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Research Article

Development of Nanocomposite adsorbent, Electrical conductivity, Photolytic degradation and Analytical applications for the treatment of metals

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ABSTRACT

In this paper we describe synthesis of nanocomposite polyanilineTi (IV) as cation exchange adsorbent, electrical conductivity, photolytic degradation and analytical applications for the treatment of metals. The experimental parameters such as mixing volume ratio, concentration and pH were established for the synthesis of the material. Ion-exchange material was synthesized at pH 1.0 shows an ion exchange capacity of 1.37 meq g-1 for Na+ ions. Bifunctional behavior of the material has been indicated by its pH titrations curves. The material was found to be granular and can be conveniently used in column operations. The synthesized composite material exhibits improved thermal stability, ion exchange capacity and selectivity for heavy metal ions. The material was characterized by using analytical techniques namely FTIR, TGA-DTA, XRD, SEM, TEM and elemental analysis. The distribution coefficient studies of metal ions on the material were performed in different concentration of surfactants and the mixture (solvent + surfactant). On the basis of Kd values the material was found to be selective for Hg (II), Bi (III), Zr (IV) and Pb (II) ions. Some binary separations of metal ions in synthetic mixtures were achieved on the column of the above cited composite ion exchanger.

Keywords: Nanocomposite polyanilineTi (IV), FTIR, TGA-DTA, XRD, SEM, TEM.

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C H E M I S T R Y   **R E S E A R C H   A R T I C L E**

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1. INTRODUCTION

Water pollution by heavy metals remains an important environmental issue associated negatively with health and economy [1]. A number of chemical and biological contaminants have affected the quality of drinking water [2]. Wastewaters containing toxic metals (Pb2+, Cd2+, Hg2+, Bi3+, Th4+, Zr4+ etc.) are generated as a by-product from metallurgical, galvanizing, metal finishing, electroplating, mining, power regeneration, electronic device manufacturing and tannery industries which were found to be hazardous to the health [3, 4].

The use of lead in the industries (lead-acid batteries, lead wire or pipes, metal recycling and foundries) is one of the causes of environmental contamination [5, 6]. Lead poisoning interferes with a variety of body processes and is toxic to many organs and tissues causing potentially permanent learning and behavior disorders. Children living near industrial areas that process lead such as smelters have been found to have unusually high blood lead levels [7]. Besides human beings, plants and animals are also affected by its toxicity. The critically endangered California condor has also been affected by lead poisoning [8]. Mercury accumulated in the body enters the brain cells through an oxidation reaction and turns into inorganic ions (Hg2+) [9, 10].

A number of techniques have been developed for the treatment of such waste streams. Among these, ion-exchange method has several advantages over other methods because it is relatively clean and energy efficient method which also features selectivity for certain ions even in solutions of low concentration of the target ion from industrial wastes [11-13]. For this

purpose, inorganic ion-exchangers and organic resins have been used but they suffer certain limitations. The main drawbacks existing with inorganic ion-exchanger is low mechanical and chemical strength and obtaining in powdered form which is not suitable for column applications. The serious limitations of organic resins are its poor thermal and chemical stability [14]. Hence, in order to overcome all these barriers, there is continuous need to investigate novel composite ion-exchangers which are capable of removing heavy metals from industrial wastes [15]. These show better exchange capacity, granulometric properties, reproducibility, chemical and thermal stability, and also possess good selectivity for heavy metals as compared to pure inorganic and organic materials. Polyaniline based composite materials have been in the forefront of the global search for commercially available conducting polymers because of its unique proton dopability, low cost, ease of synthesis, excellent redox recyclability, variable electrical conductivity, thermal and chemical stability [16, 17].

Owing to the above mentioned advantages, they can be used as a ion-exchanger [18-20], as catalyst [21], as an ion selective electrode [22], conducting material [23] and also it finds a large number of applications in pollution control and water treatment which are of economic importance. Characterization of polyanilineTi(IV)As with better thermal and chemical stability and their applications in the separation of heavy metals, photochemical degradation of dye as well as conducting material. This paper reports significant ion exchange capacity (1.37 meq g-1) and thermal stability (78 % retention of IEC up to 400°C) [24].

2. EXPERIMENTAL SECTION

A. Materials and Methods:

The main reagents for the synthesis were aniline, potassium persulphate, titanium tetra chloride, carbon tetrachloride, tween 80 and cetyl pyridinium chlorides (CPC) that were from E-Merck (India) and sodium arsenate was from CDH (India), and Acid Blue 29 (AB 29) was from Sigma Aldrich. A solution of sodium arsenate (0.25M) was prepared in

demineralized water and 1% solution of $TiCl_4$ was prepared in CCl_4 while 10% solution (v/v) of aniline and 0.1 M potassium persulphate were prepared in 1M HCl solution. For the spectrophotometric determination of Hg (II), solutions of mercury (I1) chloride (1 mg mL-1, 0.3385 g of mercury (I1) chloride in water and dilute to 250 mL), phenanthroline monohydrate (0.05%), acetate buffer (pH 4.5), Eosin (0.05 %.), EDTA (0.05 M) and Gelatine (0.05%) were prepared in demineralized water and stored in an amber-Coloured bottle.

B. Procedure for the photochemical degradation:

The degradation of composite material was carried out using UV-vis spectrophotometer. The experiment was carried out in an immersion well photochemical reactor. For the photochemical irradiation, 0.06M solution of dye (AB29) prepared in 250mL DMW and filled into the reactor. A fixed amount of composite material (0.25g) was added. The solution was stirred for 20 minutes in the dark to allow equilibration, and the reading at zero time was measured from blank solution otherwise treated similarly to the irradiated solution. The atmospheric oxygen was continuously supplied into the suspensions throughout the experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (radiant flux ≈ 2150 μWcm−2). The short-wavelength UV and IR radiations were eliminated by circulating water around pyrex glass jacket. The samples were collected in 10.0 mL fraction before and at regular intervals during irradiation for analysis after centrifugation. The calibration curve was obtained from the absorbance at different concentrations (mole L−1 min−1).

C. Synthesis of inorganic precipitate (Ti (IV) arsenate):

The gel of Ti(IV)As was synthesized by the addition of $TiCl_4$ (0.1M) and sodium arsenate tungstate (0.25M) solutions steadily with continuous stirring at 25±°C for 1h whereby a gel type slurries was obtained. The pH of the solution was adjusted (pH=1.0) by adding dilute solution of HCl or HNO_3. The resulting white precipitate so formed was kept overnight in the mother liquor for digestion.

D. Synthesis of organic-inorganic (polyanilineTi(IV)As) ion exchange material:

PolyanilineTi(IV)As was prepared by the mixing of polyaniline gel and inorganic precipitate in a volume ratio of 1:1 thoroughly with continuous stirring for 1 h at 25±2°C. The resultant green gel obtained was kept for 24 h at 25±°C for digestion. The supernatant liquid was decanted, and gel was filtered under suction. The impurity of acid was separated by washing the material with demineralized water and dried at 50±2°C. The dried material was converted into H+ form by treating with nitric acid solution (1.0M) for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess of acid was isolated by numerous washing the material with demineralized water and finally dried at 50±2°C. Thus, under diverse conditions of mixing ratio of the reactant's ratio, pH and temperature, a number of samples of 'polyanilineTi (IV) As' were prepared (Table 4.1). Based on highest uptake capacity, physical appearance of the beads together with percentage yield, sample A-6 was selected for exhaustive studies. The proposed structure of the composite material is shown below Scheme 4.0.

E. Synthesis of polyanilineTi(IV)As composite samples for the electrical measurements:

For the measurement of electrical conductivity, a number of samples of composite material were prepared by adding varied the amount of inorganic precipitate (in different weight ratios of 5, 10, 15, 20, 25 wt. % of Ti (IV) As) to the polyaniline gels using the same procedure as described above. The prepared samples of polyanilineTi (IV) As composite were labeled as As-1(PANI), As-2, As-3, As-4, As-5 and As-6 (Table 4.2).

F. Distribution (sorption) studies and quantitative separations of metal ions in synthetic binary mixtures:

The distribution coefficient (Kd) values and quantitative separations of some important metal ions of analytical utility were achieved on polyanilineTi (IV) arsenate columns by the same procedure as described.

G. Chemical composition:

The composition of the sample was determined by dissolving a portion of 0.25 g exchanger in 15 mL hot concentrated hydrochloric acid. The solution was evaporated to near dryness then cooled and diluted to 100 mL with distilled water. Titanium and arsenate were determined spectrophotometrically using standard procedures.

H. Leaching effect of arsenic:

To observed the leaching effect of arsenic into the solution, a fixed amount of the material (0.3g) was immerse into the aqueous solution of HCl, NaOH (0.1M) and DMW (30 mL each) with occasional shaking intermittently for 24 h. The solution was filtered through Millipore cellulose membrane filter (0.45μm pore size). The amount of arsenic ions in the solution was determined by EDTA back titration using Eriochrome Black T indicator [27].

I. Selective separation of Bi3+, Hg2+ and Zr4+ from synthetic mixtures of metal ions:

Selective separation of Bi3+, Hg2+ and Zr4+ from the synthetic mixtures containing (Zn2+, Ca2+, Cd2+, Mn2+, Al3+, Bi3+, La3+), (Mg2+, Zn2+, Ca2+, Mn2+, Hg2+, Ni2+, Co2+) and (Mn2+, Zn2+, Sr2+, Ca2+, Co2+, Zr4+, Al3+) were achieved on polyanilineTi(IV)arsenate columns. The amount of the Bi2+, Hg2+ and Zr4+ ions in the synthetic mixtures was varied keeping amount of the other metal ions constant.

J. Determination of Pb2+ and Zn2+ in brass industry waste using polyanilineTi (IV) As columns by FAAS:

Industrial wastes were collected from industrial area (brass industry waste) of Aligarh City. An aliquot of a solution (50 mL) was taken as the model solution. It was then converted into clear solution by adding a small amount of nitric acid, stirred thoroughly until a clear solution was obtained and filtered off. The pH of the solution was adjusted to the optimal value with HCl or NH3. The resulting solution was made passed through the column by a flow rate adjusted to the optimal value. The adsorbed metal ions on the exchanger was eluted with 10 mL of 0.5% tween 80

solution and aspirated into an air-acetylene flame for the determination of Pb2+ and Zn2+ by FAAS.

K. Determination of Hg2+ ions in brass industry waste using polyanilineTi(IV)arsenate columns by spectrophotometric method:

For the spectrophotometric determination of Hg2+, a series of solutions containing 2.5-30 µg of Hg2+ was prepared by adding 1.0 mL of 0.05 M EDTA solution, 5 mL of pH 4.5 buffer, 2 mL of 0.05% 1,10-phenanthroline solution and 1 mL of 0.05% gelatine solution. After mixing the contents 5 mL of 0.05% eosin solution added and diluted up to 25 mL. The absorbance of the sample solutions was measured at 552 nm against a reagent blank and calibration graph was prepared for 2.5-30 µg of mercury.

3. RESULTS AND DISCUSSION

Results obtained from the synthesis of composite material (Table 4.1) indicate that ion-exchange capacity of composite material depends upon the pH. In order to investigate the working capacity of the exchanger, the ion-exchange capacity of some monovalent and divalent cations were determined (Table 4.3). The affinity sequence for monovalent ions was found to be K+> Na+> Li+ and for bivalent ions it was Mg2+> Ca2+> Sr2+. The ions with smaller hydrated radii easily enter the pores of the exchanger, resulting higher adsorption [29, 30]. From these observations it was found that the material shows greater exchange capacity for alkali metal ions than that of alkaline earth metal ions.

For complete removal of H+ ions from the exchanger, optimum concentration of the eluent was found to be 1.0M (Fig. 4.1). The experiment also established the minimum volume required for the complete elution of H+ ions which reflect the column efficiency. It was observed from Fig. 4.2 that the rate of exchange was fairly fast in the beginning as only 60 mL of NaNO3 solution (1.0 M) is sufficient for complete elution of H+ ions from the column containing 1.0 g exchanger. From this observation, it has been confirmed that the efficiency of the column is quite satisfactory. For complete removal of H+

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4. CONCLUSION

Semi-crystalline polyanilineTi (IV) as nano-composite cation exchanger shows selective behavior towards heavy-metal ions and can withstand fairly high temperature. It retains significant ion-exchange capacity up to 300°C. It can be used for the quantitative separation of metal ions from a binary mixture of analytical importance. Determination of Pb2+ and Zn2+ ions from tap water and industrial wastewater samples by FAAS do not require pretreatment. The characteristics of a promising ion-exchanger which can be explored for other applications. Electrical conductivity measurement and photochemical degradation results indicate that the composite material can be used as conducting material as well as a photo catalyst for the degradation of textile industry dye.
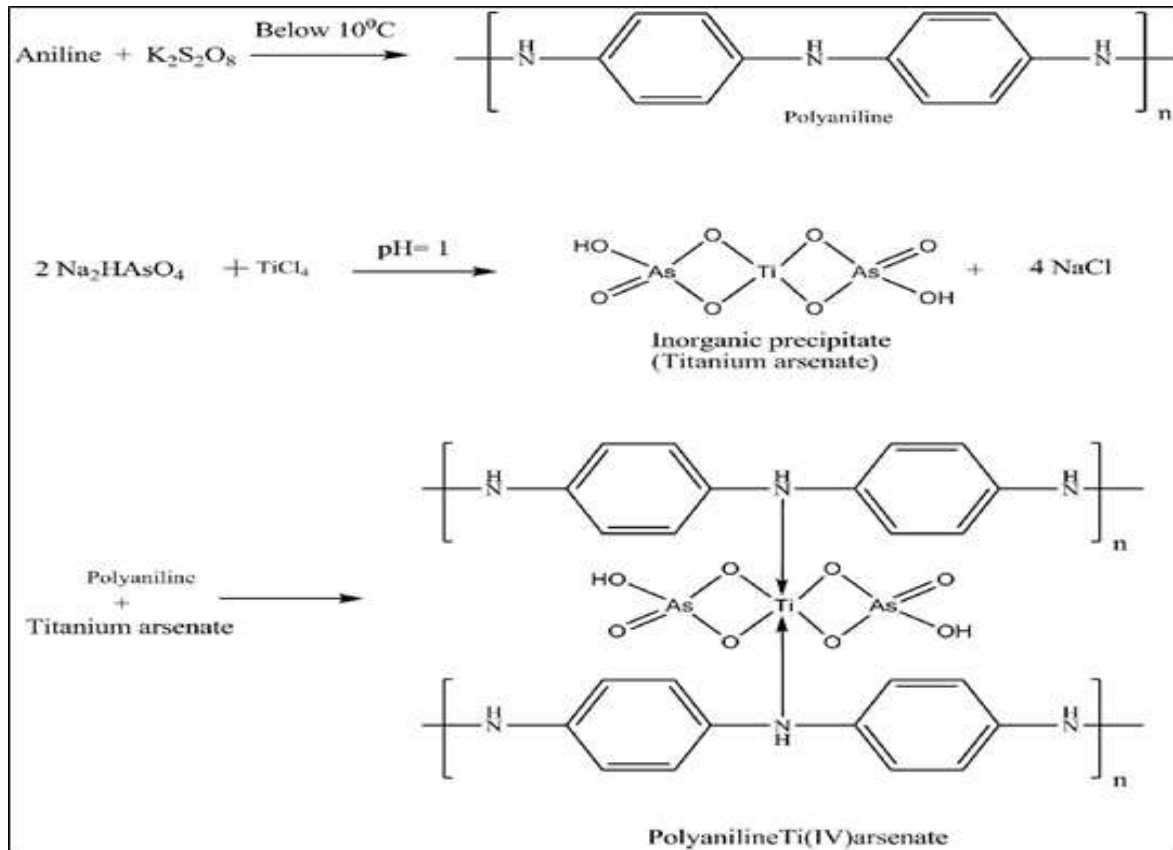
Scheme 4.0

Table 4.1 Conditions for the synthesis of polyanilineTi (IV) As cation exchanger.

S.No	A	B	C (%) v/v	Mixing ratio v/v/v	Temperature	pH	Appearance of bead	IEC for Na⁺ ions	Yield (g)
A-1	0.25	0.1	--	1:1	25±2ºC	0.5	White granular	0.75	1.62
A-2	0.20	0.1	--	1:1	25±2ºC	1.0	White granular	0.99	1.96
A-3	0.25	0.1	--	1:1	100±2ºC	1.0	White granular	0.70	2.01
A-4	0.25	0.1	--	1:1	25±2ºC	1.5	Green granular	1.00	2.90
A-5	0.25	0.1	10	1:1:1	25±2ºC	0.5	Green granular	1.10	2.30
A-6	0.25	0.1	10	1:1:1	25±2ºC	1.0	Green granular	1.37	3.99
A-7	0.25	0.1	10	1:1:1	100±2ºC	1.0	Green granular	1.00	3.30
A-8	0.25	0.1	10	1:1:1	25±2ºC	1.5	White granular	0.90	3.45

A. Sodium arsenate (Mol L-1), B. Titanium tetrachloride (Mol L-1), C. Polyaniline, IEC. Ion Exchange Capacity (meq g–1)

Table 4.2 Conditions for the synthesis of polyanilineTi (IV) as composite in different volume ratio at 25± 2ºC (pH=1).

Samples	Stock solution (10% polyaniline)/ (mL)	Ti(IV)As	Yield	Pellet thickness (mm)	Conductivity
As-1 (PANI)	100	0.0	0.290	0.92	0.028
As-2	100	5	0.449	1.55	1.77
As-3	100	10	0.519	1.20	3.20
As-4	100	15	1.956	1.45	5.61
As-5	100	20	1.640	1.39	4.31
As-6	100	25	1.587	1.44	0.043

Table 4.3 Ion-exchange capacity of exchanger on different exchanging ions on the column of polyanilineTi (IV) as.

Exchanging ions	Ionic radii (A°)	Hydrated ionic radii (A°)	IEC (meq g^{-1})
Li$^+$	0.68	3.40	0.98
Na$^+$	0.97	2.76	1.37
K$^+$	1.33	2.32	1.45
Mg^{2+}	0.78	7.00	0.78
Ca^{2+}	1.43	5.90	0.71
Sr^{2+}	1.27	6.30	0.67

IEC ion Exchange Capacity

Table 4.4 Effect of temperature on the ion-exchange capacity of polyanilineTi (IV) as cation exchanger on heating time for 1 h.

Temperature (ºC)	Colour	% Weight loss	% Retention of IEC
50	Green	0.0	100
100	Green	0.0	100
200	Dark black	0.0	100
300	Dark black	2	98
400	Black and white	36	78
500	Dirty white	44	55
600	Dark grey	75	47
700	White	76	18

Table 4.5a Distribution coefficients (mLg^{-1}) of different metal ions on polyanilineTi (IV) as cation exchanger in different surfactants systems.

Metal ions	Tween80 0.25 %(a)	Tween80 0.5 %(b)	Tween 80 1 %(c)	Tween 80 2 %(d)	CPC 0.25 %(e)	CPC 0.50 %(f)	CPC 1 %(g)	CPC 2 %(h)
Mg^{2+}	11	18	2	12	33	47	0	0
Zn^{2+}	12	5	4	13	57	6	0	0
Sr^{2+}	23	35	7	11	0	32	0	0
Ca^{2+}	13	28	3	9	0	14	0	0
Ba^{2+}	54	50	70	43	0	50	0	0
Pb^{2+}	308	111	169	134	350	304	0	0
Cd^{2+}	24	37	2	3	150	8	0	0
Mn^{2+}	14	22	11	26	6	28	0	0
Cu^{2+}	47	69	59	25	105	62	0	0
Ni^{2+}	18	50	18	34	28	34	0	0
Hg^{2+}	1900	660	1071	900	1600	11420	0	0
Co^{2+}	18	38	4	6	35	32	0	0
Al^{3+}	56	53	26	79	25	64	0	0
Fe^{3+}	100	165	145	147	138	230	0	0
La^{3+}	172	102	14	200	53	40	0	0
Bi^{3+}	88	800	1700	300	80	1900	0	0
Zr^{4+}	350	450	87	233	236	365	0	0

CPC. Cetyl pyridinium chloride.

Table 4.5b Distribution coefficients (mLg⁻¹) of different metal ions on polyanilineTi(IV)As in mixture (solvent+surfactant) systems.

Metal ions	0.1M (i)	1.0:1% (j)	0.1:1% (k)	0.01:1% (l)	0.001:1% (m)
Mg^{2+}	9	1	13	4	13
Zn^{2+}	14	6	13	4	16
Sr^{2+}	16	22	264	2	16
Ca^{2+}	22	7	6	2	16
Ba^{2+}	53	43	52	37	62
Pb^{2+}	250	538	11	194	323
Cd^{2+}	22	18	32	26	24
Mn^{2+}	27	28	6	5	8
Cu^{2+}	61	62	83	36	40
Ni^{2+}	22	4	22	14	4
Hg^{2+}	1075	600	1700	3400	27
Co^{2+}	25	25	9	18	133
Al^{3+}	90	54	52	58	83
Fe^{3+}	139	67	176	152	70
La^{3+}	230	113	217	189	150
Bi^{3+}	367	25	160	400	1600
Zr^{4+}	18	1900	133	3300	200

i. 1M DMSO, j. 1M DMSO: 1% Tween 80, k. 0.1M DMSO: 1% Tween 80, l. 0.01M DMSO: 1% Tween 80, m. 0.001M DMSO: 1%Tween80.

Table 4.6 Quantitative separation of metal ions from a binary mixture using polyanilineTi(IV)As cation exchanger columns at room temperature.

S. No.	Metal ions separation	Amount loaded (mg)	Amount found (mg)	(%) Recovery	Volume of eluent used (mL)	Eluent used
1	Zn^{2+}	6.53	6.30	96.50	70	1:0.1%
	Pb^{2+}	2.07	1.97	95.50	80	0.1:1%
2	Ca^{2+}	4.00	3.88	97.00	50	1:0.1%
	Pb^{2+}	2.07	1.95	94.50	90	0.1:1%
3	Cd^{2+}	11.24	10.84	96.50	60	1:0.1%
	Pb^{2+}	2.07	1.97	95.50	70	0.1M DMSO

4	Cd^{2+}	11.24	10.82	97.00	60	0.25 % Tween 80
	Hg^{2+}	20.05	19.14	95.50	70	0.001:1%
5	Al^{3+}	2.69	2.54	94.50	70	0.25 % Tween 80
	Hg^{2+}	20.05	18.74	93.50	70	0.001:1%
6	Fe^{3+}	5.56	5.35	96.00	70	0.01:1%
	Zr^{4+}	9.13	8.89	97.50	70	1 % Tween 80
7	Sr^{2+}	8.76	8.58	98.00	60	0.01:1%
	Zr^{4+}	9.14	8.84	97.00	80	1 % Tween 80
8	Ca^{2+}	4.00	3.86	96.50	60	0.01:1%
	Zr^{4+}	9.12	8.84	97.0	80	1 % Tween 80

Table 4.7 Selective separations of Bi^{3+} ions from a synthetic mixtures containing Zn^{2+}, Ca^{2+}, Cd^{2+}, Mn^{2+}, Al^{3+}, Bi^{3+} and La^{3+} ions on the columns of polyanilineTi(IV)As cation exchanger.

S. No.	Amount of Bi^{3+} loaded (mg)	Amount of Bi^{3+} found* (mg)	% Recovery	Eluent used	Eluent volume (mL)
1	2.95	2.80	94	CPC (0.50%)	90
2	5.90	5.74	97	CPC (0.50%)	90
3	8.86	8.50	95	CPC (0.50%)	100

* Average of five replicate determinations

Table 4.8 Selective separations of Hg^{2+} ions from a synthetic mixtures containing Mg^{2+}, Zn^{2+}, Ca^{2+}, Mn^{2+}, Hg^{2+}, Ni^{2+} and Co^{2+} ions on columns of polyanilineTi(IV)As cation exchanger.

S. No.	Amount of Hg^{2+} loaded (mg)	Amount of Hg^{2+} found* (mg)	(%) Recovery	Eluent used	Eluent volume (mL)
1	2.85	2.72	95	0.25 % Tween 80	90
2	5.72	5.49	96	0.25 % Tween 80	110
3	8.56	8.14	95	0.25 % Tween 80	100

* Average of five replicate determinations

Table 4.9 Selective separations of Zr^{4+} from a synthetic mixtures containing Mn^{2+}, Zn^{2+}, Sr^{2+}, Ca^{2+}, Co^{2+}, Zr^{4+} and Al^{3+} ions on the columns of polyanilineTi(IV)As cation exchanger.

S. No.	Amount of Zr^{4+} loaded (mg)	Amount of Zr^{4+} found* (mg)	% Recovery	Eluent used	Eluent volume (mL)
1	1.30	1.24	94	0.01M DMSO: 1% Tween	100
2	2.60	2.46	95	0.01M DMSO: 1% Tween	90
3	3.91	3.76	96	0.01M DMSO: 1% Tween	100

* Average of five replicate determinations

Table 4.10 Determination of Pb^{2+}, Hg^{2+} and Zn^{2+} ions in electroplating industrial waste and natural water samples on the columns of polyanilineTi(IV)As cation exchanger. Experimental conditions: 100mL solution, sorption flow rate 2.0mLmin^{-1}, 0.25 g exchanger.

Samples	Method	Amount of Pb^{2+} found[a] ($\mu g\ L^{-1}$) (%RSD)[b]	Amount of Hg^{2+} found[a] ($\mu g\ L^{-1}$) (%RSD)[b]	Amount of Zn^{2+} found* ($\mu g\ L^{-1}$) (%RSD)[b]
Brass industry wastewater	Direct[a]	9.1 (3.2)	9.9 (2.8)	11.4 (2.8)
	SA[c]	9.3 (2.9)	10.5 (2.2)	11.5 (2.2)
Aligarh Tap water (A.M.U. Campus, Aligarh)	Direct	--	--	10.1 (1.81)
	SA	4.3 (3.8)	10.0 (2.3)	10.0 (2.3)

a. Average of three replicate determinations, b. % RSD, Relative standard deviation, '–' indicates not detected, c. Recommended procedure applied without spiking, c. Recommended procedure after spiking (standard addition method).

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