0	Refluxed for 6 h in 0.1 M HCl	White	1.53

A, zirconium oxychloride; B, sodium arsenate; C, acrylamide.

the overall ability of the material to remove the ion of interest under set condition. 300 mg portions of the *acrylamide zirconium (IV) arsenate* in H⁺ form were taken in Erlenmeyer flasks mixed with 30 mL of different metal nitrate solution in required medium and shaken for 6 h in temperature controlled shaker at 25 ± 2 °C to attain the equilibrium. The metal ion concentration before and after the equilibrium was determined by EDTA titration. The distribution coefficients were calculated using the equation

$$K_d = \frac{\text{Amount of metal ion in the exchanger phase/g of exchanger}}{\text{Amount of metal ion in the solution phase/mL of solution}}$$

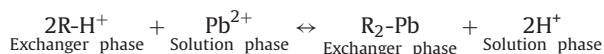
In our case

$$K_d = \frac{I - F/300 \text{ mg}}{F/30 \text{ mL}}$$

where *I* is the volume of EDTA used before treatment of metal ion. *F* is the volume of EDTA consumed by metal ion left in solution phase.

The sorption of metal ions involves the ion exchange of the H⁺ ions in exchanger phase with that of metal ions in solution phase.

For example,



where R = *acrylamide zirconium (IV) arsenate*.

2.16. Separations

2.16.1. Quantitative separations of metal ions in synthetic binary mixtures

Important separations of metal ions were achieved on columns of *acrylamide zirconium (IV) arsenate* (height 35 cm, i.d. 0.6 cm, bed height 2.5 cm) containing 2.0 g of exchanger in H⁺ form. The column was washed thoroughly with demineralized water and then with the suitable solvent. The column flow experiments were performed in acidic to neutral medium. The binary mixture of metal ions was loaded and eluted using suitable solvent. The effluent was collected in 10 mL fractions at a flow rate of 5–6 drops per minute. The metal ions in the effluent were determined titrimetrically using standard solution of disodium salt of EDTA.

2.16.2. Selective separation

Selective separation of Pb²⁺ ions from the synthetic mixtures containing Mg²⁺, Ca²⁺, Sr²⁺, Zn²⁺, Pb²⁺ and Cu²⁺, Al²⁺, Ni²⁺, Fe³⁺, Pb²⁺ were achieved on *acrylamide zirconium (IV) arsenate* columns. The amounts of the Pb²⁺ loaded in the column were varied keeping amount of the synthetic mixture constant.

2.16.3. Quantitative separation of Cu²⁺ and Zn²⁺ in a commercially available brass sample

The commercially available brass sample (2.0 g) was dissolved in minimum quantity of aqua regia. The mixture was heated to evaporate excess of acid and finally diluted to 100 mL with demineralized water and used as stock solution for the determination Cu²⁺ and Zn²⁺. The composition of the brass sample was determined after separation of Cu²⁺ and Zn²⁺ on *acrylamide zirconium (IV) arsenate* columns. The subsequent steps remained same as described earlier.

3. Results and discussion

Different samples hybrid ion-exchanger *acrylamide zirconium (IV) arsenate* were prepared. The exchanger appears to be a promising cation exchange material with fairly good ion-exchange capacity, thermal and chemical stability. Table 1 shows the effect of mixing ratio of reagents, temperature and pH on the synthesis of *acrylamide zirconium (IV) arsenate*. Different samples of the exchanger were synthesized in the pH range from 0.5 to 2.0. Results show that an increase in pH decreases the ion-exchange capacity because at higher pH the formation of metal hydroxide precipitate may occur. The most favorable pH for the synthesis was found to be pH 1. Increase in the ratio of arsenate enhances the ion-exchange capacity whereas increase in acrylamide in the reaction mixture has no such effect. The temperature has also the appreciable effect on the ion exchange property. The material synthesized at 70 ± 2 °C has higher ion-exchange capacity (1.53 meq/g) as compared to material obtained at 25 ± 2 °C (1.13 meq/g).

Table 2 shows the ion-exchange capacity for alkali and alkaline earth metal ions. The results reveal comparatively higher ion-exchange capacity for alkaline earth metal ions than alkali metal ions. Further the ion-exchange capacity increase with the decrease in hydrated ionic radii down the group that is ions with smaller hydrated radii easily enter the pores of the exchanger resulting in higher adsorption. The pH titration curve (Fig. 1) shows that the *acrylamide zirconium (IV) arsenate* is monofunctional strong cation exchanger as evident from low initial pH 2.8 of the solution when

Table 2
Ion exchange capacity of various exchanging ions on *acrylamide zirconium (IV) arsenate*

Exchanging ions	Ionic radii (Å)	Hydrated ionic radii (Å)	IEC (mmol g ⁻¹)
Li ⁺	0.68	3.40	1.40
Na ⁺	0.97	2.76	1.53
K ⁺	1.33	2.32	1.63
Mg ²⁺	0.78	7.00	1.42
Sr ²⁺	1.27	6.30	1.97
Ba ²⁺	1.43	5.90	2.4

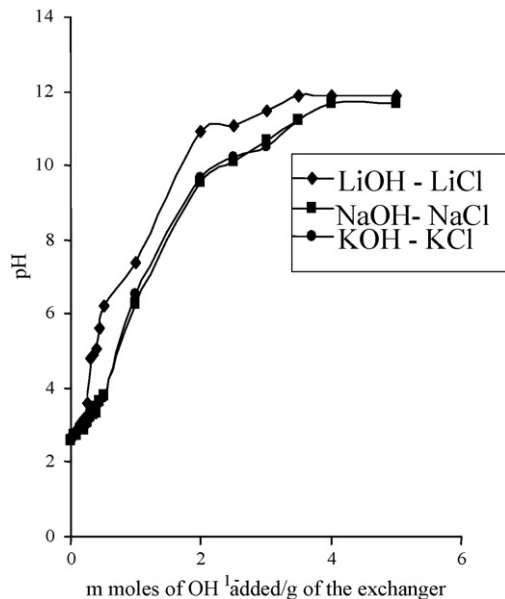


Fig. 1. pH titration curves for acrylamide zirconium (IV) arsenate hybrid cation exchanger with various alkali metal hydroxides in the presence of corresponding salts.

no OH^- ions were added to the system; further the steep rise in pH at 1.8 mmol of the OH^- ions indicates the complete neutralization of H^+ ions of the exchanger. The chemical stability data (Table 3) shows that the acrylamide zirconium (IV) arsenate is fairly stable in common solvents, strong acids HCl, HNO_3 , H_2SO_4 up to 2 M, reasonably stable in strong base NaOH and in some organic solvents up to 1 M concentration. Thus exchanger is chemically resistant to most of the solvents and can be successfully used with diverse solvents in column operation. The chemical composition analysis reveals that the molar ratios of Zr:As:C:H:N is 1:2:0.5:12.24:0.5.

An optimum concentration of the eluent was found to be 1.0 M for the complete removal of H^+ ions from the above column. The experiment also established that the minimum volume required for the complete elution of H^+ ions, which reflects the column efficiency. It was found that the rate of elution is governed by the concentration of eluent used (Fig. 2). Fig. 3 illustrates that the exchange is quite fast and almost all the H^+ ions are released in the first 150 mL of the effluent from the column containing 1.0 g exchanger with a standard flow rate of (0.5 mL/min). Further, it

Table 3
Chemical stability of acrylamide zirconium (IV) arsenate in different solvents (250 mg of the material was initially taken of treatment)

Solvent	Zirconium released (mg/25 mL)	Arsenate released (mg/25 mL)
0.1 M HCl	0.10	0.00
1 M HCl	0.16	0.21
2 M HCl	0.24	0.25
0.1 M HNO_3	0.00	0.25
1 M HNO_3	0.12	0.20
2 M HNO_3	0.62	1.40
0.1 M H_2SO_4	0.08	0.75
1 M H_2SO_4	0.38	1.50
2 M H_2SO_4	0.48	1.96
0.1 M NaOH	0.06	1.6
1 M NaOH	0.10	2.7
0.1 M succinic acid	0.00	0.42
0.1 M DMSO	0.20	0.42
0.1 M oxalic acid	0.00	0.22
4% Tween	0.14	0.25
8% Tween	0.24	0.45

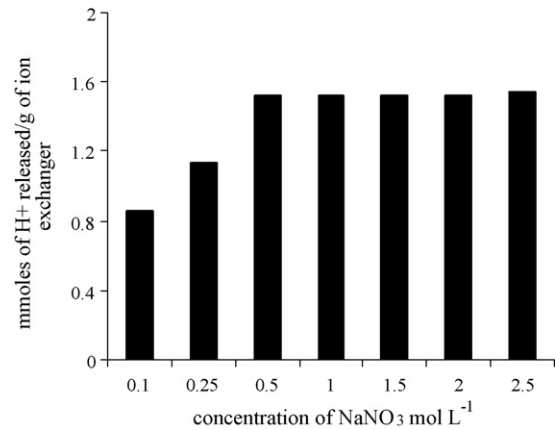


Fig. 2. Effect of eluent concentration on ion-exchange capacity of acrylamide zirconium (IV) arsenate a hybrid cation exchanger.

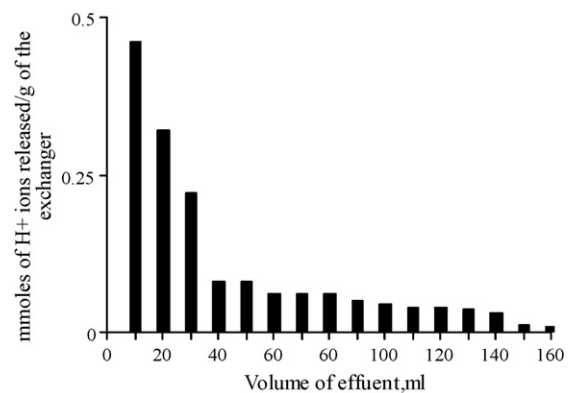


Fig. 3. Elution behavior of acrylamide zirconium (IV) arsenate a hybrid cation exchanger.

is clear from the breakthrough curve Fig. 4 of the ion exchanger column that the total ion-exchange capacity of the column is indicated at the point where the appearance of the hydrogen and disappearance of the sodium ions occurs in the effluent. Therefore the maximum ion-exchange capacity experimentally obtained is 2.2 meq.

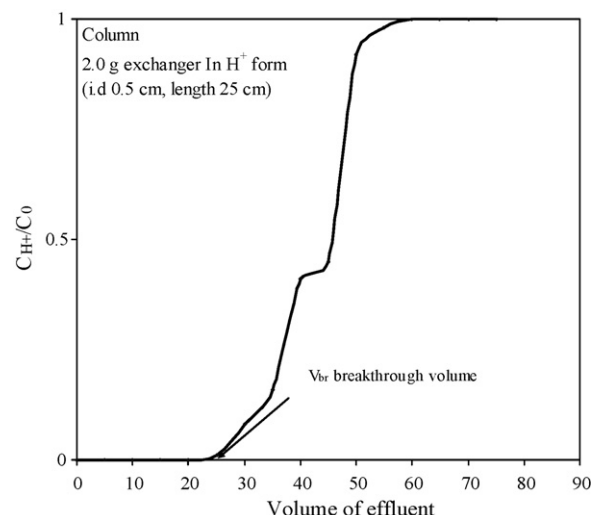


Fig. 4. Breakthrough curve for the acrylamide zirconium (IV) arsenate.

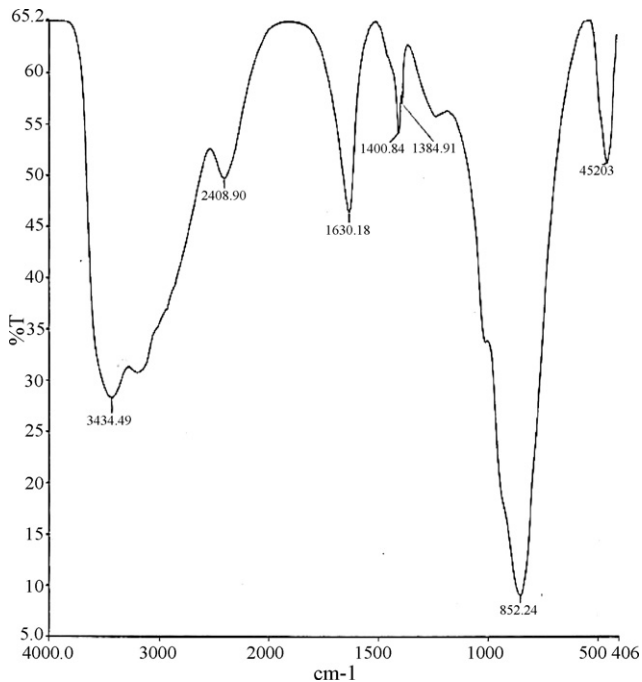


Fig. 5. FTIR spectrum of acrylamide zirconium (IV) arsenate.

The FTIR spectrum (Fig. 5) of acrylamide zirconium (IV) arsenate shows the presence of external water molecules [21] (peak 3434 cm^{-1}) in addition to metal oxygen and metal –OH stretching bands. The absorption peak at 1630 cm^{-1} may be due to the amide bond stretching [22]. The peaks at 1400 and 1384 cm^{-1} indicate the presence of considerable amount of acrylamide in acrylamide zirconium (IV) arsenate [23]. Presence of sharp peak at 852 can attributed to presence of arsenate and the band at 452 may be due to presence of Zr–O stretching vibration. The X-ray diffraction pattern (Fig. 6) indicates that the material is slightly crystalline in nature. It is apparent from the TGA curve (Fig. 7) that the initial loss of about 12% up to 100°C which may be due to loss of external water molecules [24] from the material. The gradual weight loss above 100°C may be due to partial hydrolysis of amide groups which continue up to 200°C . Further weight loss of about 8% from

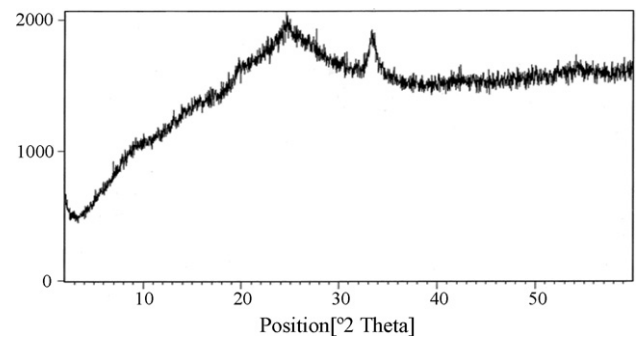


Fig. 6. X-ray diffraction pattern of spectrum of acrylamide zirconium (IV) arsenate.

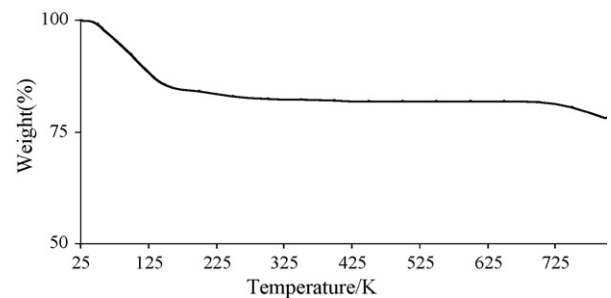


Fig. 7. TGA curve of acrylamide zirconium (IV) arsenate.

Table 4

Effect of temperature on the ion-exchange capacity of acrylamide zirconium (IV) arsenate a cation exchanger on heating time for 1h temperature

Temperature ($^\circ\text{C}$)	Color	% Weight loss	% Retention of IEC
50	White	0.00	100.0
100	Brown	6.02	97.38
200	Light brown	7.80	93.50
300	Dirty white	8.22	92.65
400	Dirty white	12.08	88.82
500	White	12.50	86.23
600	White	14.90	84.25

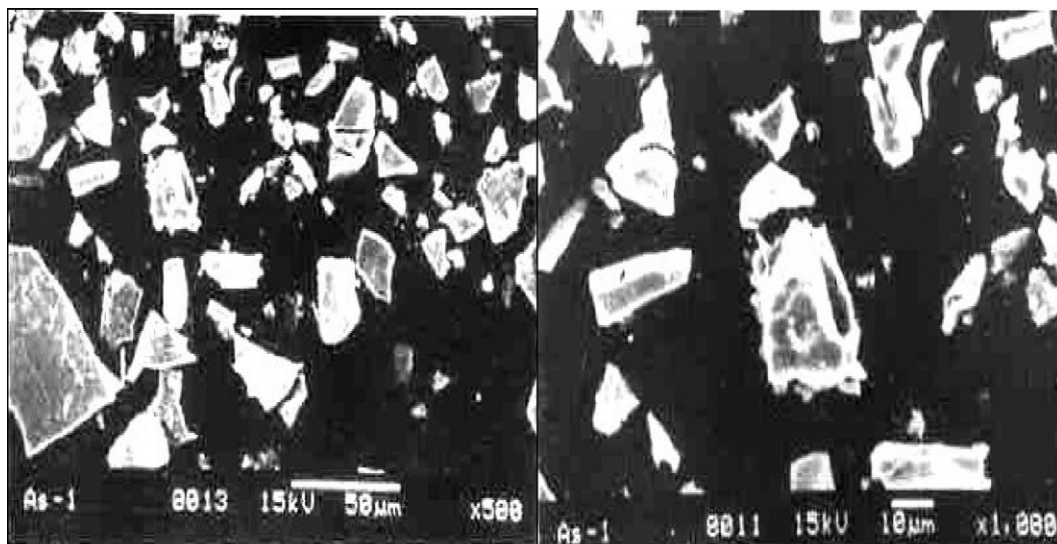


Fig. 8. Scanning electron micrographs of acrylamide zirconium (IV) arsenate obtained at two different magnifications.

Table 5
Distribution coefficients of different metal ions on *acrylamide zirconium (IV) arsenate* in different solvent systems

Metal ion	DMW	Formic acid	DMSO	Acetonitrile	Acetic acid	Succinic acid	Nitric acid
Mg ²⁺	20.0	22.4	28.0	34.9	36.6	48.0	12.4
Ca ²⁺	12.0	14.8	21.0	40.6	55.4	60.0	12.4
Sr ²⁺	20.0	28.4	32.4	46.5	72.0	78.8	25.5
Ba ²⁺	110.2	400.0	400.0	140.0	288.4	444.4	96.6
Pb ²⁺	650.0	700.0	812.2	920.0	1200.0	1444.5	220.0
Hg ²⁺	162	160.0	122.2	44.4	56.0	25.0	45.2
Zn ²⁺	20.0	22.0	22.0	50.0	52.7	58.4	18.6
Cd ²⁺	27.7	30.7	32.2	40.0	48.1	50.0	22.5
Mn ²⁺	23.0	34.4	46.6	49.8	43.0	50.0	17.11
Cu ²⁺	70.0	88.4	156.9	166.6	152.8	170.0	45.5
Al ³⁺	17.0	50.4	88.8	90.4	150.4	242.0	25.3
Ni ²⁺	12.0	12.0	20.0	23.4	26.4	38.4	12.0
Fe ³⁺	30.0	50.4	54.4	55.5	55.5	75.0	30.5
Th ⁴⁺	20.0	32.3	50.7	50.0	70.0	90.0	18.2
Ce ³⁺	125.0	200.0	263.4	300.0	365.4	400.4	100.2
La ³⁺	125.0	160.0	166.6	225.0	235.0	381.4	115.4

Table 6
Quantitative separation of metal ions from a binary mixture using *acrylamide zirconium (IV) arsenate* columns at room temperature

Separation achieved	Amount loaded (mg)	Amount found (mg)	% Recovery	Eluant used	pH of eluant used	Volume of Eluant (mL)
Zn ²⁺	5.88	5.86	99.6	0.1 M succinic acid	2.7	60
Pb ²⁺	19.68	19.06	96.8	0.1 M nitric acid	1.0	80
Cd ²⁺	9.77	9.77	100	0.1 M acetic acid	2.9	60
Pb ²⁺	19.68	19.60	99.5	0.1 M nitric acid	1.0	80
Mn ²⁺	4.4	4.4	100	0.1 M formic acid	2.3	70
Pb ²⁺	19.68	19.20	97.5	0.1 M nitric acid	1.0	80
Ca ²⁺	3.60	3.50	97.2	0.1 M formamide	6.2	50
Pb ²⁺	19.68	19.47	98.9	0.1 M nitric acid	1.0	70
Zn ²⁺	5.88	5.75	98.1	0.1 M succinic acid	2.7	50
Ba ²⁺	13.04	12.77	97.9	0.1 M nitric acid	1.0	70
Zn ²⁺	5.88	5.86	99.6	0.1 M DMSO	5.8	60
Cu ²⁺	6.20	5.97	96.2	0.1 M nitric acid	1.0	70
Mg ²⁺	2.40	2.22	92.5	0.1 M succinic acid	2.7	50
Al ³⁺	2.98	2.60	87.6	0.1 M nitric acid	1.0	80
Ce ⁴⁺	20.60	20.55	99.75	0.1 M acetic acid	2.9	50
Th ⁴⁺	12.95	12.70	98.4	0.1 M nitric acid	1.0	80

Table 7
Selective separation of Pb²⁺ ion from the synthetic mixture of Mg²⁺, Ca²⁺, Sr²⁺, Zn²⁺ and Pb²⁺ on *acrylamide zirconium (IV) arsenate* columns

S. No.	Amount loaded (mg)	Amount recovered (mg)	Recovery (%)	Eluant used	Eluant volume (mL)
1	3.45	3.40	98.50	0.1 M nitric acid	30.0
2	6.90	6.83	98.90	0.1 M nitric acid	40.0
3	10.36	10.20	98.40	0.1 M nitric acid	40.0

250 to 550 °C may due complete decomposition of the organic part present in the material. Above 800 °C the curve shows the sharp depression may be due formation of metal oxides residues. Comparing *acrylamide zirconium (IV) arsenate* with other ion exchangers reported [3,11,12,16,17] the material retains 86% of its ion-exchange capacity up to 500 °C and also the weight loss is minimum in case of *acrylamide zirconium (IV) arsenate* (Table 4). Fig. 8 shows the surface properties of the *acrylamide zirconium (IV) arsenate* obtained at two different magnification (500× and 1000×) using Scanning Electron Microscopy. The results reveal that the material shows the irregular zigzag particle size.

In order to explore the separation potentiality of *acrylamide zirconium (IV) arsenate*, sorption behavior of 16 metal ions was studied

and the values obtained for distribution coefficients are given in Table 5. It was found that the increase in dielectric constant of solvents causes decrease in distribution coefficient of almost all the metal ions studied except in case of Ba²⁺ and Hg²⁺ where no regular trend was observed. The increase in polarity of the solvent increases the interaction between metal ion and solvent due to ion–dipole interaction as a result exchange of metal ion between solvent phase and exchanger phase will be less. The low metal ion uptake such as in nitric acid is due to the presence of large excess of H⁺ ions in the external solution. Pb²⁺ ions show higher K_d values in all the solvent system studied. Thus the promising feature of the material is its selectivity for Pb²⁺ ions, which is the one of the most toxic and polluting metal ions in the environment. The

Table 8
Selective separation of Pb²⁺ ion from the synthetic mixture of Cu²⁺, Al³⁺, Ni²⁺, Fe³⁺ and Pb²⁺ on *acrylamide zirconium (IV) arsenate* columns

S. No.	Amount loaded (mg)	Amount recovered (mg)	Recovery (%)	Eluant used	Eluant volume (mL)
1	4.14	4.12	99.5	0.1 M nitric acid	40.0
2	8.28	8.16	98.5	0.1 M nitric acid	50.0
3	12.43	12.27	98.4	0.1 M nitric acid	50.0

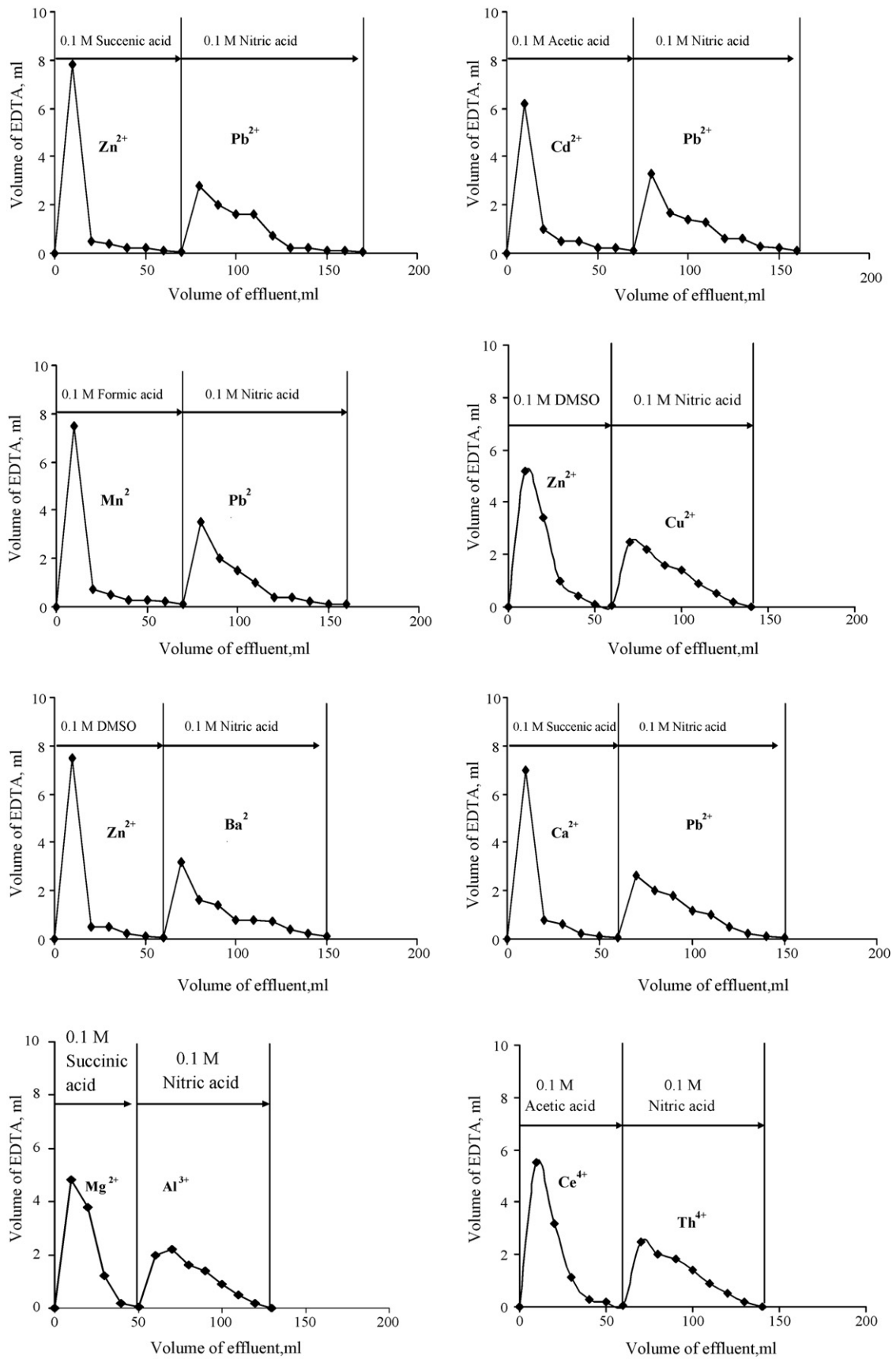


Fig. 9. Elution curves of binary separations of metal ions on acrylamide zirconium (IV) arsenate columns.

Table 9Quantitative separation of Cu²⁺ and Zn²⁺ in commercially available brass sample on acrylamide zirconium (IV) arsenate columns

Binary mixtures	Amount loaded (mg)	Amount recovered (mg)	Recovery (%)	Eluant used	Eluant volume (mL)
Zn ²⁺	3.0	2.80	93.30	0.1 M DMSO	50
Cu ²⁺	7.0	6.66	95.10	0.1 M nitric acid	60
Zn ²⁺	6.0	5.41	90.12	0.1 M DMSO	60
Cu ²⁺	14.0	12.96	92.51	0.1 M nitric acid	70
Zn ²⁺	9.0	8.24	91.50	0.1 M DMSO	60
Cu ²⁺	21.0	20.0	95.20	0.1 M nitric acid	70

analytical application of the acrylamide zirconium (IV) arsenate was explored by achieving different binary separations of metal ions on its columns. The results are given in Tables 6–9. The orders of elution of these metal ions are depicted in Fig. 9. It is evident from the elution profile that the elution is quite fast and resolution and recovery of the metal ions is satisfactory. Pb²⁺ ions were selectively removed from synthetic mixtures containing Mg²⁺, Ca²⁺, Sr²⁺, Zn²⁺, Pb²⁺ and Cu²⁺, Al³⁺, Ni²⁺, Fe³⁺, Pb²⁺ hence Pb²⁺ ions can be separated out in presence of the other metal ions present in waste waters. In order to demonstrate the practical utility of the material, quantitative separations of Zn²⁺ and Cu²⁺ from a commercially available brass sample were achieved acrylamide zirconium (IV) arsenate columns.

4. Conclusion

New semicrystalline acrylamide zirconium (IV) arsenate was synthesized, characterized and its analytical application explored. The material is fairly stable in inorganic acids, bases and organic solvents up to 2.0M. The promising feature of the material is its selectivity for Pb²⁺ ions, which is one of the most toxic metal ions present in environment. Further work is in progress for synthesizing the ion-selective electrode of this material for determination of Pb²⁺ ions.

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