



# Development of Titanium-Supported Ion-Exchange Adsorbent for Removal of Metal Pollutants

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## Abstract

An ethylenediaminetetraacetate-supported ethylenediaminetetraacetate–Ti(IV) phosphate (ETP) hybrid ion-exchange material has been synthesized using sol–gel chemical route. Characterization of ETP has been carried out using Fourier transform infrared spectroscopy, thermogravimetric analysis (TGA/DTA), X-ray diffraction (XRD), and scanning electron microscopy (SEM) analyses. Semicrystalline morphology of the material was identified via XRD and SEM analyses. The material was explored for the removal of metal ions from real and synthetic wastewaters. The hybrid material showed good ion-uptake capacity for Ba<sup>2+</sup> ion (2.9 eq kg<sup>-1</sup>). In terms of thermal stability, ETP has potential to resist up to 200 °C with retention of 98% initial ion-uptake capacity. Studies on the distribution coefficients using solvents (CH<sub>3</sub>CN, ACOH) and surfactant (CTAB) verified their selective behavior toward Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Bi<sup>3+</sup> and Th<sup>4+</sup>. Separations of some metal ion in binary mixtures and natural waters have been achieved using columns of this material.

**Keywords** Wastewater treatment · Separation of metal ion · Synthesis · Characterization · Environmental application · Water pollution

## 1 Introduction

Wastewater streams from textile and battery industries, mining and mineral processing industries contain heavy metals, which has become a serious environmental problem [1–5]. Heavy metal ions are necessary for living beings as micronutrient; however, their excessive absorption has severe lethal effects [6–8]. These metal ions are commonly introduced to the water bodies through the textile, chemical and paints effluents and result in affecting lives of flora and fauna [9–15]. The metals get slowly accumulated in the different parts of body (e.g., kidneys, liver, pancreas, bones, central nervous system, reproductive system and brain) and ultimately result in organ failure or produce a number of diseases [16–19]. The impairments by metal ions to the environment has made the treatment of such metals a top

priority in wastewater treatment [20,21]. Different physical and chemical methods including adsorption, precipitation, filtration and ion-exchange have been reportedly used for the removal of metal ions [22–27]. Among these methods, ion-exchange method is found to be the most favoured method due to its high efficiency, easy handling, low cost as well as easy regeneration [28]. For treatment of waters, a number of organic–inorganic ion-exchange materials are studied [25,29–38]. Titanium-based hybrid ion-exchange adsorbents have been fabricated [32,37,39–42] possessing highly selective behavior for certain metal ions in environmental waters. In the present study, the fabrication of ethylenediaminetetraacetic acid (EDTA)–Ti(IV) phosphate and its application for the treatment of metal ions from natural and industrial wastewaters have been analyzed.

## 2 Materials and Methods

### 2.1 Chemicals and Reagents

All chemicals used were of analytical grade and employed without further purification. Titanium tetrachloride (TiCl<sub>4</sub>), carbon tetrachloride (CCl<sub>4</sub>), orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>),

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hydrochloric acid (HCl), perchloric acid (HClO<sub>4</sub>), nitric acid (HNO<sub>3</sub>), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), acetone (CH<sub>3</sub>COCH<sub>3</sub>), methanol (CH<sub>3</sub>OH), acetic acid (CH<sub>3</sub>COOH) (ACOH), formaldehyde (HCHO), formic acid (HCOOH), sodium hydroxide (NaOH), potassium hydroxide (KOH) and ammonia (NH<sub>3</sub>) were procured from Merck (New Delhi, India), and EDTA was obtained from Qualigens Fine Chemicals (New Delhi, India). Solutions of EDTA (0.1 mol L<sup>-1</sup>) and orthophosphoric acid (0.1 mol L<sup>-1</sup>) and cetyl trimethylammonium bromide (CTAB) (0.1 mol L<sup>-1</sup>) were prepared with demineralized water (DMW), and a TiCl<sub>4</sub> (1%) solution was prepared in CCl<sub>4</sub>.

## 2.2 Apparatus

Thermogravimetric analysis/differential thermal analysis (TGA/DTA) was carried out (DTG—60 H; C305743 00134, Shimadzu, Kyoto, Japan) at a rate of 10 °C min<sup>-1</sup> in nitrogen atmosphere. A digital pH meter (EL-10, Elico, New Delhi, India) was used for pH measurements. Fourier transform infrared (FTIR) spectra (1730, Perkin Elmer, Waltham, Massachusetts 02451, USA) were recorded using the KBr disk method. An analytical diffractometer (X' Pert PRO PW-3040/60, PANalytical, Almelo, The Netherlands, with CuK  $\alpha$  radiation  $\lambda = 1.5418 \text{ \AA}$ ) was used for X-ray diffraction measurements. Flame atomic absorption spectrometric (FAAS) measurements were recorded (Model 932-Plus, GBC Scientific, Braeside, Australia). A scanning electron microscope (SEM); LEO, 435 VF) was used to observe surface morphology at different magnifications. A temperature-controlled shaker (MSW-275, Rurkee, India) and a muffle furnace (Narang Scientific Works, New Delhi, India) were employed for heating material at different temperatures.

## 2.3 Synthesis of EDTA–Ti(IV) Phosphate

EDTA–Ti(IV) phosphate was synthesized by adding gradually a 1:1 mixture of aqueous solutions of EDTA and H<sub>3</sub>PO<sub>4</sub> (0.1 mol L<sup>-1</sup> each) to a solution of 1% TiCl<sub>4</sub> in CCl<sub>4</sub> (1:1) under continuous stirring for 1 h at room temperature (25 ± 2 °C). The obtained white precipitate was kept for 24 h at 25 ± 2 °C for digestion. An aqueous nitric acid solution (1.0 mol L<sup>-1</sup>) was used to adjust the pH to 0.5–1.5. The supernatant liquid was pour out, and precipitate was filtered through Whatman No.1 filter paper under suction. Excess reagents were removed by washing with DMW, and the precipitate was dehydrated in an oven at 50 ± 2 °C for 24 h. It was then ground in a pestle mortar to reduce into smaller particles and sieved with wire mesh cloth to get particle fractions in the size range of 100–150 mesh. The desired sized particles (100–150 mesh) were converted into the H<sup>+</sup> form by treating with 1.0 mol L<sup>-1</sup> nitric acid solution for 24 h, intermittently

replacing the supernatant liquid with fresh acid. The material was washed several times with DMW to remove excess acid and was finally dried at 50 ± 2 °C for 24 h.

## 2.4 Ion-Exchange Potential (IEP)

An aliquot of 1.0 g composite material (the H<sup>+</sup> form) was fit in a glass column with a fixed internal diameter (0.5 cm, length 25 cm) consisting glass wool at the bottom. The H<sup>+</sup> ions were excluded by passing a fixed volume (250 mL) of NaNO<sub>3</sub> solution (0.1 mol L<sup>-1</sup>) at a constant flow rate (2.0 mL min<sup>-1</sup>). The concentration of H<sup>+</sup> ion in the effluent was determined by using standard method of sodium hydroxide titration [13].

## 2.5 The pH Titration

According to Topp and Pepper [43,44], aliquots of 0.5 g exchanger in the H<sup>+</sup> form were taken into 50-mL conical flasks followed by addition of 0.1 mol L<sup>-1</sup> aqueous solutions containing LiCl, NaCl, or KCl (0, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 10, 15, 20, 30, 40, 45 and 50 mL) and 0.1 mol L<sup>-1</sup> of the corresponding hydroxides LiOH, NaOH or KOH (50, 45, 40, 30, 20, 15, 10, 5.0, 4.0, 3.0, 2.5, 2.0, 1.5, 1.0, 0 mL). The total volume of the solution was maintained as 50 mL.

## 2.6 The Consequence of Concentration

A fixed volume (250 mL) of different contents (0.25, 0.50, 0.75, 1.0, 1.25 and 1.50 mol L<sup>-1</sup>) of sodium nitrate solutions was used at a fixed flow rate (2.0 mL min<sup>-1</sup>) for elution of the counter ions consisting in a column containing 0.5 g adsorbent. The effluent was titrated using standard method of NaOH titration (1.0 mol L<sup>-1</sup>).

## 2.7 The Effect of Solvent Elution

A fixed amount of composite adsorbent (0.5 g) fit in a glass column and the H<sup>+</sup> was eluted using 1.0 mol L<sup>-1</sup> sodium nitrate solution. The flow rate of effluent was 2.0 mL min<sup>-1</sup>, and the effluent was collected in 10.0 mL fraction. Each volume (10 mL) of effluent was titrated using standard solution method of NaOH.

## 2.8 Distribution (Sorption) Studies

A fixed amount of (300 mg) hybrid adsorbent was taken in each 50-mL Erlenmeyer flask and mixed with a fixed volume (30 mL) of different metal nitrate solutions (0.1 mol L<sup>-1</sup>) in different solvents (as shown in Table 4), subsequently shaken for 6 h at 25 ± 2 °C to attain equilibrium [43,45]. The concentration of metal ion before and after equilibrium

was calculated using EDTA (0.005 mol L<sup>-1</sup>) standardization method [46]. The values of distribution coefficient were calculated as:

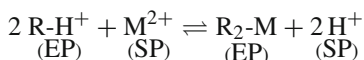
$$K_d = \frac{\text{Amount of metal ion retained in one gram of the exchanger phase (mg g}^{-1}\text{)}}{\text{Amount of metal ion in unit volume of the supernatant solution (mg mL}^{-1}\text{)}}$$

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

where *I* is the volume of EDTA used before treatment of metal ion exchanger.

*F* is the volume of EDTA consumed by metal ion left in solution phase.

For example:



EP = Exchanger phase, SP = Solution phase

R = EDTA–Ti(IV) phosphate

### 3 Results and Discussion

#### 3.1 Physicochemical Properties of EDTA–Ti(IV) Phosphate

Recently, various organic–inorganic ion-exchange composite materials have been prepared by incorporating transition metals ions (e.g., Zr, Mn, Ti, V, Mo, Cr, Sc, Sn, As) into the matrix of organic framework [25]. Among different metal ions, titanium-supported hybrid materials were established to have advantages over other composite materials owing to their significant chemical and thermal stability. In this regard, the samples of EDTA–Ti(IV) phosphate were synthesized using sol gel chemical route at different volume ratios of reactants and pH values as listed in Table 1 affecting the ion-uptake efficiency of adsorbent. On increasing the pH, the IEC may have decreased due to metal oxide formation.

**Table 1** Synthesis of EDTA–Ti(IV) phosphate cation exchanger

S. No	A (mol L <sup>-1</sup> )	B (mol L <sup>-1</sup> )	C (%)	Mixing ratio	pH	IEC (eq kg <sup>-1</sup> )	Yield (g)
M-1	0.10	0.10	–	1:1	0.5	1.80	1.98
M-2	0.10	0.10	–	1:1	1.0	1.60	2.20
M-3	0.10	0.10	–	1:1	1.5	2.10	2.40
M-4	0.10	0.10	1.0	1:1:1	0.5	2.52	2.58
M-5	0.10	0.10	1.0	1:1:1	1.0	2.44	3.13
M-6	0.10	0.10	1.0	1:1:1	1.5	2.15	2.16

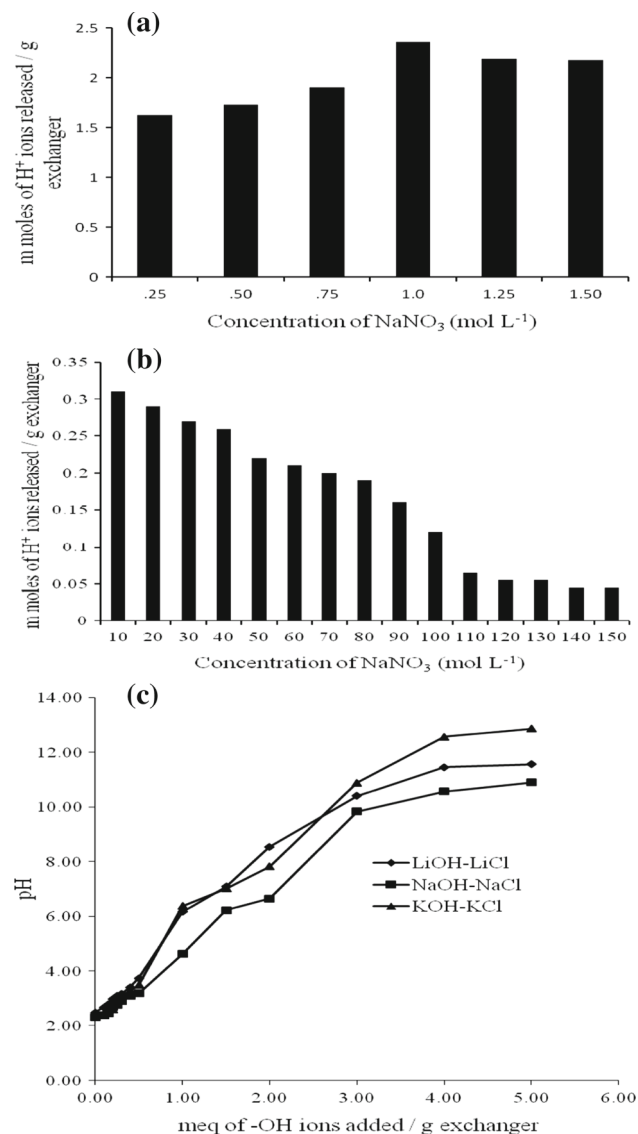
A. EDTA, B. orthophosphoric acid, C. TiCl<sub>4</sub> in CCl<sub>4</sub>

It is inferred from the date of ion-uptake potential (Table 2) of alkali and alkali earth metal ions that the affinity sequence of hydrated ionic radii for alkali and alkaline metal ions was

found to be as; K<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup> and Ba<sup>2+</sup> > Sr<sup>2+</sup> > Ca<sup>2+</sup> > Mg<sup>2+</sup>, respectively [35]. The ions with smaller hydrated radii easily enter the cavity of adsorbent resulting in improvement in adsorption capacity. The consequence of eluent dose and elution potential was determined to examine column effectiveness. The effect of eluent concentration (Fig. 1a) on the material was studied to estimate the attainable optimum ion-uptake efficiency of composite adsorbent using 1.0 mol L<sup>-1</sup> NaNO<sub>3</sub> solution. The elution behavior (Fig. 1b) indicated that only 50 mL NaNO<sub>3</sub> solution (1.0 mol L<sup>-1</sup>) was required for the elution of H<sup>+</sup> ions from the column (0.5 g adsorbent; ETP). From these examinations, it was established that the efficiency of material is good for column operation. Functional group of ETP (mono-, bi- and tri-functional) was determined using pH titration curves studies (LiOH–LiCl, NaOH–NaCl, or KOH–KCl) as shown in Fig. 1c. The pH titration curves showed two inflection points which estab-

**Table 2** Ion-exchange capacity (IEC) of EDTA–Ti(IV) phosphate cation exchanger for alkali and earth alkali ions

Exchanging ions	Ionic radii (A°) [53]	Hydrated ionic radii (A°)	IEC for Na <sup>+</sup> ions (eq kg <sup>-1</sup> )
Li <sup>+</sup>	0.68	3.40	1.75
Na <sup>+</sup>	0.97	2.76	2.52
K <sup>+</sup>	1.33	2.32	2.63
Mg <sup>2+</sup>	0.78	7.00	2.71
Ca <sup>2+</sup>	1.43	5.90	2.80
Sr <sup>2+</sup>	1.27	6.30	2.87
Ba <sup>2+</sup>	1.43	5.90	2.92

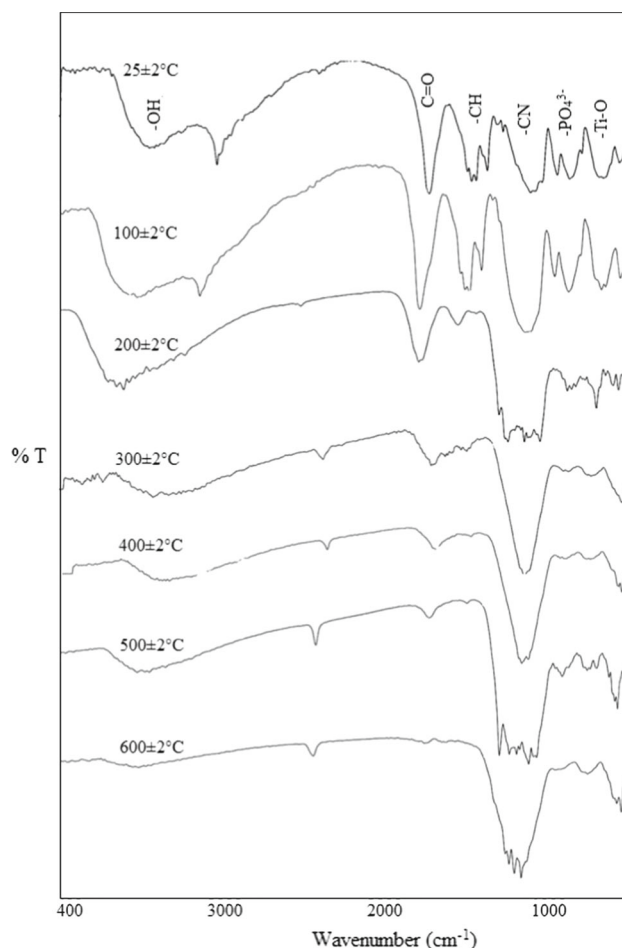


**Fig. 1** The effect of eluent concentration (a), the effect of elution behavior (b), the pH titration curves (c) of EDTA-Ti(IV) phosphate

lished bifunctional cation-exchange characteristics of ETP. The strong cation-exchange characteristic of the material was specified at the solution pH of 2.20. In the beginning, a sharp decrease in pH was observed owing to absence of OH<sup>-</sup> ions (the discharging of H<sup>+</sup> ions from the exchanger). Further, addition of base increased the pH of solution quickly, and beyond pH 10 the material started to hydrolyze.

### 3.2 FTIR, SEM and TEM Analyses

The FTIR spectra of EDTA-Ti(IV) phosphate (Fig. 2) showed merged bands in the region (3590–3100 cm<sup>-1</sup>) ascribed to OH<sup>-</sup> [47] and C–H symmetric and asymmetric stretching [48]. A sharp band at ~ 1665 cm<sup>-1</sup> may



**Fig. 2** FTIR spectra of EDTA-Ti(IV) phosphate at different temperatures

be attributed to the C=O stretching mode of EDTA [49], while an assembly of peaks near 1445 and ~ 750 cm<sup>-1</sup> was due to the presence of in plane bending of the CH-bands [50]. A middle intensity peak at 1320 cm<sup>-1</sup> revealed the existence of tertiary amine group [50]. The peaks at ~ 900 and ~ 550 cm<sup>-1</sup> could be attributed to P=O stretching and Ti–O bonding [51]. The X-ray diffraction pattern showed sharp as well as low-intensity peaks revealing the semicrystalline nature of the material. The SEM micrographs (Fig. 3) confirmed single rod-shaped phase of composite material.

### 3.3 Thermal Stability

To examine the consequence of heating on ion-uptake efficiency of ETP, the FTIR spectra heated for 1 h at different temperatures up to 700 °C were studied. Up to 250 °C physisorbed and interlayer water is released from the material. Onward 250–400 °C, decomposition of organic part of composite material took place in the form of oxides of car-

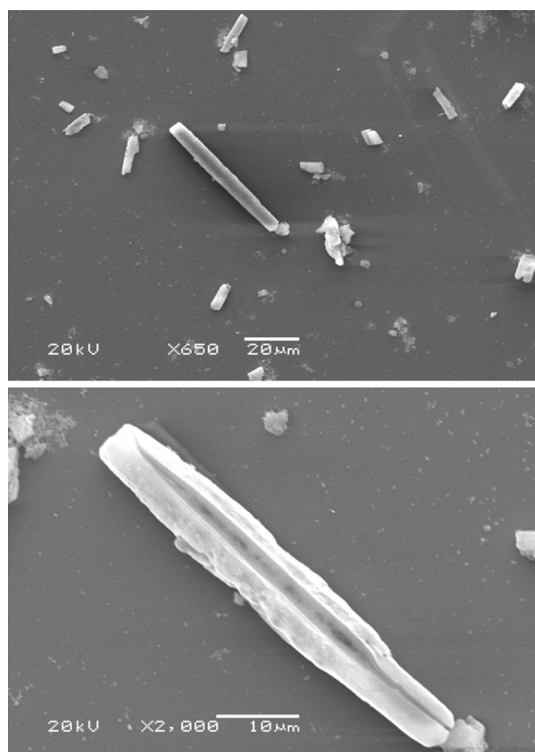


Fig. 3 SEM micrographs of EDTA–Ti(IV) phosphate

Table 3 The effect of temperature on the IEC EDTA–Ti(IV) phosphate cation exchanger on heating for 1 h

Temperature (°C)	Color	% Weight loss	% Retention of IEC
25	White	0.0	100
50	White	0.0	100
100	White	0.0	100
200	Brown	2.0	98
300	Black	10	92
400	Black	34	72
500	Light brown	45	62
600	Dirty white	56	45
700	white	64	40

IEC ion-exchange capacity

bon, nitrogen and hydrogen. However, at higher temperature (above 700 °C) complete degradation composite material functional group was found in the form of oxides of titanium and phosphorous which resulted in a decrease in the IEC. The data indicated that the appearance and ion-uptake efficiency of the ETP got altered with increasing temperature as listed in Table 3.

The material appeared to be thermally stable as it retained 98% significant ion-exchange capacity up to 200 °C. The TGA/DTA curves for breakdown of EDTA–Ti(IV) phos-

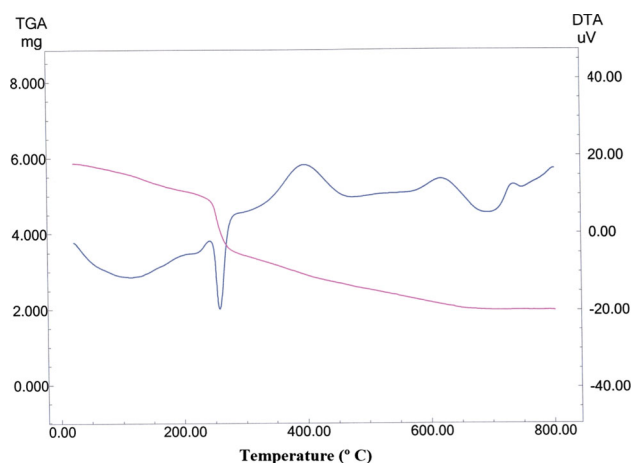


Fig. 4 TGA/DTA curves for decomposition of EDTA–Ti(IV) phosphate

phate are shown in Fig. 4. TGA demonstrated weight loss in three steps 250, 400 and 700 °C, while DTA confirmed two endothermic and one exothermic peak in the same temperatures range. The endothermic peak at 250 °C is owing to physisorbed and interlayer water from the material; however, the exothermic peak at 400 °C is associated with recrystallization by decomposition of organic part. The other endothermic peak at 700 °C indicates the completion of degradation of composite adsorbent due to the formation of metal oxides as residue.

### 3.4 Chemical Stability

The composite material showed excellent chemical stability in various solvent systems up to 2M concentration of solvents (e.g., HCl, HClO<sub>4</sub>, HNO<sub>3</sub>, DMSO, DMF, CH<sub>3</sub>COCH<sub>3</sub>, methanol, CH<sub>3</sub>COOH, NaOH, KOH, HCHO, HCOOH and NH<sub>3</sub>), while it was found to be slightly soluble in H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>. Based on good chemical stability, EDTA–Ti(IV) phosphate can be effectively used for removal of metal ions in different solvents.

## 4 Application

### 4.1 Separation of Toxic Heavy Metal Ions from Industrial Wastewaters

In order to explore the potentials of the EDTA–Ti(IV) phosphate for the removal of metal ions, *K<sub>d</sub>* values of different metal ions (Table 4) were determined in DMW, different concentrations of solvents (e.g., CH<sub>3</sub>CN, CH<sub>3</sub>COOH) and surfactant (CTAB). The adsorption of metal ions on composite adsorbent exclusively depends on the nature of solvent



**Table 4** Distribution coefficient studies ( $K_d$  values) of different metal ions in pure and mixed solvent systems on the columns of EDTA–Ti(IV) phosphate

S.No	Metal ion	DMW	0.1M CH <sub>3</sub> CN	0.01M CH <sub>3</sub> CN	0.001M CH <sub>3</sub> CN	0.1M ACOH	0.01M ACOH	0.001M ACOH	0.1M ACOH:CH <sub>3</sub> CN (1:1)	0.1% CTAB	0.01% CTAB
1	Al <sup>3+</sup>	196	533	137	217	476	217	342	459	296	375
2	Ca <sup>2+</sup>	49	55	49	83	77	67	74	149	2110	1100
3	Sr <sup>2+</sup>	74	1257	111	9400	840	990	1400	400	189	1780
4	Cd <sup>2+</sup>	730	2871	511	395	10300	5100	1287	2871	20700	20000
5	Pb <sup>2+</sup>	2090	209	320	1209	20900	10400	10900	3090	21900	1090
6	La <sup>3+</sup>	7400	111	400	541	332	1150	400	249	18500	18500
7	Bi <sup>3+</sup>	2.5	4000	200	1400	23090	20400	22400	20400	2090	20400
8	Ce <sup>3+</sup>	72	91	93	136	105	91	113	124	107	2140
9	Zn <sup>2+</sup>	826	4160	610	752	1231	868	21200	21200	21200	21200
10	Zr <sup>4+</sup>	2880	1390	7350	7350	148	1800	1480	2800	292	1390
11	Ba <sup>2+</sup>	125	233	5900	8900	900	1300	1790	1700	1900	2000
12	Cu <sup>2+</sup>	4020	20500	1273	2475	1273	2010	10500	1050	984	4020
13	Co <sup>2+</sup>	388	489	242	375	5600	4175	470	1040	350	55
14	Th <sup>4+</sup>	2050	500	900	1205	20500	20500	5000	2500	10500	10500
15	Mg <sup>2+</sup>	250	36	30	40	45	52	69	64	25300	20300
16	Hg <sup>2+</sup>	7500	7500	7500	6600	6600	7500	7500	7500	0.0	0.0
17	Fe <sup>3+</sup>	2757	1076	1150	18900	19900	13500	14900	18900	15900	16900
18	Ni <sup>2+</sup>	750	1600	25400	2090	885	1400	507	24400	442	25000
19	Mn <sup>2+</sup>	100	30	51	63	250	130	81	85	66	576



**Table 5** Quantitative binary separation of metal ions from mixtures using EDTA–Ti(IV) phosphate cation-exchange columns

Metal ion	Amount loaded (mmole)	Amount found (mmole)	% Recovery	Volume of eluent (mL)	Eluent used
Co <sup>2+</sup>	8.55	8.40	98.25	50	CH <sub>3</sub> CN 0.01M
Ni <sup>2+</sup>	12.75	12.50	98.04	60	ACOH 0.001M
Ce <sup>3+</sup>	11.20	10.95	97.77	50	CH <sub>3</sub> CN 0.001M
Fe <sup>3+</sup>	10	9.45	94.50	120	CH <sub>3</sub> CN 0.01M
Al <sup>3+</sup>	9.5	9.3	97.89	80	ACOH 0.01M
Fe <sup>3+</sup>	10	9.5	95.00	120	CH <sub>3</sub> CN 0.01M
Ca <sup>2+</sup>	10.6	10.45	98.58	60	ACOH 0.01M
Th <sup>4+</sup>	10.3	9.75	94.66	150	HNO <sub>3</sub> 1.0 M
Ce <sup>3+</sup>	11.2	10.25	91.52	50	ACOH 0.01M
Th <sup>4+</sup>	10.3	10.2	99.03	80	CTAB 1.0%
Zn <sup>2+</sup>	10.65	10.05	94.37	80	CH <sub>3</sub> CN 0.01M
Pb <sup>2+</sup>	10.50	9.95	94.76	140	ACOH 0.01M
Zn <sup>2+</sup>	10.65	10.45	98.12	70	CH <sub>3</sub> CN 0.01M
Th <sup>4+</sup>	10.03	9.95	96.60	100	HNO <sub>3</sub> 1.0 M

**Table 6** Determination of Ni<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup> and Fe<sup>3+</sup> ions from environmental wastewater samples using columns of EDTA–Ti(IV) phosphate

Samples	Method	Amount of Ni <sup>2+</sup> found <sup>a</sup> (mg L <sup>-1</sup> ) (%RSD) <sup>b</sup>	Amount of Cd <sup>2+</sup> found <sup>a</sup> (mg L <sup>-1</sup> ) (%RSD) <sup>b</sup>	Amount of Cu <sup>2+</sup> found <sup>a</sup> (mg L <sup>-1</sup> ) (%RSD) <sup>b</sup>	Amount of Fe <sup>3+</sup> found <sup>a</sup> (mg L <sup>-1</sup> ) (%RSD) <sup>b</sup>
Ganga river water, Garh, U.P	Direct <sup>c</sup>	1.67 (2.9)	0.09 (2.4)	N.D	22.93 (3.3)
	SA <sup>d</sup>	1.72 (2.7)	0.10 (2.3)	N.D	23.00 (3.2)
Narora canal water, U.P	Direct <sup>c</sup>	59.30 (2.7)	0.07 (2.9)	41.40 (2.9)	N.D
	SA <sup>d</sup>	60.10 (3.0)	0.08 (3.1)	42.60 (3.3)	N.D
Lock industry wastewater, Aligarh, U.P	Direct <sup>c</sup>	1.35 (3.1)	0.14 (2.5)	N.D	31.96 (2.9)
	SA <sup>d</sup>	1.43 (3.0)	0.16 (2.3)	N.D	32.20 (3.2)
Battery industry waste, water, Aligarh, U.P	Direct <sup>c</sup>	1.40 (2.9)	0.14 (3.2)	N.D	9.04 (3.5)
	SA <sup>d</sup>	1.54 (3.1)	0.15 (3.0)	N.D	9.21 (3.1)
Tap water, Aligarh, U.P	Direct <sup>c</sup>	0.22 (3.2)	0.05 (3.1)	N.D	N.D
	SA <sup>d</sup>	0.24 (3.0)	0.07 (2.9)	N.D	N.D

Experimental conditions: 100 mL solution, sorption flow rate 2.0 mL min<sup>-1</sup>, 0.50 g cation exchanger

N.D. not detected

<sup>a</sup> Average of three replicate determinations

<sup>b</sup> % RSD, Relative standard deviation

<sup>c</sup> Recommended procedure applied without spiking

<sup>d</sup> Recommended procedure after spiking (standard addition method)

medium. Different solvent systems show diverse behaviors; consequently, the selectivity of metal ions plays different role in different mediums. The distribution coefficient values of metal ions by using hybrid material did not show any particular trend in all solvent systems. However, Pb<sup>2+</sup>, Fe<sup>3+</sup> and Th<sup>4+</sup> ions showed higher  $K_d$  values in 0.1M acetic acid

solution, while Cd<sup>2+</sup> and Mg<sup>2+</sup> ions showed higher values in 0.1% CTAB solution and Ni<sup>2+</sup> ions had high value in 0.01M CH<sub>3</sub>CN solution. On the basis of relatively higher  $K_d$  values, EDTA–Ti(IV) phosphate was found to be selective for Pb<sup>2+</sup>, Fe<sup>3+</sup>, Th<sup>4+</sup>, Cd<sup>2+</sup>, Mg<sup>2+</sup> and Ni<sup>2+</sup> ions.



The efficacy of the composite adsorbent has been demonstrated by accomplishing quantitative separation of metal ions (e.g.,  $\text{Co}^{2+}$ - $\text{Ni}^{2+}$ ,  $\text{Ce}^{3+}$ - $\text{Fe}^{3+}$ ,  $\text{Fe}^{3+}$ - $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ - $\text{Th}^{4+}$ ,  $\text{Ce}^{3+}$ - $\text{Th}^{4+}$ ,  $\text{Zn}^{2+}$ - $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ - $\text{Th}^{4+}$ ) from binary mixtures up to 98 % recovery (Table 5). The separations were quite sharp together with substantial and reproducible recovery. The sensible usefulness of ETP composite was demonstrated by the removal and recovery of  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Fe}^{3+}$  ions from the natural water as well as from industrial wastewaters.

For the determination of  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Fe}^{3+}$ , water samples were collected from Ganga river canal, industrial wastewater (collected from lead storage batteries) and tap water (AMU, University) Aligahr, U.P, India. These water samples were instantly filtered through Millipore cellulose membrane filter (0.45  $\mu\text{m}$  pore size) acidified to pH 4 by using concentrated  $\text{HNO}_3$ . The content of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Fe}^{3+}$  ions in real water samples was successfully determined using flame atomic absorption spectrophotometer, and their results are shown in Table 6.

#### 4.2 Column Procedure for the Measurement LOD and LOQ

The limit of detection (LOD) and the limit of quantitation (LOQ) were calculated using standard addition method followed by adding a known content (10  $\mu\text{g}$ ) of particular metal ions to the wastewater samples before subjecting it to FAAS determination. The limit of detection and quantification were measured by applying previously reported method [52]. The limit of detection was found to be 9.12 (0.0020), 1.78 (0.0012), 0.88 (0.0013) and 1.05 (0.0004)  $\mu\text{gL}^{-1}$  for  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions, respectively.

## 5 Conclusion

Newly synthesized semicrystalline, EDTA-Ti(IV) phosphate shows good sorption behavior for the removal of toxic metal ions. It has potential to be employed at fairly high temperature (up to 200 °C) with retaining 98% of ion-uptake capacity. Quantitative separation of metal ions in water sample has been effectively achieved with significant recovery. The EDTA-Ti(IV) phosphate exchanger, thus, reveals the characteristics of a promising ion-exchange adsorbent which can be employed for treatment of wastewaters.

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