

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/319310802>

Antimony (V) silicate as a new inorganic ion-exchanger useful for the removal of chromium (VI), copper (II) and cadmium (II)

Article in Pollution Research · August 2017

CITATIONS

0

READS

47

3 authors:



Naresh Kumar Mishra

BSNVPG College

31 PUBLICATIONS 42 CITATIONS

[SEE PROFILE](#)



Abhyanshi Tripathi

Ashoka University

18 PUBLICATIONS 0 CITATIONS

[SEE PROFILE](#)



Nimish Mishra

Indian Institute of Information Technology, Kalyani

28 PUBLICATIONS 19 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Quantum Error Correction [View project](#)



Analysis of the story 'Beauty and the Beast' by Clarice Lispector. [View project](#)

ANTIMONY (V) SILICATE AS A NEW INORGANIC ION-EXCHANGER USEFUL FOR THE REMOVAL OF CHROMIUM (VI), COPPER (II) AND CADMIUM (II)

NARESH KUMAR MISHRA¹, ABHYANSHI TRIPATHI² AND NIMISH MISHRA³

¹ Analytical Lab, Department of Chemistry, Bappa Sri Narain Vocational Post Graduate College,
Lucknow 226 001, India

^{2,3} Freelancer, City Montessori Inter College, Aliganj I, Lucknow 226 021, India

(Received 23 May, 2017; accepted 28 July, 2017)

ABSTRACT

A new inorganic ion-exchanger antimony (v) silicate (AS) has been synthesized under varying conditions. Distribution coefficients (K_d) of 20 transition metal ions have been studied in DMW, 0.1 mol/dm³ HCl, 0.1 mol/dm³ HCl-10% DMSO (1:10) and 1 mol/dm³ NH₄Cl systems. Some analytically important separations of metal ions have been investigated. The greater selectivity behaviour of the exchanger for Cr (VI), Cu (II) and Cd (II) has been utilized for the removal and recovery of these metal ions from dilute water samples.

KEY WORDS : Ion Exchanger, Antimony (V) Silicate, Analytical Separation

INTRODUCTION

Recently heteropoly acid salts have received considerable attention as inorganic ion-exchangers due to their different ion-exchange behaviour and selectivity in comparison to simple salts (Mukherjee *et al.*, 1984; Inamuddin *et al.*, 2007; Qureshi *et al.*, 1972 and Pekarek *et al.*, 1972). Two component ion-exchangers have been much studied. The input of industrial and human wastes into estuaries and coastal water is often associated with elevated levels of heavy metals in the water and the sediment (Parekh *et al.*, 2001 and Millward *et al.*, 1982). Heavy metals such as Cu and Cd produce their chronic harmful effects through what is known as a "Cumulative action". Chromium is one of the recognized environmental human carcinogens. Due to their specific selectivity, inorganic ion-exchangers have been found more successful than the adsorbents for the removal and recovery of toxic metal ions from dilute aqueous solutions (Janardanan *et al.*, 2001; Yavari *et al.*, 2009 and Singh *et al.*, 2003). Antimonates of Zr(IV), Ti(IV), Fe(III) and Sn (IV) have been studied as inorganic ion-exchangers. These materials are generally

temperature resistant and stable under chemical attack. Their utility has been shown in separation science. This note reports the synthesis, ion-exchange behaviour towards transition metal ions and analytical applications of antimony (V) silicates as a new two component inorganic ion-exchanger.

MATERIALS AND METHODS

Antimony (V) Chloride was obtained from B.D.H England and sodium silicate (Merck) was used. All other reagents were of A.R grade and used as such.

Antimony (V) silicate was prepared by mixing decimolar solutions of antimony (v) chloride and sodium silicate under various conditions. pH of the mixture was adjusted by adding ammonia solution dropwise. After ~ 24 hrs, the product was filtered, washed with demineralised water and dried at ~ 60° C. The material was finally ground, sieved to 60-100 mesh and was converted to the H⁺ form by treatment with HNO₃ (1 mol/dm³). The ion-exchange capacity of various samples of antimony (v) silicate was determined for Na⁺ ions by column method. The neutral salt decomposition capacity with different univalent and bivalent ions were reported.

0.50g of the powdered exchanger (AS_1) was dissolved in Conc HCl (20ml). Antimony was precipitated as sulphide and determined titrimetrically with potassium iodide (Furman., 1962) and silica was determined as SiO_2 (Scott., 1939). The molar ratio of Sb : Si was found to be 1 : 2.5. *Chemical Stability*- 0.25 g of the ion –exchanger was shaken with 25 mL of the solution concerned at $\sim 30^\circ C$ for 6 hrs. The solution was then analysed for dissolved antimony and silica spectrophotometrically (snell *et al.*, 1959).

Thermal stability- 1g samples of AS_1 were heated at various temperatures in a muffle furnace for 1h each, and the ion – exchange capacity was determined by column method after cooling the material upto room temperature.

pH titrations – The pH titrations were performed by Topp and Pepper's method using NaOH – NaCl system. 0.25 g samples of the exchanger in H^+ form were shaken with 25 ml in several conical flasks $\sim 30^\circ C$. After shaking ~ 6 hrs for equilibrium , pH of the solution of each flask was measured and plotted against the meq of the OH^- added. Infrared analysis of the sample antimony (v) silicate (AS_1) was performed by KBr technique.

The distribution studies (Kd values) of 20 transition metal ions in DMW, HCl, HCl + 10% DMSO (1:10) and NH_4Cl systems were determined by batch process (Singh *et al.*, 1988), Pt(IV) with potassium iodide, Ru (VIII) with thiourea and Cr(VI) with diphenyl – carbazide were determined spectrophotometrically (Snell *et al.*, 1959) and other metal ions were determined using EDTA titrations.

Kd values were calculated from :

K_d (mL/g) = Amount of metal ion in exchanger phase / Amount of metal ion in solution phase

On the basis of differences in K_d values, some quantitative separations of analytically important metals ions were performed on the small columns of antimony (V) silicate. For quantitative separations of metal ions of analytical interest, the ion – exchanger in H^+ form (2g) was taken into a column of i.d 0.4 cm. The column was first washed with 20 ml of DMW and then the mixture of metal ions were introduced into the column and allowed to be adsorbed. The metal ions were eluted separately using eluents selected on the basis of observed K_d values and determined by EDTA titrations, or by spectrophotometric methods. The flow rate was maintained at ~ 0.4 ml min^{-1} .

An aliquot of standard metal solution, Cu (II), or

Cd (II), or Cr (VI) was taken in a 100 ml standard flask, foreign metal ions were added and the solution was diluted to the volume with DMW. This solution was passed through the column 30 cm x 0.39 cm^2 cross-sectional area containing 2 g exchanger (AS_1) at flow rate ~ 1 ml min^{-1} . Then the column was washed with about 50 ml of DMW at the same flow rate. The retained metal ion Cd (II) was eluted with 40 ml of 1 mol / dm^3 NH_4Cl – 0.1 mol / dm^3 HCl , Cu (II) was eluted with 40 ml of 0.1 mol / dm^3 HCl and Cr (VI) was eluted with 50 mL of 0.1 % diphenylcarbazide in 0.1 mol / dm^3 HCl.

RESULTS AND DISCUSSION

The results of ion – exchange capacity studies for various samples of antimony (V) silicate (Table 1) reveal that AS_1 prepared by mixing 0.1 mol / dm^3 solutions of antimony (V) chloride and sodium silicate had maximum ion- exchange capacity [1.20 meq/(dry g)], highest chemical and thermal stability and good appearance; it was thus chosen for further studies

Table 1. Synthesis and ion exchange capacity for Na^+ ion of antimony (v) silicate

Sample No.	Mixing ratio (V/V)		pH	Ion exchange capacity (meq g^{-1})
	Sb :	Si		
AS_1	1	1	1	1.20
AS_2	1	1	2	1.10
AS_3	1	1	3	0.90
AS_4	1	2	1	0.85
AS_5	2	1	1	0.80

The ion – exchange capacity data determined for various cations (Table 2) show that the values for alkali metals are higher than the alkaline earth metals.

Table 2. Ion exchange capacity of antimony (V) silicate for various cations (Sample AS_1)

Cations	pH	Hydrated radii/nm	Ion-exchange capacity, meq / g dry exchanger
Li(I)	6.8	0.340	0.92
Na(I)	6.7	0.276	1.10
K(I)	6.8	0.232	1.26
Mg(II)	6.5	0.700	0.69
Ca(II)	6.5	0.630	0.95
Sr(II)	6.4	-	0.99
Ba(II)	6.1	0.590	1.03

The chemical stability of the exchanger AS_1 was studied in different solvents, viz HNO_3 (1 and 4 mol / dm^3), HCl (1 and 2 mol/ dm^3) and $NaOH$ (0.1 mol/ dm^3). The results indicate that the material is fairly stable in DMW, 1 mol / dm^3 NH_4Cl , 0.5 mol / dm^3 NH_4OH and upto 2 mol/ dm^3 HNO_3 and HCl .

The effect of drying temperature of ion-exchanger capacity revealed that the exchanger can be used upto 100°C without loss in ion-exchange capacity.

The results of pH – titration (figure 1) indicate that the exchanger AS_1 (H^+ form) behaves as a mono – protic weak acid. The total ion-exchange capacity is 1.9 meq g^{-1} calculated at the neutralization point. This gives the maximum number of replaceable counter ions and is independent of nature of cation.

Chemical analysis of AS_1 was as follows: Sb: 22.6%, Si: 47.7 % (calculated for Sb: 22.5, Si: 47.2%). IR spectrum of sample AS_1 is shown in figure 2. It revealed IR data at 3700 – 3100 cm^{-1} (Interstitial water molecules and OH), 1660 cm^{-1} (def. of interstitial water molecules), 740, 695, 625, 560, 502, 440 and 430 (polymerization through M-O linkage), 1330 cm^{-1} (antimonic acid) ¹² and 1040 cm^{-1} corresponds to the silicates.

Based on the above results the following tentative formula has been assigned:



In order to study the selectivity behaviour of the exchanger for transition metal ions, the distribution

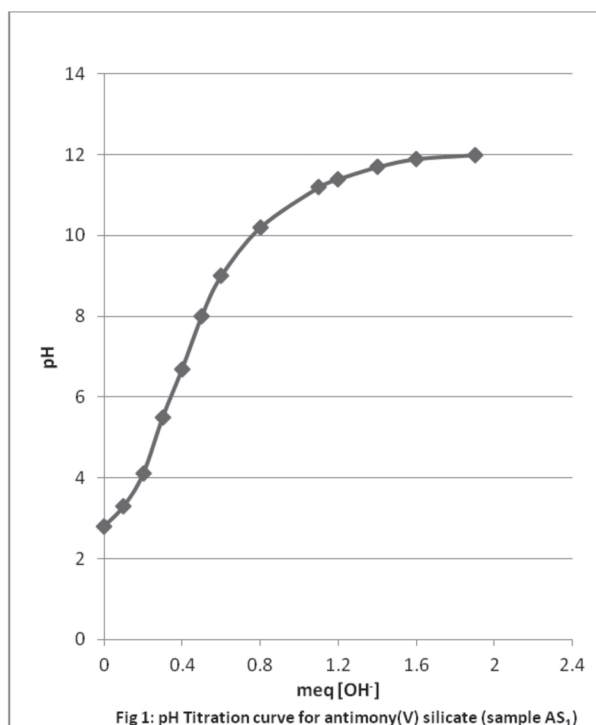


Fig. 1. pH Titration curve for antimony(V) silicate (sample AS_1)

co-efficients of 20 metal ions were measured in four different systems. The results are plotted in Table 3. The ion-exchanger material showed high selectivity K_d values for Pb(II), Cd(II), Mo(VI), Cu(II), Hg(II),

Table 3. K_d values of metal ions on antimony (V) silicate (sample AS_1)

Metal ions	DMW	0.1 mol/ dm^3 HCl	0.1 mol/ dm^3 HCl+10%DMSO(1:10)	1 mol/ dm^3 NH_4Cl
Ni(II)	275	238	141	80
Pb(II)	612	301	387	83
Cu(II)	1082	232	1052	235
Hg(II)	475	430	370	320
Co(II)	408	121	112	98
Zn(II)	97	12	20	10
Mn(II)	121	32	95	14
Cd(II)	865	582	652	246
Pd(II)	252	36	100	36
Cr(VI)	980	582	900	590
Ru(VIII)	750	410	603	370
Pt(IV)	260	138	198	178
Zr(IV)	208	138	75	20
Fe(III)	71	30	26	10
Ca(II)	36	16	35	27
Mg(II)	15	12	30	18
Au(III)	102	15	42	4
Ba(II)	54	39	45	35
Sr(II)	40	33	45	30
Mo(VI)	670	418	152	280

Ru(VIII), Co(II).

The utility of the material was demonstrated by achieving the separations of metal ions of great analytical significance (Table 4). Only small volume of eluents was required to give compact chromatograms and no tailing was observed during the elution of metal ions.

The material was highly selective for some toxic transition metal ions. Owing to the greater selectivity behaviour of the exchanger for some toxic transition metal ions, it may be utilized for the removal and recovery of these ions from dilute water samples. The exchanger is useful in environmental analysis and pollution control.

Recoveries of Cu(II), Cd(II) and Cr(VI) from 1000 ml water samples (pH ~2) were studied. The method is quite simple and highly selective for some ions. The samples were spiked with Cu(II), Cd(II) and Cr(VI) solutions respectively and analyzed by standard procedure. The average values of five determinations are summarized in Table 5. The results revealed quantitative recoveries. Sample solutions containing Cu(II) and Cr(VI) and foreign metal ions Zn(II), Mn(II), Ni(II), Au(III) and Pt(IV) (2mg each) were prepared. All the foreign metal ions were washed away with 50 mL of HCl (0.2 mol / dm³). The determination of Cu (II) or Cr (VI) was carried out by standard procedure. The recovery

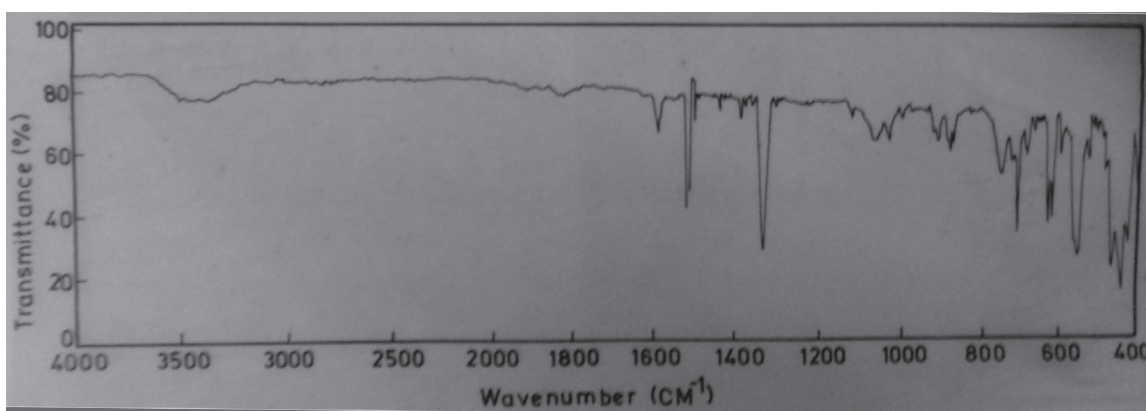


Fig. 2. Infrared spectrum of antimony (V) silicate (Sample AS₁)

Table 4. Quantitative separations of metal ions on antimony (V) silicate (Sample AS₁) columns.

Sl. No.	Metal ions	Eluents	Eluate (ml)	Amount loaded (µg)	Amount recovered (µg)	Error (%)
1.	Zn(II)	0.5 mol/dm ³ NH ₄ Cl	40	187	185	1.06
	Cd(II)	1mol/dm ³ NH ₄ Cl + 0.1mol/dm ³ HCl	40	236	233	1.27
	Hg(II)	0.01mol/dm ³ EDTA+0.1 mol/dm ³ HCl	50	250	252	0.80
2.	Fe(III)	0.5 mol/dm ³ NH ₄ Cl	40	223	225	0.89
	Ni(II)	1mol/dm ³ NH ₄ Cl + 0.1mol/dm ³ HCl	50	225	222	1.33
	Cr(VI)	0.1% DPC + 0.1mol/dm ³ HCl	50	262	266	1.52
3.	Cu(II)	0.1 mol/dm ³ NH ₄ Cl	50	317	313	1.26
	Co(II)	1mol/dm ³ NH ₄ Cl	40	118	116	1.69
	Hg(II)	0.01 mol/dm ³ EDTA+0.1mol/dm ³ HCl	50	212	213	0.47
4.	Au(III)	1mol/dm ³ Thiourea+0.1mol/dm ³ HCl	30	197	197	0.00
	Cu(II)	0.1 mol/dm ³ HCl	40	327	323	1.22
	Al(III)	0.01 mol/dm ³ EDTA+0.1mol/dm ³ HCl	50	260	260	0.00
5.	Fe(III)	1mol/dm NH ₄ Cl	30	223	223	0.00
	Pt(IV)	5% KI +0.1mol/dm ³ HCl	40	195	194	0.50
	Ru(VIII)	0.1mol/dm ³ Thiourea+0.1mol/dm ³ HCl	50	200	202	1.00
6.	Mn(II)	0.1mol/dm ³ HCl	30	440	440	0.00
	Ni(II)	1mol/dm ³ NH ₄ Cl +0.1mol/dm ³ HCl	50	228	226	0.87
7.	Zn(II)	0.5 mol/dm ³ NH ₄ Cl	30	262	262	0.00
	Pb(II)	1mol/dm ³ NH ₄ Cl +0.1mol/dm ³ HCl	50	404	408	0.99

Table 5. Recovery of Cu (II), Cd (II) and Cr (VI) ions from 1000 mL water samples of each (five replicates)

Ions Measured	Added (µg)	Found (µg)	Recovery (%)
Cu (II)	157	155	98.7
	638	632	9.0
Cd(II)	238	236	99.1
	1123	1115	9.3
Cr(VI)	266	263	98.8
	520	512	8.4

Table 6. Recovery of Cu(II) and Cr(VI) ions in the presence of foreign metal ions : Zn (II), Mn(II), Ni(II), Au(III) and Pt (IV).

Ions Measured	Added (µg)	Found	Recovery (%)
Cu (II)	159	160	100.6
Cu (II)	235	239	101.7
Cu (II)	634	639	100.8
Cu (II)	262	264	100.8
Cu (II)	522	527	101.0

data reveal that the presence of these foreign metal ions does not cause a significant error (Table 6).

CONCLUSIONS

The results of the present study indicate the potential of antimony (V) silicate as a filtration/ ion exchange media for the removal of some toxic metal ions from water. These are common pollutants in industrial waste effluents and are hazardous if present in higher concentrations than the limit permitted. Water filters prepared from such material may prove useful for the treatment of industrial effluents.

ACKNOWLEDGEMENTS

All necessary research assistance from B.S.N.V P.G. College, Lucknow University, and from CDRI, Lucknow, Uttar Pradesh, India is gratefully acknowledged.

REFERENCES

- Furman, N.H. 1962. *Standard Methods of Chemical Analysis*. Van Nostrand, New York
- Inamuddin., Khan, S.A., Siddiqui, W.A and 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, Issue 2 : 841.
- Janardanan, C. and Aravinda, K. and Shan, K.K. 2001. *Separation of mercury (II) using antimony (III) tungstovanadate as an inorganic ion - exchanger*. *Indian J. Chem.* 40A (12) : 1356.
- Millward, G.E. and Moore, R.M. 1982. *The adsorption of Cu, Mn and Zn by iron oxy hydroxide in model estuarine solutions*. *Wat. Res.* 16 : 981.
- Mukherjee, A.K. and Mandal, S.K. 1984 *Studies on the lanthanum arsenate: Preparation, physiochemical properties and applications*. *Talanta*. 31(3): 195.
- Parikh, K., Pandit, B., Sudhakar, P. and Chaudasama, U. 2001. *Application of an inorganic ion - exchanger in waste water treatment*. *Pollution Research*. 20 (2) : 291.
- Pekarek, V. and Vesely, V. 1972. *Synthetic inorganic ion - exchangers - II salts of heteropolyacids, insoluble ferrocyanides, synthetic aluminosilicates and miscellaneous exchangers*. *Talanta*. 19(11) : 1245.
- Qureshi, M. and Nabi, S.A. 1972. *Synthesis and ion - exchange properties of thermally stable stannic selenite*. *Talanta*. 19 (9) : 1033.
- Scott, W.W. 1939. *Standard Methods of Chemical Analysis*. Van Nostrand, New York, 5 edn.
- Singh, D.K. and Darbari, A. 1988. *Synthesis, ion - exchange properties and analytical applications of anilinium tin (IV) phosphate*. *Bull. Chem. Soc. Jpn.*, 61: 1369.
- Singh, P., Rawat, J.P. and Rahman, N. 2003. *Synthesis and characterization of zirconium (IV) iodovanadate and its use as electron exchanger*. *Talanta*., 59, Issue 3 : 443. .
- Snell, F.D. and Snell, C.T. 1959 *Colorimetric Methods of analysis*. D. Van Nostrand, New York,
- Yavari, R., Ahmadi, S.J., Huang, Y.D., Khanchi, A.R., Bagheri, G. and He, J.M. 2009. *Synthesis, characterization and analytical applications of a new inorganic cation exchanger - Titanium (IV) molybdophosphate*. *Talanta*. 77 (3) : 1179.