Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

New Organic-Inorganic Type *Acrylamide Aluminumtungstate*: Preparation, Characterization and Analytical Applications as a Cation Exchange Material

S. A. Nabi[a]; Sajad A. Ganai[a]; Aabid H. Shalla[a]
[a] Department of Chemistry, Aligarh Muslim University, Aligarh, U.P., India

To cite this Article Nabi, S. A. , Ganai, Sajad A. and Shalla, Aabid H.(2008) 'New Organic-Inorganic Type *Acrylamide Aluminumtungstate*: Preparation, Characterization and Analytical Applications as a Cation Exchange Material', Separation Science and Technology, 43: 14, 3695 — 3711

To link to this Article: DOI: 10.1080/01496390802212674

URL: http://dx.doi.org/10.1080/01496390802212674

Separation Science and Technology, 43: 3695–3711, 2008

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802212674

Taylor & Francis
Taylor & Francis Group

New Organic-Inorganic Type *Acrylamide Aluminumtungstate*: Preparation, Characterization and Analytical Applications as a Cation Exchange Material

S. A. Nabi, Sajad A. Ganai, and Aabid H. Shalla
Department of Chemistry, Aligarh Muslim University, Aligarh, U.P., India

Abstract: A crystalline sample of organic-inorganic cation exchanger *acrylamide aluminumtungstate* has been synthesized. The material behaves as a mono-functional cation-exchanger with an ion–exchange capacity 1.25 meq/g for Na^+ ions. The material has been characterized on the basis of thermal stability, chemical stability, FTIR, TGA-DTA, X-ray, and SEM studies. The effect of time and temperature on the distribution coefficient of metal ion was studied. It was concluded that 30°C appeared to be the most favorable temperature. Sorption behavior of the metal ions was studied in different solvent systems. On the basis of distribution studies, the material was found to be selective for Pb^{2+} ions. Its selectivity was examined by achieving some important binary separations like Mg^{2+}-Pb^{2+}, Hg^{2+}-Pb^{2+}, Ca^{2+}-Pb^{2+} Zn^{2+}-Pb^{2+}, Ni^{2+}-Pb^{2+}, and Al^{3+}-Pb^{2+}. The practical applicability of the cation-exchanger was demonstrated in the separation of Pb^{2+} ions from a synthetic mixture.

Keywords: *Acrylamide aluminumtungstate*, cation-exchanger, crystalline, organic-inorganic

Received 13 September 2007; accepted 6 April 2008.

Address correspondence to Syed Ashfaq Nabi, Department of chemistry, Aligarh Muslim University, Aligarh, U.P., India. E-mail: sanabi@rediffmail.com, ssajad16@rediffmail.com

INTRODUCTION

Ion exchangers have received much attention because of their versatility in different fields. The role played by ion exchangers to control the atmospheric pollution is unparalleled. Inorganic ion exchangers are used in place of organic exchangers that were found to be unstable at high temperatures and strong radiations. However, the inorganic ion exchangers have their own limitations. The main disadvantage of inorganic ion exchangers is their morphology. They are generally fine powdery materials not suitable for column separations. These materials are usually amorphous and quite often non- reproducible in behavior. Further, their chemical stability is less but their mechanical strength is high as compared to their organic counterpart. These drawbacks of organic resins and inorganic adsorbents have compelled many researchers to introduce organic-inorganic hybrid ion exchangers consisting of inorganic ion exchangers and organic binding matrices (1–9). Organic-inorganic hybrid materials have attained a great deal of attention because of their greater resistance to high temperature and radiation stability, which is of greater importance to nuclear technology. Organic-inorganic hybrid materials enable the integration of useful organic and inorganic characteristics within a single molecular-scale composite. The synthesis of hybrid ion exchangers could open new avenues for analytical chemistry, hydrometallurgy, antibiotic purification and separation of radioactive isotopes, and find large-scale application in water treatment and pollution control (10). In the continuing quest for these materials a large number of hybrid ion exchangers based on acrylamide (4), acrylonitrile (11), Nylon-6,6 (9), triethylammonium (12), and polyaniline (6) have been synthesized. The present paper describes synthesis, characterization, and ion-exchange behavior of a highly thermally and chemically stable new organic-inorganic hybrid cation exchanger, *acrylamide aluminumtungstate*. Efforts have been made to explore the effect of temperature, time, and concentration of solvents on the distribution coefficient of metal ions. The practical utility of the material was explored in carrying out the selective separation of lead from synthetic mixture. Lead is considered as a highly toxic element. The main source of lead contamination of the environment is the combustion of petroleum fuel. Due to its toxicity, lead inhibits the function of certain enzymes necessary for the formation of haeme in bone marrow, the pigment that combines with protein to form haemoglobin. Lead poisoning can produce brain damage. Lead is therefore a potential pollutant in the environment. Thus, the relatively emerging field of organic-inorganic hybrids offers a variety of exciting technological opportunities to decrease the environmental pollution.

EXPERIMENTAL

Reagents and Instrument

Acrylamide (Loba Chemie, India), aluminum nitrate (Merck, India), and sodium tungstate (Merck, India). All other chemicals and reagents used were of analytical grade.

The main instruments used during the study were a UV-vis spectrophotometer (Elico EI 301E, India). FTIR spectrophotometer (Perkin-Elmer spectrum BX, USA), an automatic thermal analyzer (V2.2A DuPont 99000, a PW 1148/89 based X-ray diffractometer (Phillips, Holland), a water bath incubator shaker (MSW-275, India), and muffle furnace (G1-111, India).

Syntheses

The organic-inorganic hybrid, *acrylamide aluminumtungstate* was prepared by adding a mixture of 0.25 M sodium tungstate and 0.1 M acrylamide in different proportions into 0.25 M aluminum nitrate solution with constant stirring. The pH was adjusted by 1 M nitric acid or 1 M ammonia solutions. The gelatinous precipitate so formed was allowed to stand for 24 h at room temperature (25 ± 2°C) for digestion. The supernatant liquid was filtered by suction. The excess acid was removed by washing with demineralized water (DMW) and finally dried in an oven at 50°C. The dried products were immersed in DMW to obtain small granules. The granules were converted into H^+ form by placing in 1 M HNO_3 solution for 24 h. The excess acid was removed after several washings with DMW and finally dried at 50 ± 2°C. The particles of size 50–100 µm of the material were obtained by sieving. In this way samples of *acrylamide aluminumtungestate* were prepared in different experimental conditions. On the basis of the Na^+ ion-exchange capacity, sample(S-5) was selected for detailed studies (Table 1).

Ion-Exchange Capacity

To determine the ion-exchange capacity, a column process was used. 1.0 g of a dry cation-exchanger in H^+ form was packed in a column (1.0 cm id) fitted with glass wool at the bottom. Metal nitrates as eluent were used to elute the H^+ ions completely from the cation-exchanger column. The effluent was titrated against a standard solution of 0.1 M NaOH.

Table 1. Experimental conditions for the synthesis of *acrylamide aluminumtungstate*

	Condition of synthesis						
Sample no	A	B	C	Mixing ratio	pH	Appearance	IEC meq/g
S-1	0.25	0.25	0.1	1:1:1	0.5	Brown	0.25
S-2	0.25	0.25	0.1	1:1:1	1.0	Brown	0.50
S-3	0.25	0.25	0.1	1:1:1	1.25	Brown	0.45
S-4	0.25	0.25	0.1	1:1:1	1.5	Brown	0.45
S-5	0.25	0.25	0.1	1:2:1	1.0	Brown	1.25
S-6	0.25	0.25	0.1	2:1:1	1.0	Brown	1.00
S-7	0.25	0.25	0.1	1:1:2	1.0	Brown	1.04

A: aluminumnitrate, B: sodium tungstate, C: acrylamide.

pH Titration

The Topp and Pepper method was used for pH titration studies in NaCl-NaOH and KCl- KOH systems (13). 0.5 g of the exchanger was treated with 50 mL of the solution mixture.

Chemical Composition

0.50 g of the sample was dissolved in 10 ml aqua regia. The dissolved sample was diluted to 50 mL. The amount of aluminum and tungstate were determined by standard spectrophotometric methods. Carbon, hydrogen, and nitrogen contents of the material were determined by elemental analysis.

Thermal Stability

In order to determine the effect of heating temperature on ion-exchange capacity, 1.0 g sample of the material (S-5) in H^+ form was heated at different temperatures in a muffle furnace for 1 h and Na^+ ion-exchange capacity was determined by the standard column process as described above. Thermogravimetric analysis and differential thermal analysis studies (TGA-DTA) were performed at a heating rate of 10°C/min in a nitrogen atmosphere.

FTIR Studies

For FTIR analysis, 10 mg (dry mass) of the exchanger in H^+ form was thoroughly mixed with 100 mg (dry mass) of KBr and ground to a fine powder. A transparent disc was formed by applying a pressure of 80 psi (1 psi = 6894.76 pa) in a moisture free atmosphere. The FTIR absorption spectrum was recorded between 450–400 cm^{-1}.

X-ray Studies

The X-ray diffraction pattern of the ion-exchange material (sample S-5) was recorded by a PW 1148/89 based diffractometer with Cu Kα radiation.

Scanning Electron Microscopy

Electron micrographs were recorded for acrylamide *aluminumtungstate* by using a scanning electron microscope at 20.0 KV. The details are shown in the SEM photographs.

Distribution Studies

The distribution coefficient (K_d) for various metal ions were determined in a number of solvent systems viz. 2%DMF, 10%DMF, 2%DMSO, 10%DMSO, 2%Formamide, 10%Formamide, 2%Triton X-100, and 10%Triton X-100. The effect of the temperature and time on the distribution coefficient was also studied. *Acrylamide aluminumtungstate* (0.3 g) in H^+ form was put into 100 ml conical flasks each containing 30 ml solution of 0.1 M concentration of metal ions. The mixture was continuously shaken for 5 h at 30°C, 35°C, 45°C, and 55°C. The amount of metal ions present in the solution was determined by titrating it against disodium salt of EDTA (0.01 M) using standard procedures. The distribution coefficient values were calculated by using the following relationship:

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

$$\text{In our case} \quad K_d = \frac{I - F/300\,\text{mg}}{F/30\,\text{ml}}$$

Table 2. Ion exchange capacity of *acrylamide aluminumtungstate* for different metal ions

Exchanging ions	Ionic radii A^0	Hydrated ionic radii A^0	IEC m mol g^{-1}
Li^+	0.68	3.40	0.86
Na^+	0.97	2.76	1.25
K^+	1.33	2.32	1.30
Mg^{2+}	0.78	7.00	0.82
Ba^{2+}	1.43	5.90	1.00

Where I is the initial amount of the metal ion in the solution phase and F is the final amount of the metal ion in the solution phase.

Quantitative Separation of Metal Ions in Binary Synthetic Mixtures

Quantitative binary separations of some metal ions of analytical interest were achieved on *acrylamide aluminumtungstate*. 2.0 g of the exchanger in H^+ form was packed in a glass column (i.d 1.0 cm) with a glass wool support at the end. The column was washed thoroughly with DMW. 2.0 ml

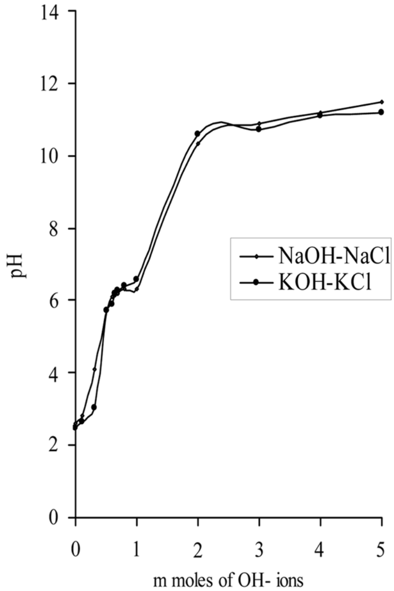

Figure 1. pH titrations curves of *acrylamide aluminumtungstate*.

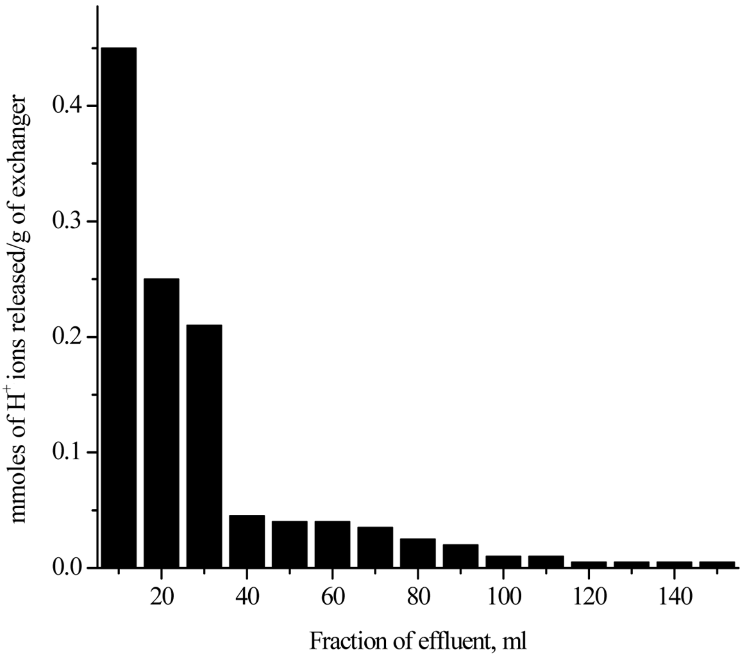

Figure 2. Elution behavior of H^+ ions on *acrylamide aluminumtungstate*.

binary mixture of the metal ions to be separated was poured on to the column and allowed to flow at a rate of 0.25 ml min^{-1} till the solution level was just above the surface of the material. The column was then rinsed with DMW. Individual metal ions were eluted using appropriate

Table 3. Effect of temperature on the ion–exchange capacity of *acrylamide aluminumtungstate* cation ion–exchanger

Temperature °C	Color	Retention of IEC (%)
50	Brown	100.00
100	Brown	99.00
200	Brown	96.00
300	Light green	92.00
400	Yellow	84.00
500	Yellow	79.00
600	Yellow	76.00

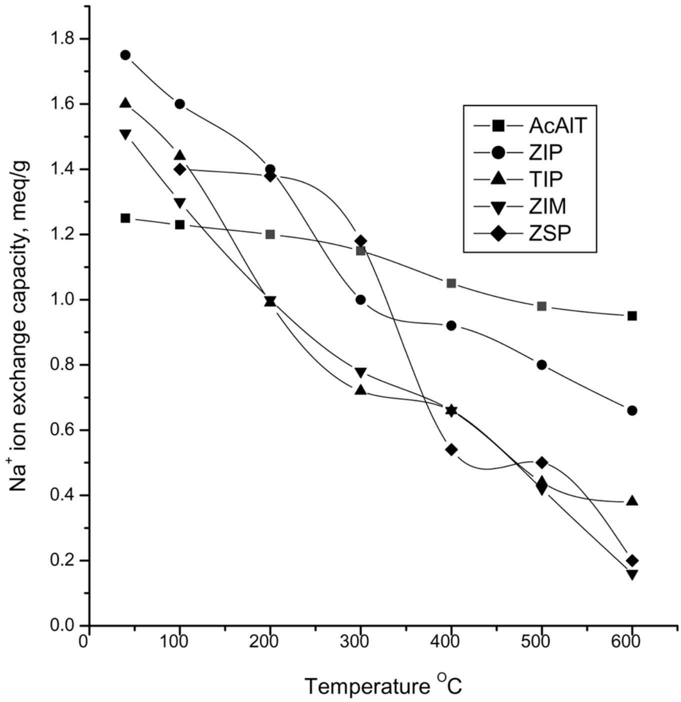

Figure 3. Comparison of ion exchange capacity of different ion exchange materials at different temperatures. *AcAlT*: *Acrylamide aluminumtungstate*; *ZIP*: *Zirconium iodophosphate*; *TIP*: *Titaniumi odophosphate*; *ZIM*: *Zirconium iodomolybdate*; *ZSP*: *Zirconium stannicphosphate.*

eluting reagents. The flow rate of the eluent was maintained (1.0 ml min^{-1} throughout the elution process. The effluent was collected in 10 ml fractions and was titrated against the standard solution of 0.01 M di-sodium salt of EDTA.

Selective Separation of Pb^{2+} from the Synthetic Mixture of Mg^{2+}, Ca^{2+}, Sr^{2+}, Pb^{2+}, Cd^{2+}, and Hg^{2+} on *Acrylamide Aluminumtungstate* Columns

For selective separation different sets of the synthetic mixtures were taken in which the amount of the Pb^{2+} was varied keeping the amount of other metal ions constant. The subsequent procedure remains the same as described earlier.

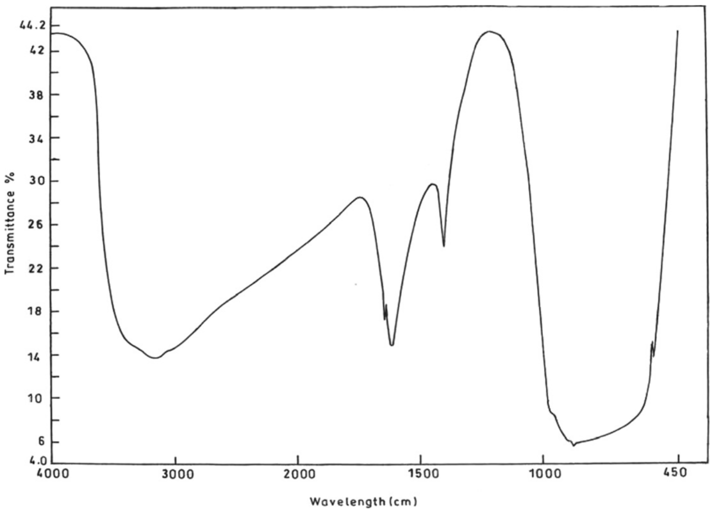

Figure 4. FTIR spectrum of *acrylamide aluminumtungstate*.

RESULT AND DISCUSSION

In the present work various samples of *acrylamide aluminumtungstate* were synthesized under varying experimental conditions. The material appears to be a promising hybrid material with good ion-exchange

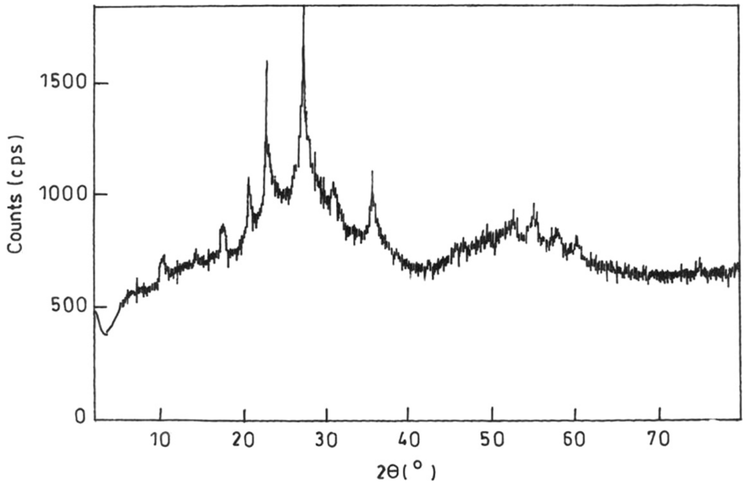

Figure 5. Powder X-ray diffraction pattern of *acrylamide aluminumtungstate*.

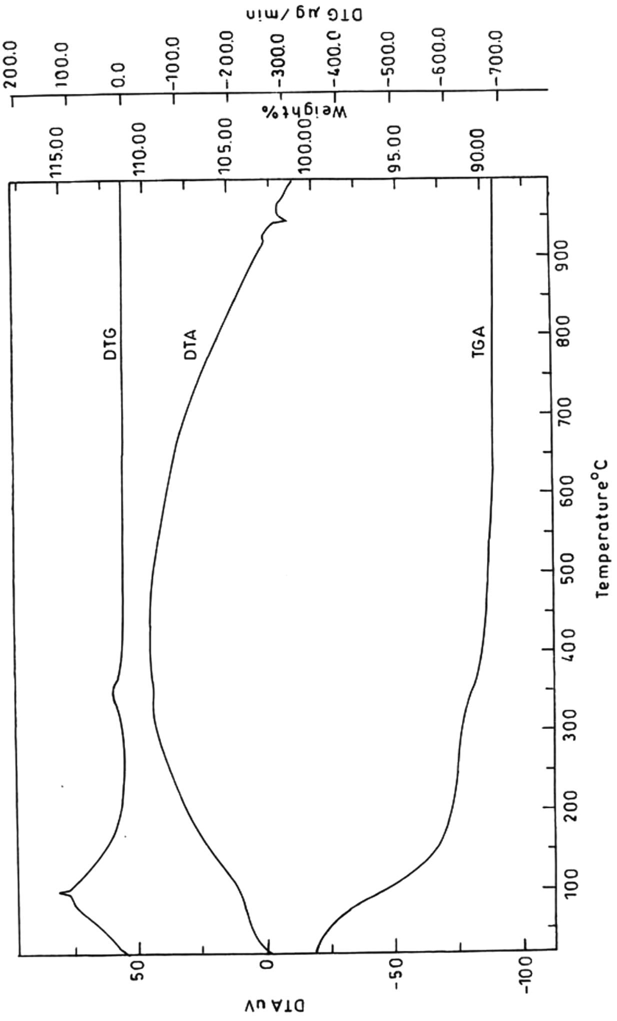

Figure 6. Simultaneous DTA-TGA curves of *acrylamide aluminumtungstate*.

capacity, thermal, and chemical stability. It was evident from (Table 1) that the mixing ratio of reactants and pH affect the ion-exchange capacity of the material. It was found that the anionic part contributed towards the ion-exchange capacity of the material as the replaceable ions are attached to this group. The size and charge of the exchanging ion affects the ion exchange capacity of the material. As evident from (Table 2) the ion-exchange capacity for alkali metal ions and alkaline

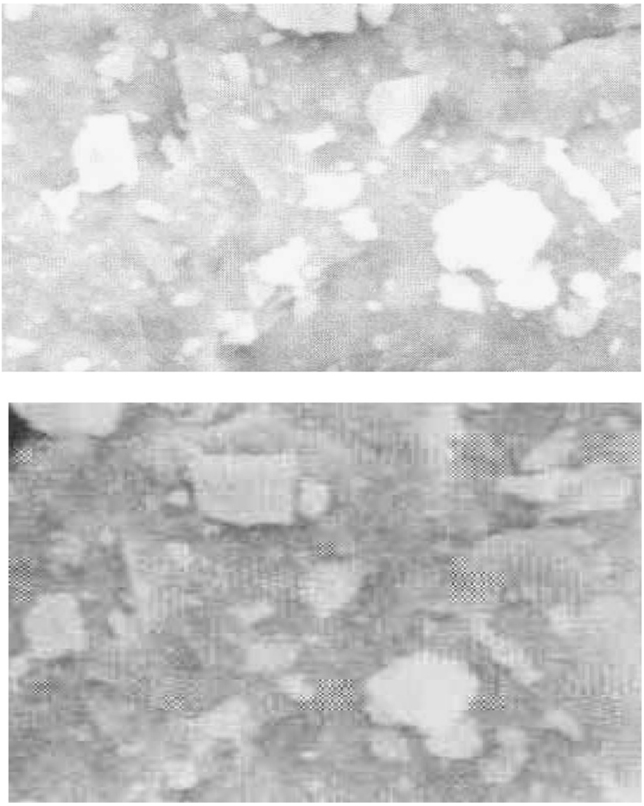

Figure 7. SEM images of *acrylamide aluminumtungstate*.

earth metal ions increases according to the decrease in the hydrated ionic radii (14,15). The ions with smaller hydrated radii easily enter the pores of the exchanger, resulting in higher adsorption (16). The pH titration for the systems NaCl-NaOH and KCl-KOH show two breaks in the curves indicate bi-functional behavior of the material (Fig. 1). The chemical composition analysis reveals that the molar ratio of Al:W:C:H:N:O is 1:2:4.9:16.9:1:27. The material works efficiently as almost all the H^+ are eluted in first 100 ml of the eluent as evident from Fig. 2. On heating the material at different temperatures for 1 h (Table 3), the weight, the physical appearance, and the ion–exchange capacity of *acrylamide aluminumtungstate* was changed. An important characteristic of *acrylamide aluminumtungstate* that differentiates it from other exchange materials is that it can withstand temperature as high as 600°C and retain reasonable ion exchange capacity (76%). On the other hand Zirconium(IV)

Table 4. Distribution coefficients (ml/g) of metal ions

	Dimethylformamide		Dimethylsulphoxide		Formamide		Tritron X-100	
Metal ions	2%	10%	2%	10%	2%	10%	2%	10%
Mg^{2+}	304.00	238.70	320.0	240.00	267.85	257.14	152.50	164.10
Ba^{2+}	566.66	458.82	447.05	361.90	578.57	669.23	268.00	246.15
Ca^{2+}	390.00	182.85	400.00	230.00	354.54	308.00	206.06	241.66
Sr^{2+}	345.00	338.00	330.00	245.00	425.00	252.00	113.33	155.55
Cd^{2+}	385.71	274.07	343.47	225.80	410.00	300.00	201.47	207.14
Hg^{2+}	546.66	478.57	542.85	416.66	341.17	400.00	325.00	328.57
Zn^{2+}	316.66	253.33	304.00	225.80	392.30	360.86	185.71	186.48
Mn^{2+}	370.00	217.24	336.36	239.28	380.00	300.00	310.00	340.00
Pb^{2+}	1328.00	870.00	2000.00	669.23	3233.3	1900.00	462.50	845.00
Cu^{2+}	349.16	340.00	300.00	286.36	337.50	309.52	420.00	388.09
Ni^{2+}	30.00	233.33	216.12	215.55	259.25	257.14	320.83	275.00
Al^{3+}	229.03	248.27	226.66	177.14	200.00	209.52	203.33	201.66

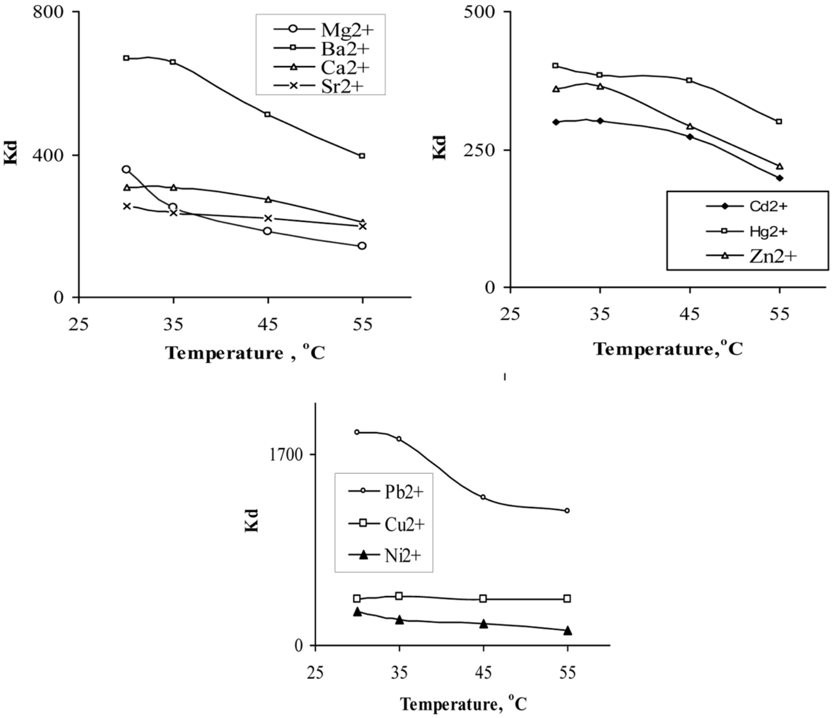

Figure 8. Effect of temperature on distribution coefficient of metal ions on *acrylamide aluminumtungstate*.

iodophosphate, tin(IV) iodophosphate, Zirconium(IV) iodomolybdate, Zirconium(IV) selenophosphate experience a significant loss in the ion exchange capacity (Fig. 3). In this way *acrylamide aluminumtungstate* appears to be superior to other ion exchange materials mentioned here (16). The FTIR spectrum (Fig. 4) of *acrylamide aluminumtungstate* shows the presence of external water molecule in addition to M-O and M-OH groups present in the material. The position of the board IR peak at $3137\,cm^{-1}$ indicates N-H vibration from the amino group of acrylamide as well as of water and hydroxyl groups. A sharp peak with a maximum at $1614.93\,cm^{-1}$ corresponds to the deformation vibration of free water molecules. The peak at $1401.45\,cm^{-1}$ indicates the presence of a considerable amount of acrylamide in *acrylamide aluminumtungstate* (17). The presence of a broad peak at $875.28\,cm^{-1}$ may be due to the presence of aluminum and tungstate. The X-ray diffraction pattern (Fig. 5) indicates that the material is semi-crystalline in nature. As evident from the thermogravimetric (Fig. 6) curve of *acrylamide aluminumtungstate* shows the initial weight loss about (6%) upto 150°C may be due to the removal of external water molecules per mole of the material present. A slow weight loss observed 3.5% between 150°C and 400°C may be due to the complete decomposition of the organic component of the material and is in agreement by the appearance of peak with T_{max} at 352°C in the DTG curve. The Scanning Electron Micrograph (Fig. 7) at different magnification indicates that the material has a sheet like appearance. Assuming all the external water molecules are lost upto 150°C, then the weight loss as calculated from the TGA curve was 6%. The number of water molecules (n) per mole of the material can be calculated from the Alberti equation (18)

$$18\,n = \frac{X\,(M + 18\,n)}{100}$$

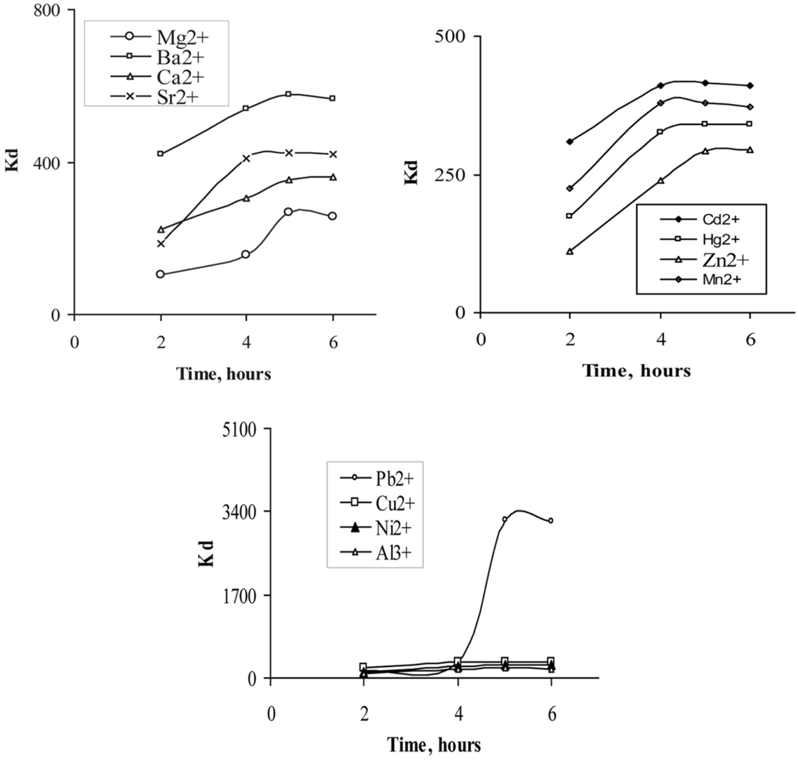

Figure 9. Effect of time on distribution coefficient of metal ions on *acrylamide aluminumtungstate*.

Where X is the percent weight loss (−6%) in the exchanger by heating upto 150°C and M + 18 n is the molecular weight of the material, the calculation gives −3 for the external water molecules (n) per molecule of the hybrid cation exchanger (sample S-5).

In order to explore the potentiality of this hybrid cation-exchange material in the separation of metal ions, distribution studies for various metal ions were performed in different solvents (Table 4). It was observed that for most of the metals, K_d values decrease with the increase in concentration of solvents except Al^{3+}. However, in Triton X-100 the K_d value increases with the increasing surfactant concentration except Ba^{2+}, Cu^{2+}, Ni^{2+}, and Al^{3+}. The distribution studies showed that the material was found to be selective for Pb^{2+}. Figure 8 shows a variation of the K_d value with the change in temperature in 10% formamide. All the metal ions except Zn^{2+} and Cu^{2+} studied exhibit a general trend of a highest K_d value at 30°C and then a gradual decrease with the increase in temperature. Therefore, the optimum temperature for sorption studies is 30°C. The effect of time on the sorption (Fig. 9) infers that the maximum sorption occurs after 4.5 hours of shaking. The separation capability of the material has been demonstrated by achieving some important binary separations of analytical interest (Table 5) such as Mg^{2+}-Pb^{2+}, Ca^{2+}-Pb^{2+}, Hg^{2+}-Pb^{2+}, Zn^{2+}-Pb^{2+}, Ni^{2+}-Pb^{2+}, and Al^{3+}-Pb^{2+}. Thus, separation of zinc from lead can be utilized for recovery of zinc from galvanizing wastes. The specificity of the material towards the lead is the promising feature of the material, as lead is one of the most potential

Table 5. Quantitative separations of metal ions of binary mixtures using acrylamide aluminumtungstate columns

Separation achieved	Amount loaded, mg	Amount found, mg	Recovery (%)	Eluent used	Volume of eluent, mL
Mg^{2+}	2.43	2.35	96.70	2% Triton X-100	80
Pb^{2+}	20.72	19.16	92.47	10%DMSO	70
Ca^{2+}	4.00	4.00	100.00	10% DMF	110
Pb^{2+}	20.72	20.40	98.45	2%Tritin X-100	80
Hg^{2+}	20.05	20.05	100.00	2%Triton X-100	90
Pb^{2+}	20.72	20.20	97.49	10%DMSO	110
Zn^{2+}	6.53	6.47	99.08	10%Triton X-100	90
Pb^{2+}	20.72	20.51	98.98	2%Triton X-100	70
Ni^{2+}				10%DMSO	100
Pb^{2+}	20.72	19.06	91.98	2%Triton X-100	70
Al^{3+}	2.69	2.65	98.51	2%DMSO	80
Pb^{2+}	20.72	19.06	91.98	2%Triton X-100	80

Table 6. Selective separation of Pb^{2+} ion from synthetic mixture of Mg^{2+} Sr^{2+}, Ca^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} on *acrylamide aluminumtungestate* columns

S. no	Amount loaded, mg	Amount recovered, mg	(%) Recovery	Eluent used	Volume of eluent, mL
1	1.72	1.71	99.40	2% Triton X-100	70.00
2	3.44	3.44	100.00	2% Triton X-100	100.00
3	5.16	5.15	99.80	2% Triton X-100	120.00

pollutants in the environment that leads to many disorders in the body. Lead ion can be removed from waste waters in the presence of other metal ions. The separations are quite sharp and the recovery is quantitative and reproducible. The practical utility of the material was demonstrated in the quantitative analysis of Pb^{2+} from a synthetic mixture of Pb^{2+}, Mg^{2+}, Sr^{2+}, Ca^{2+}, Hg^{2+} and Cd^{2+} (Table 6).

ACKNOWLEDGEMENT

The authors are thankful to the chairman, Department of Chemistry, Aligarh Muslim University, Aligarh. One of the authors (Sajad Ahmad Ganai) is thankful to the University Grants Commission (UGC), India, for financial support. The authors are also thankful to Dr. Amjad Mumtaz Tahir Khan, Lecturer, Department of Applied Chemistry, Aligarh Muslim University, Aligarh in the preparation of the manuscript

REFERENCES

1. Siddiqui, W.A.; Khan, S.A.; Inamuddin. (2007) Synthesis, characterization and ion-exchange properties of a new and novel organic-inorganic hybrid cation-exchange: Poly (methyl methacrylate) Zr(IV) phosphate. *Colloids and Surfaces A: Physiochemical and Eng. Asp. 295*: 193.
2. Khan, A.A.; Inamuddin. (2006) Applications of Hg(II) sensitive polyaniline Sn(IV) phosphate composite cation-exchange material in determination of Hg^{2+} from aqueous solutions and in making ion-selective membrane electrode, sensors and Actuators B. *120*: 10.
3. Varshney, K.G.; Agrawal, A.; Mojundar, S.C. (2005) Pectin based cerium(IV) and thorium(IV) phosphates as novel hybrid fibrous ion exchangers, synthesis characterization and thermal behavior. *J. of Thermal Analysis and Calorimetry*, *81*: 183.

4. Varshney, K.G.; Gupta, P. (2003) Synthesis and characterization of a mercury selective phase of acrylamide tin(iv) phosphate hybrid ion exchanger: Separation of Hg(I) from Cd(II), Pb(II) and Sr(II). *Indian Journal of Chemistry*, *12A*: 2974.
5. Khan, A.A.; Alam, M.M. (2004) New and novel organic-inorganic type crystalline Polypyroll/Polyantimonic acid composite system: Preparation, characterization and analytical applications as a cation-exchange material and Hg^{2+} ion-selective membrane electrode. *Analytical Chemical Acta*, *504*: 253.
6. Khan, A.A.; Alam, M.M. (2003) Synthesis, characterization and analytical applications of a new and novel organic-inorganic composite material as a cation-exchanger and Cd(II) ion-selective membrane electrode: polyaniline Sn(IV) tungstoarsenate. *Reactive and Functional Polymers*, *55*: 277.
7. Niwas, R.; Khan, A.A.; Varshney, K.G. (1999) Synthesis and ion exchange behavior of polyaniline Sn(IV) arsenophosphate: A polymeric inorganic ion exchanger. *Colloids and Surfaces A: Physicochemical and Eng. Asp.*, *150*: 7.
8. Gupta, U.; Tayal, N. (2003) Synthesis, characterization and applications of a new phase of crystalline and mercury selective acrylamide cerium(IV) phosphate: of novel fibrous ion exchanger. *Indian Journal of Chemistry*, *42A*: 89.
9. Inamudin; Khan, S.A.; Siddiqui, W.A.; Khan, A.A. (2007) Synthesis, characterization and ion-exchange properties of a new and novel organic-inorganic hybrid cation-exchanger: Nylon-6,6, Zr(IV) phosphate. *Talanta*, *71*: 841.
10. Helfrich, F. (1962) Ion-Exchange; MacGraw-Hill: New York.
11. Varshney, K.G.; Tayal, N.; Gupta, U. (1998) Acrylonitrile based cerium(IV) phosphate as a new mercury selective fibrous ion exchanger-synthesis, characterization and analytical application. *Colloids and Surfaces A: Physicochemical and Eng. Asp.*, *145*: 71.
12. Singh, D.K.; Singh, S.; Srivastava, B. (2002) Synthesis, characterization and ion exchange properties of zirconium(IV)triethylammonium phosphate. *Indian Journal of Chemistry*, *41A*: 2526.
13. Topp, N.E.; Pepper, K.W. (1949) *J. Chem. Soc.*, 3299.
14. Nabi, S.A.; Khan, A.M. (2006) Synthesis, ion-exchange properties and analytical applications of stannic silicomolybdate: Effect of temperature on distribution coefficients of metal ions. *React. Funct. Polym.*, *66*: 495.
15. Khan, A.A.; Inamuddin.; Alam, M.M. (2005) Determination and separation of Pb^{2+} from aqueous solutions using a fibrous type organic-inorganic hybrid cation-exchange material: Polypyrrol thorium(IV) phosphate. *React. Funct. Polym.*, *63*: 119.
16. Nabi, S.A.; Usmani, S.; Rahman, N. (1996) Synthesis, characterization and analytical applications of an ion-exchange material: Zirconium(IV) iodophosphate. *Ann. Chim. Fr.*, *21*: 521.
17. Socrates, G. (1980) Infrared Characteristic Group Frequencies; John Wiley: Toronto.
18. Alberti, G.; Toracca, E.; Conte, A. (1996) Stoichiometry of ion exchange materials containing zirconium and phosphate. *J. Inorg. Nucl. Chem.*, *28*: 607.