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Synthesis and Characterization of Graphene Th(IV) Phosphate Cation Exchanger

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Abstract—*Graphene Th(IV) phosphate composite cation exchanger was prepared by sol-gel precipitation method. Several physicochemical properties as Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) study, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies were carried out. The material possessed an IEC of 1.56 meq g^{-1} of the exchanger. The selectivity studies showed that the material was selective towards Pb^{2+} ions. The selectivity of this cation-exchanger was demonstrated in the binary separation of Pb^{2+} ions from mixture with other metal ions.*

Keywords*: cation-exchanger; graphene Th(IV) phosphate; ion-exchange capacity, nano-composite; selectivity studies.*

1. INTRODUCTION

The rapid growth of industry and technology has improved the standard of life, but at the same time it has created a complicated web of environmental pollution [1-2]. In order to meet the demands of modern society, natural resources get overburdened, producing harmful and toxic materials that must be disposed of. One of the major threats is that of toxic metals that are released into the environment through anthropogenic activities. Most of the heavy toxic metals from industries, factories, and agricultural use end up in water streams [3]. The presence of these heavy metal ions renders water useless for drinking, owing to their toxic and bio-accumulative nature. Therefore, the detection and removal of these pollutants is of utmost importance in order to get safe potable water. Lead is considered as one such major toxic metal. It is a potent threat to human life and the ecosystem [4]. The main sources of lead production include the manufacture of lead acid batteries, lead pipes, metal processing plants, printing, mining, and tannery [5]. It gets accumulated in the tissues and causes severe renal, reproductive, and central nervous system failure [6]. The Indian standard drinking water specification (Second revision) has set the tolerance limit of lead in drinking water as 0.01 mg/L [7]. As a result of these harmful effects, there is a constant need to monitor, separate, and remove the lead from water sources.

Ion-exchange materials have emerged as a viable option for the separation of metal ions compared to chemical precipitation, membrane filtration, electrochemical, and thermal treatment in terms of simple procedure and cost effectiveness [8,9]. The incorporation of organic conducting polymer into the matrices of multivalent inorganic metal salts such Th(IV), Sn(IV), Zr(IV), Sb(V), etc. has resulted in the development of hybrid ion-exchangers with superior ion-exchange, granulometric, mechanical properties, and higher selectivity for heavy metals. Recently, several studies have been reported for the adsorption of Pb(II) ions on tartaric acid-modified graphene oxide, L-glutamic acid-functionalized graphene oxide, diiodocarbene-modified graphene, dibromocarbene-modified graphene, and 3D hierarchical flower-like nickel ferrite/manganese dioxide. In this study, a graphene Th(IV) phosphate composite cation-exchanger was synthesized and was evaluated for its ion-exchange property.

2. MATERIALS AND METHODS

2.1. Reagents and Instruments

The main reagents used in the synthesis were thorium nitrate, orthophosphoric acid, nitric acid, and N-cetyl-N,N,N-trimethylammonium bromide (CTAB). These reagents and chemicals were purchased from Central Drug House, India. Graphene oxide powder (<20 µm) with 98% purity was purchased from Sigma Chemicals, India. All reagents and chemicals were of analytical grade. A digital muffle furnace (Macro Scientific Works, MSW-251, Thane, India), digital balance (MAB 220, Rajasthan, Wensar India), and a magnetic stirrer (LMMS-1L4P, LABMAN Scientific Instruments) were used.

2.2. Preparation of the Reagent Solutions

Thorium nitrate (0.1 M) was prepared in 1 M HNO_3, while orthophosphoric acid (2 M) was prepared in demineralized water (DMW). A dispersion of graphene was prepared in CTAB

2.3. Synthesis of Composite Cation-Exchanger

The inorganic precipitates of Th(IV) phosphate were synthesized as reported earlier [10] by mixing a solution of 0.1 M$Th(NO_3)_4.5H_2O$ in 1 MHNO_3 at the flow rate at 0.5 ml min^{-1} to a solution of H_3PO_4 in different molarities. Further, a dispersion of graphene was added to the slurry.

2.4. Characterization

Fourier transform infrared study

The Fourier transform infrared (FTIR) spectra of the inorganic Th(IV) phosphate and composite graphene Th(IV) phosphate in the range 4,000–500 cm^{-1}were recorded using FTIR spectrometer (Spectrum-Two, Perkin-Elmer, USA).

X-ray diffraction study

The X-ray diffraction (XRD) pattern of the grapheneTh(IV) phosphate composite cation exchanger was recorded by an X-ray diffractometer (mniflex-II, Rigaku, Japan) with Cu Kα radiations.

Scanning electron microscopic

Scanning electron microscopic images of graphene Th(IV) phosphate composite cation-exchanger were taken by scanning electron microscope (JEOL, JSM, 6510-LV, Kyoto, Japan) at an accelerating voltage of 20 kV.

Transmission electron microscopy

TEM studies were carried out to determine the particle size of graphene Th(IV) phosphate composite cation-exchanger using transmission electron microscope (JEM 2100, JEOL, Kyoto, Japan).

2.5. Determination of Ion-Exchange Capacity

The standard column process as described elsewhere [11] was used to determine the ion-exchange capacity.

2.6. Distribution Studies

The batch method was used to determine the distribution coefficients (Kd-values) of various metal ions on graphene Th(IV) phosphate. The initial metal ion concentration was adjusted such that it did not exceed 33% of its total ion-exchange capacity. Titration against standard 0.005 M solution of EDTA gave the metal ions in the solution before and after equilibrium [12].

2.7. Separation of Metal Ions

Quantitative binary separations of some metal ions of analytical utility were achieved on graphene Th(IV) phosphate column. The metal ions in the effluent were determined quantitatively by EDTA titration [12].

3. RESULTS AND DISCUSSION

In this study, graphene Th(IV) phosphate was prepared by sol-gel precipitation method. The graphene provides the mechanical stability to the inorganic cation-exchanger and contributes to enhancing the ion-exchange capacity. The inorganic thorium phosphate possessed the ion-exchange capacity of 1.20 meq g^{-1}, which is lower than that of the composite ion-exchange capacity of 1.56 meq g^{-1}. The enhancement in the ion-exchange capacity results from the binding of graphene with inorganic ion-exchanger, and hence leaching of inorganic ion-exchanger was not prominent.

FTIR spectra of the inorganic phosphate and composite cation exchanger are shown in Figure 1. The FTIR spectrum of the composite exhibits a broad band in the region -3,400 cm^{-1} (O–H stretching), a band around -2,900 cm^{-1} (C–H stretching), a band at $^{-1}$, 620 cm^{-1}, a sharp peak around -1,050 cm^{-1} (P=O stretching) and the presence of two bands at -630 and -500 cm^{-1} may be attributed to the presence of metal oxygen bond. The XRD pattern of this material shows the absence of sharp peaks indicating the amorphous nature of the composite cation exchanger (Figure 2).

The SEM micrograph of graphene Th(IV) phosphate (Figure 3) shows that the surface of inorganic precipitate of Th(IV) phosphate was

uniformly covered with graphene. The organic conducting polymer is tightly binding to the inorganic precipitate, providing mechanical stability and preventing the leaching out of the inorganic precipitate.

The TEM studies (Figure 4) reveal that the composite has a varying particle size (i.e., 16.2, 21.8, 35.0, 44.6, and 47.8 nm), and hence the above-prepared material can be considered a nano-composite. It was observed from the higher Kd-values (Table 1) that the lead is highly adsorbed as compared to other metal ions under study. It was also observed that Kd-values or selectivity is dependent on the nature and composition of contacting solvents. The separation capability of this cation-exchanger was also demonstrated in the binary separation of lead from a mixture of the lead with other metal ions (Table 2). The weakly adsorbed metal ions elute first from the column, while the strongly held ions were eluted last. It was observed that the recovery of lead was found to be quantitative and reproducible by three replicate measurements.

Table 1. Kd-values of some metal ions on graphene Th(IV) phosphate column in different solvent systems.

Solvents / Metal ions	K_d-values (mL g^{-1})									
	DDW	10^{-2} M $HClO_4$	10^{-1} M $HClO_4$	1 M $HClO_4$	10^{-2} M HNO_3	10^{-1} M HNO_3	1 M HNO_3	10^{-2} M HCl	10^{-1} M HCl	1 M HCl
Mg^{2+}	95	46	28	17	30	26	22	25	20	14
Ca^{2+}	134	140	107	83	112	94	81	104	85	67
Cd^{2+}	80	85	69	45	92	77	52	81	63	47
Pb^{2+}	560	640	593	548	580	523	470	500	430	380
Co^{2+}	135	155	128	117	137	123	115	140	117	104
Hg^{2+}	380	470	426	377	390	362	284	360	337	246
Mn^{2+}	75	87	71	46	73	56	37	78	52	33
Sr^{2+}	127	133	114	92	167	142	109	125	103	72
Cu^{2+}	66	57	39	28	62	45	32	50	31	26
Ba^{2+}	110	116	94	81	100	86	71	110	93	79

Table 2. Some binary separations of metal ions achieved on graphene Th(IV) phosphate.

Separation achieved	Amount loaded (µg)	Amount Found (µg)	Error (%)	Eluent used	Volume of eluent (mL)
Cu2+ Pb2+	1271.00 4144.00	1261.60 4144.00	-0.74 0.00	1 M HCl 1 M HCl	50 60
Ba2+ Pb2+	2746.60 4144.00	2724.63 4144.00	-0.80 0.00	1 MHNO3 1 M HCl	60 60
Cd2+ Pb2+	2248.20 4144.00	2225.72 4088.06	-1.00 +1.35	1 MHClO4 1 M HCl	50 60
Ca2+ Pb2+	4723.00 4144.00	4677.66 4117.88	+0.96 -0.63	1 M HCl 1 M HCl	60 60

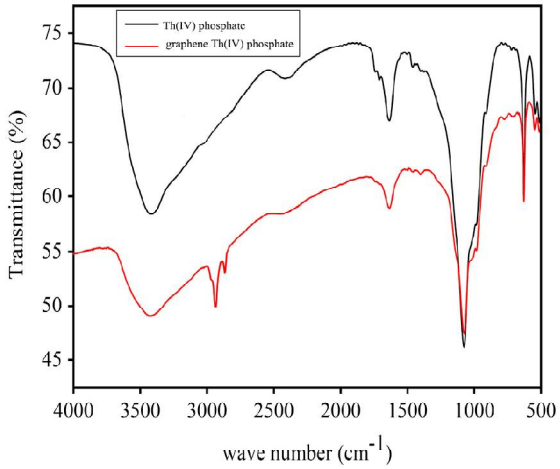

Figure 1. FTIR spectra of as prepared Th(IV) phosphate and graphene Th(IV) phosphate.

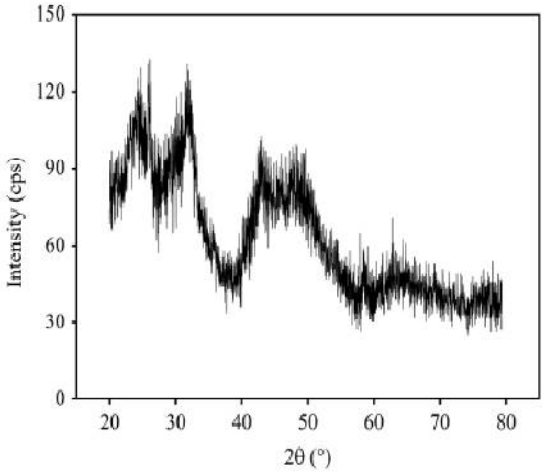

Figure 2. Powder XRD pattern of graphene Th(IV) phosphate composite cation exchanger.

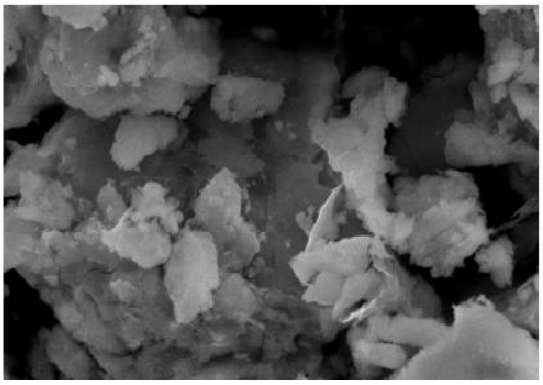

Figure 3. Scanning electron micrograph (SEM) of graphene Th(IV) phosphate cation-exchanger at ×5000.

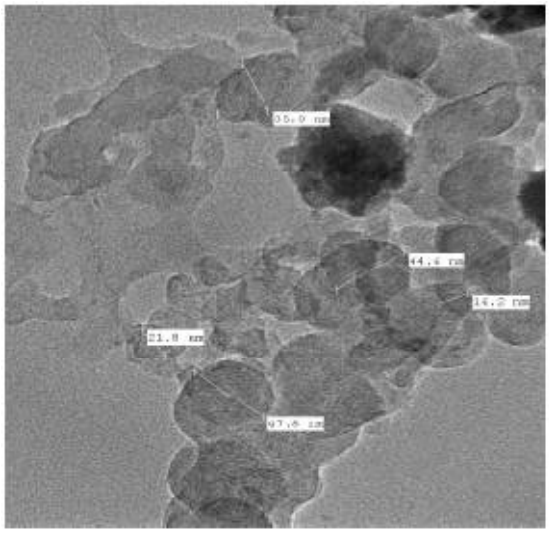

Figure 4. Transmission electron micrograph (TEM) of graphene Th(IV) phosphate cation exchanger.

4. CONCLUSIONS

In the present study, a Pb^{2+} ion-selective nano-composite ion-exchanger graphene Th(IV) phosphate having an IEC of 1.56 meq g^{-1} of exchanger was prepared. The TEM analysis revealed that the particle size of the prepared composites was in the range of 16-45 nm. Thus, the cation-exchanger can be considered as a nano-composite material. The composite material was successfully used in the separation of Pb^{2+} ions quantitatively from various metal ions. The environmental monitoring requires quick detection as well as effective separation of pollutants, and hence the selective behavior of this cation-exchanger can be of great significance.

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