

Synthesis and Characterization of Poly-o-Toluidine Bi (III) Phosphotungstate Nano-composite Cation Exchanger

N. Kohila^{1,*}, Sheila Agnes Vidot², Fatma Bassyouni³, Fatima Hamouche⁴, Selçuk Bulat⁵, Jaime Alfonso Flores Navas⁶

¹Department of Chemistry, Aditanar College of Arts and Science, Affiliated to Manonmaniam Sundaranar University, Tirunelveli, Tamil Nadu, India.

²Department of Medical Consultants, IPS Health, Mahe, Seychelles.

³Department of Chemistry of Natural and Microbial Products, National Research Centre, Giza, Egypt.

⁴Department of Chemistry, Ibn Tofail University, Kenitra, Rabat-Salé-Kénitra, Morocco.

⁵Department of Nanoscience and Nanoengineering, Institute of Natural Sciences, Sakarya University, Serdivan, Sakarya, Turkey.

⁶Faculty of Sciences, National Autonomous University of Mexico, Coyoacán, Mexico City, Mexico.
nkohila302@gmail.com¹, vidotsheila@gmail.com², fatma.nrc@hotmail.com³, fatima.hamouche@uit.ac.ma⁴,
sbulat@tse.org.tr⁵, jaguarnegro175@gmail.com⁶

Abstract: An advanced organic–inorganic hybrid nano-composite cation exchanger, poly-O-toluidine-bismuth (III) phosphotungstate (POT/Bi (III)PT), was successfully synthesised via a sol–gel mixing method. Researchers systematically characterized the material's physicochemical and structural properties using FT-IR, UV-visible spectroscopy, XRD, and SEM, confirming the formation of a distinct nano-composite structure. The size and charge of the exchanging ions governed ion-exchange behaviour. The hybrid material exhibited enhanced ion-exchange capacity, following the selectivity sequence $K^+ > Na^+$ for alkali metals and $Ba^{2+} > Sr^{2+}$ for alkaline earth metals, indicating that smaller hydrated ionic radii facilitate smoother intra-pore diffusion. Elution kinetics showed optimised H^+ ion release at a minimum NaCl eluent concentration of 0.4 M, with the material reaching equilibrium at 5 hours. Chemical stability trials demonstrated that the POT/Bi(III)PT composite is remarkably robust in distilled water, metal salt solutions, and highly concentrated acidic media. However, it undergoes hydrolytic degradation in alkaline environments. Combining superior ion-exchange performance, high reproducibility, and strong structural stability, this newly developed nano-composite holds significant promise as an effective candidate for column operations and environmental remediation applications.

Keywords: Hybrid Cation Exchanger; Chemical Stability; Conductive Polymer; Nano-Composite Ion Exchanger; Sol-Gel Synthesis; Ion-Exchange Capacity; Scanning Electron Microscopy; Chemical Stability.

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1. Introduction

*Corresponding author.

A conductive polymer is a semiconductor, or an organic semiconductor; common classes of organic conductive polymers include polyacetylene, polypyrrole, polyaniline, polythiophene, polyindole, polytoluidine, etc. [1]. Conjugated polymers, or conducting polymers, are characterised by alternating single and double bonds along the polymer backbone [2]. Because of its high stability and unique combination of properties, PANI was the first conducting polymer used in practice as an antistatic coating, electrode material for batteries and condensers, a corrosion inhibitor and a sensing material. Polyaniline (PANI) has attracted much attention because doping with protic acids or treatment with oxidants such as iodine can control its interesting chemical, electrochemical and optical properties. PANI has been reported for use as an electrode in secondary batteries, an active material in electrochromic display devices, and a corrosion inhibitor. However, PANI applications have been limited because it has poor solubility in common organic solvents. Researchers have tried to improve PANI solubility and electronic properties by introducing substituents such as alkyl, alkoxy and carboxylic acid groups on the monomer. Among conducting polymers, aniline (O-toluidine) polymers have been of particular interest because of their environmental stability and redox properties associated with the chain nitrogens [3]. Polyaniline polymers also exhibit crystallinity and solution- or counter-ion-induced processability; furthermore, secondary doping can substantially improve their electrical properties [4]. This excellent processability, together with several intrinsic redox states, has significantly expanded the potential applications of aniline polymers in practical devices [21].

Ion exchange materials have extensive applications in analytical and industrial chemistry because of their desirable characteristics, such as an insoluble matrix, stoichiometric exchange, good selectivity and suitability for column operations [6]. One major driver for these investigations is that such ion exchangers generally exhibit superior selectivity for given aqueous metal cations compared to more traditional organic-based ion-exchange resins, even in the presence of high concentrations of competing cations Na, K and H₃O⁺ [8]. They play a vital role in treating environmental pollutants [9]. Interest in using inorganic ion exchangers with rare earths stems from their ability to increase acid sites in the material's structure, thereby improving adsorption [5]. Insoluble salts of heteropolyacids with polyvalent metals show selective ion-exchange behavior and are preferred over other ion exchangers. Qureshi et al. [7] have studied "Vanadophosphate, vanadotungstates, and phosphotungstates of tin (IV), studies on Ce(IV)arsenate and Ce(IV)vanadate have already been reported by Rao [10]. Heteropolyacid exchangers based on Bismuth(III) have not been studied in detail; phosphosilicates and phosphomolybdates, and some cerium(IV) exchangers, have been studied [11]. Analytical and industrial chemistry have widely used ion-exchange materials because of their elegant features, such as an insoluble matrix, stoichiometric exchange, good selectivity, specificity and applicability to column operations [12]. Important inorganic ion exchangers, such as trivalent metal acid salts, are promising materials because they have robust properties, good ion-exchange characteristics, thermal stability and chemical resistance [13].

Interest in using organic ion exchangers with rare earths stems from their ability to increase acid sites in the material structure and thus improve adsorption [14]. Among polyvalent metal acid salt mixed materials, those containing a cation and two different anions show improved ion-exchange properties and selectivity for particular metal ions compared to their single-salt counterparts [15]. Heteropolyacid salts can be used as inorganic ion exchangers. These exchangers are stable in moderately concentrated acid. However, they dissolve in alkaline solutions. Heteropolyacids have a high affinity for heavy alkali metals, thorium and silver. The size of univalent ions of these elements is compatible with their entrapment in the crystal lattice of heteropolyacids. Second, they are selective, have higher ion-exchange capacity than their simple salts, and are more thermally and chemically stable. Inorganic ion exchangers and organic resins, commonly referred to as ion exchange media, have been widely investigated for remediating wastewater containing heavy metal ions as by-products from a variety of industries [22]. However, two principal challenges still hamper the practical use of organic and inorganic ion exchange media. One is the poor thermal and radiation stability of organic resins compared with inorganic ion exchangers; the other is the non-reproducible character, lower stability in highly acidic and basic media, and high cost of inorganic ion exchangers [23]. In addition, inorganic ion exchangers are not convenient for purifying impurities from large volumes of effluent. In this connection, research has motivated investigations into organic-inorganic hybrid ion exchangers with better mechanical, chemical, thermal and radiation stability, reproducibility and good selectivity for highly toxic heavy metals [16].

Ion exchange materials have been proven to be a suitable tool for various environmental problems [17]. One major limitation of organic resins is their low thermal stability [24]. They are unstable at high temperatures and under strong radiation. The non-granulometric nature of inorganic ion exchangers makes them unsuitable for column operation [18]. To overcome these limitations, many investigators have introduced organic-inorganic composite ion exchangers [19]. Most composites have been developed to improve a combination of mechanical characteristics such as stiffness, toughness and high-temperature strength [20]. Thus, the synthesis of polymeric inorganic composites has received considerable attention because it provides new materials with special mechanical, chemical, electrochemical, optical and magnetic properties. In 2007, Khan et al. [27] reported that the organic polymer nylon-6,6 framework with Zr(IV) phosphate, an inorganic ion exchanger, was highly selective for Hg(II), a highly toxic environmental pollutant. This helps reduce environmental pollution. In 2007, Siddiqui et al. [26] reported that incorporating a polymer material into an inorganic ion exchanger provides a class of hybrid ion exchangers with good ion-exchange capacity, high stability and high selectivity for heavy metals [25]. A new organic-inorganic hybrid cation exchanger, poly(Methyl methacrylate) Zr(IV) phosphate, was reported for heavy metal removal. In 2007, Khan et al. [27]

reported that ion-exchange membranes obtained by embedding ion exchangers as electroactive materials in a polymer binder (i.e., PVC) have been extensively used as potentiometric sensors (i.e., ion sensors), chemical sensors or, more commonly, ion-selective electrodes.

A nano-composite cation exchanger is used to determine Hg(II) ions present in the sample solution. The material can be considered a nano-composite material using poly(O-toluidine) Th(IV) phosphate. In 2009, Khan et al. [28] reported that the organic poly (O-anisidine) framework with Sn(IV)arsenophosphate, an inorganic ion-exchanger, was found to be highly selective for Pb²⁺ in water; a heterogeneous precipitate-based ion-selective membrane electrode was developed by means of this composite cation exchanger as an electroactive material. The selectivity coefficients were calculated by the mixed-solution method and showed that the electrode is sensitive to Pb(II) in the presence of interfering cations. The main objective of the present work is to synthesize, characterize and conduct ion-exchange studies of a new hybrid organic – inorganic cation exchanger, poly-O-toluidine Bi(III) phosphotungstate, by incorporating organic polymers (i.e., poly-O-toluidine and an inorganic ion exchanger, Bi(III) phosphotungstate, with good ion-exchange capacity and high selectivity for heavy metals. Researchers studied the physicochemical characteristics of the organic-inorganic composite cation exchanger using FT-IR, UV-Vis spectroscopy, XRD and SEM. In addition, researchers studied the ion-exchange capacity of the organic-inorganic hybrid cation exchanger, POT/Bi(III)phosphotungstate, by the column method. Researchers studied the chemical stability of the hybrid cation exchanger in acidic, neutral and basic media.

2. Experimental Section

2.1. Chemicals

O-toluidine-[Sigma-Aldrich CHEM Pvt. Ltd. (AR)], potassium perdisulphate-[Sigma-Aldrich CHEM Pvt. Ltd. (AR)], bismuth nitrate-[HIMEDIA. CHEM Ltd. (AR)], trisodium phosphate-[HIMEDIA. CHEM Ltd. (AR)], sodium tungstate-[HIMEDIA. CHEM Ltd (AR)], sodium hydroxide-[S.R & CHEM Pvt. Ltd], sodium chloride-[S.R & CHEM Pvt. Ltd], potassium chloride-[S.R & CHEM Pvt. Ltd], barium chloride-[S.R & CHEM Pvt. Ltd], strontium chloride-[S.R & CHEM Pvt. Ltd], acetone, sulphuric acid, methanol, nitric acid, N-methyl pyrrolidone (NMP) are the chemicals used in this work. O-toluidine was purified by zinc dust distillation.

2.2. Preparation of Reagent Solutions

0.1 M solutions of potassium perdisulphate and O-toluidine were prepared in demineralised water and 1 M H₂SO₄, respectively. 0.1 M solutions of bismuth nitrate, trisodium phosphate and sodium tungstate were prepared in demineralised water.

2.3. Synthesis of Poly-O-Toluidine-Sulphuric Acid Salt

Poly-O-toluidine emeraldine salt is easily synthesised by oxidative polymerisation of O-toluidine in aqueous acidic media with KPS as the oxidising agent. The organic polymer, poly-o-toluidine, was prepared by mixing 0.1 M KPS solution with 0.1 M O-toluidine in 1 M sulphuric acid, with continuous stirring using a magnetic stirrer for 30 minutes to form an emulsion of POT/H₂SO₄ (Figure 1).



Figure 1: Formation of green coloured poly-O-toluidine

A green precipitate was obtained and kept for 24 hours at 0 °C in a refrigerator. The emeraldine salt was washed with organic solvents, methanol and acetone, to remove oligomers. The POT salt was vacuum-dried for 24 hrs to give a green-black powder of POT-H₂SO₄ emeraldine salt.

2.4. Synthesis of Bismuth(III) Phosphotungstate Ion-Exchanger

Bismuth(III) phosphotungstate was synthesised by mixing equimolar (0.1 M) solutions of bismuth nitrate, trisodium phosphate and sodium tungstate in a 1:1:2 volume ratio, with slow, continuous stirring at pH 2. Nitric acid was added to the precipitate to obtain the desired pH. The white precipitate so formed was allowed to stand for 24 hrs in the mother liquor and then filtered. The precipitate was filtered and dried at room temperature. It was continuously washed with distilled water to remove excess acid.

2.5. Synthesis of Poly-O-Toluidine-Bi(III) Phosphotungstate Cation Exchanger

The composite cation exchanger was prepared by sol-gel mixing of poly-O-toluidine, an organic conducting polymer, with the inorganic precipitate of bismuth(III) phosphotungstate. In the synthesis of poly-O-toluidine-Bi(III) phosphotungstate, the gels of poly-O-toluidine were added to the white precipitate of Bi(III) phosphotungstate with constant stirring for 7 hrs. The resulting mixture was slowly converted into greenish-black slurries and maintained for 24 hrs at 0 °C. The poly-O-toluidine-based composite gels were then filtered and washed thoroughly with demineralised water to remove excess acid and trace KPS. The dried product was washed with methanol and acetone to remove oligomers that were present in the material.

2.6. Synthesis of H⁺ Form of Poly-O-Toluidine-Bi(III) Phosphotungstate Cation Exchanger

The dried product was ground into small granules and converted to the H⁺ form by keeping it in 1 M HNO₃ for 24 h, with occasional shaking at room temperature. After several washings with demineralised water, the excess acid was removed, and the product was dried.

2.7. IEC Studies of Poly-O-Toluidine-Bi(III) Phosphotungstate Cation- Exchanger

The exchange capacity, generally taken as a measure of hydrogen ions liberated by a neutral salt flowing through the composite cation exchanger, was determined by the standard column process. A glass column was packed with dry cation exchanger in the H⁺ form (Figure 2).



Figure 2: Ion exchange column for ion exchange experiment

Alkali and alkaline earth metal chlorides/nitrates were used as eluents to elute H⁺ ions from the cation exchanger column at a very slow rate (0.5 ml min⁻¹) [29]. The effluent was titrated against a standard NaOH solution to determine the total ion liberated in solution, using phenolphthalein as the indicator.

2.8. Effect of Size and Charge of Metal Ions on IEC

The IEC of the POT/bismuth(III) phosphotungstate cation exchanger was also determined by the column process for different alkali and alkaline earth metals similarly. The cation exchanger was divided into five equal parts (0.2 g each), packed into five different columns, and washed with distilled water to settle the granules and form the bed. Five solutions of metal ions of equimolar concentrations (0.4 M) were prepared. Each column was treated with a specific salt solution to perform the ion exchange. The effluents were collected and titrated separately against standard NaOH solution to determine the hydrogen ion concentration.

2.9. Influence of Eluent Concentration on IEC

The elution extent depends on eluent concentration. A fixed volume of NaCl solution of different concentrations was passed through a column of 0.2 g of the exchanger in H⁺ form at a flow rate of (0.5 ml min⁻¹) to find out the optimum concentration of eluent for complete elution of H⁺ ions. The H⁺ ions eluted were determined by titrating the effluent against a standard solution of NaOH.

2.10. Elution Behavior

For this study, a 0.4 M NaCl solution of optimum concentration was passed through a column containing 1g of the poly-O-toluidine- Bi(III) phosphotungstate composite cation-exchanger in H⁺ form at a flow rate of 0.5 ml min⁻¹ for complete elution of H⁺ ions. The effluent was collected in 10ml fractions, and each fraction was titrated against a standard alkali solution to quantify the eluted H⁺ ions. The experiment determined the minimum volume required for complete elution of H⁺ ions, which measures the column's exchange efficiency.

2.11. Effect of Time on IEC

The optimum shaking time of the ion exchanger with NaCl solution for complete elution of H⁺ ions was determined. The liberated H⁺ ions were determined by titration with standard NaOH solution at different time intervals by shaking 0.2 g of ion-exchanger with 25mL of NaCl solution.

2.12. Chemical Stability

To determine the extent of dissolution of the material in different chemical solvents, viz. demineralised water, solutions of metal chlorides, and different concentrations of HCl, H₂SO₄, organic solvents like acetone, methanol, and bases. Equilibrate 0.1 g of material with 25mL of the solution of interest and leave the mixture as such for 24 hours at room temperature. If residual material remained in solution, it was decanted and washed with demineralized water to remove excess acid and base. The color and weight changes were noted. This method was used to study the stability of the composite cation exchanger in various solutions.

3. Results and Discussions

3.1. FT-IR Spectral Studies

The FT-IR study was performed to determine the presence of different groups and structures in the material (Table 1).

Table 1: FT-IR absorption data of POT emeraldine salt

Frequency (cm ⁻¹)	Assignment
3745.08	N-H stretching
1521.56	Stretching of N=Q=N
1420	Stretching of benzenoid ring
1005.7	C-H bending vibrations
588.182	Aromatic ring deformation

FT-IR spectra of POT, Bi(III) phosphotungstate, the POT/Bi(III) phosphotungstate composite cation exchanger, and the H⁺ form of the composite in its original form, dried at 50 °C, were recorded by the KBr disc method at room temperature (Table 2).

Table 2: FT- IR absorption data of Bi(III) phosphotungstate

Frequency (cm ⁻¹)	Assignment
3489.56	Presence of interstitial water molecules and hydroxyl groups
1602.56	Due to H- bonded OH group
1015.34	Due to the presence of PO ₄ ³⁻
536.11, 592	M-O stretching vibrations

Figure 3 shows the FT-IR spectrum of H₂SO₄-doped POT. The FT-IR spectrum of POT emeraldine salt shows a band at 3745.08 cm⁻¹, which is assigned to the N-H stretching mode. The intense bands at 1521.56 cm⁻¹ are assigned to the ring-stretching modes of quinoid rings.

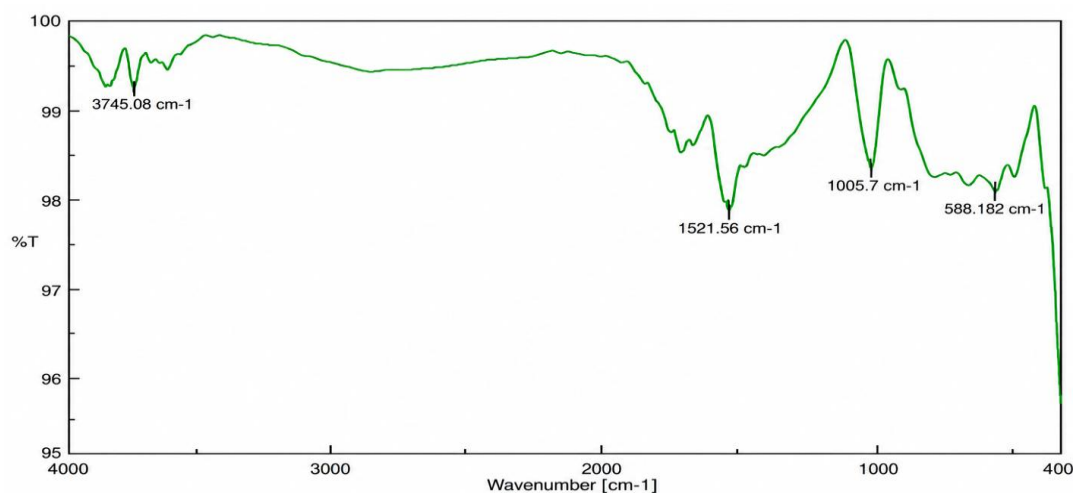


Figure 3: FT-IR spectrum of POT emeraldine salt

The band at 1420 cm⁻¹ is assigned to benzenoid ring-stretching vibrations. The spectral data given above confirm the formation of poly-O-toluidine salt.

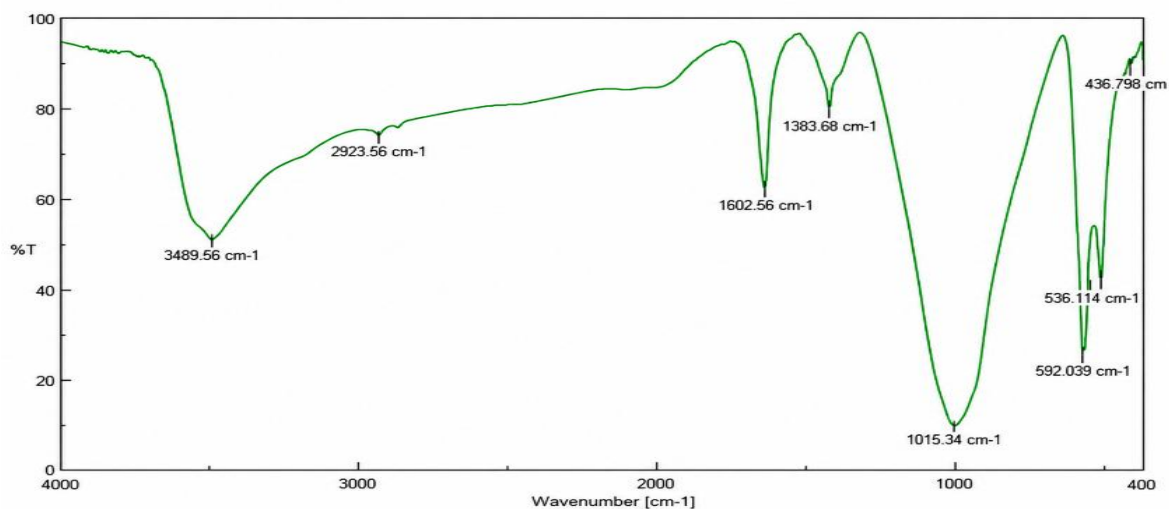


Figure 4: FT-IR spectrum of Bi(III) phosphotungstate

The FT-IR spectrum of Bi(III) phosphotungstate (Figure 4) shows a peak at 3489 cm⁻¹ indicating the presence of external water. The sharp peak at 1602 cm⁻¹ confirms the presence of a strongly H-bonded OH group (Table 3).

Table 3: FT-IR absorption data of poly-O-toluidine-Bi(III) phosphotungstate

Frequency (cm ⁻¹)	Assignment
3214.75	NH stretching vibrations
2922.59	Aromatic C-H Stretching vibrations
1588.09	Stretching of N=Q=N
1492.63	Stretching of N-B-N
1382.71	C-N stretching in QB, Q
1266.07	C-N stretching of primary aromatic amines

1110.8, 1009.55	- H bending vibrations & due to the presence of the phosphate ion.
874	Due to W- O stretching vibration mode
808, 609	Aromatic ring deformation as well as presence of metal – oxygen stretching vibrations

The sharp peak at 1015 cm⁻¹ indicates the presence of the PO₄³⁻ ion. An absorption band at 536 cm⁻¹ further confirms the ionic phosphate group. The spectrum shows an intense band at 592 cm⁻¹, indicating M-O stretching vibrations (Bi-O group).

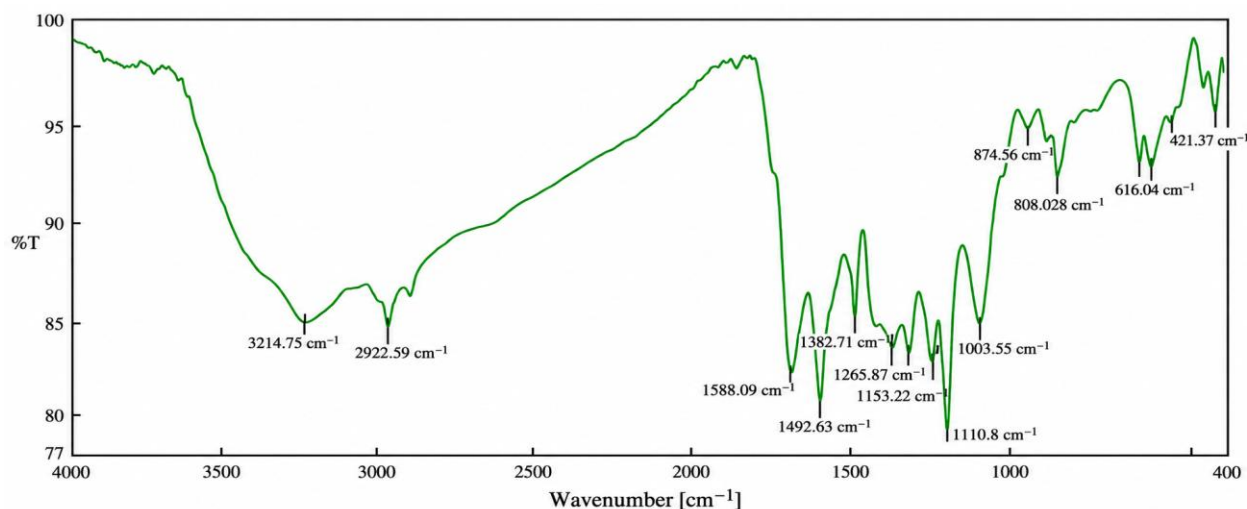


Figure 5: FT-IR spectrum of POT/ Bi (III)phosphotungstate nano-composite

The FT-IR spectrum of the POT/Bi(III) phosphotungstate cation-exchanger (Figure 5) shows vibration bands at 3214 cm⁻¹, 2922 cm⁻¹, 1588 cm⁻¹, 1492 cm⁻¹, and 1266 cm⁻¹, which are characteristic of poly-O-toluidine. The main absorption peaks at 1588 cm⁻¹ and 1492 cm⁻¹ in this spectrum are attributed to the ring-stretching modes of the quinoid and benzenoid rings, respectively (Table 4).

Table 4: FT-IR absorption data of H⁺ form of poly-o-toluidine-Bi(III) phosphotungstate nanocomposite

Frequency (cm ⁻¹)	Assignment
3216.68	NH Stretching vibrations
1599.66	Stretching of N=Q=N
1492.63	Stretching of N-B-N
1382.71	C-N stretching vibration
1264.11	C-N stretching in QB, Q, QBB
1172.51	C-H in-plane bending of 1, 2,4 ring
1012.45	Due to the presence of a phosphate ion
875.52,	W-O stretching vibration mode
820.56	C-H out-of-plane bending of 1,4 ring
559.25, 513	Aromatic ring deformation as well as the presence of M-O stretching vibrations

The peak at 874 cm⁻¹ is assigned to the W-O stretching mode. Peaks at 808 cm⁻¹, 609 cm⁻¹ etc. indicate the presence of an ionic phosphate group and M-O stretching vibrations in the material, and the broad peak at 1009.55 cm⁻¹ indicates the presence of a phosphate ion. Therefore, the IR spectrum shows both the organic polymer and the inorganic ion exchanger present in the POT/Bi(III) phosphotungstate nano-composite. The absorption peak at 3216.68 cm⁻¹ was assigned to the N- H stretching vibration. The vibration bands at 1599.66, 1492.63, and 1264.11 cm⁻¹ in the FT-IR spectrum of the H⁺ form of the organic – inorganic hybrid nano-composite ion-exchanger (Figure 6) imply the presence of poly-o-toluidine in the composite. The presence of phosphate and metal-oxygen stretching vibrations indicates binding of the inorganic precipitate to the organic polymer and the formation of an organic-inorganic hybrid. UV-visible absorption spectra of chemically synthesised poly-O-toluidine emeraldine salt and poly-O-toluidine-Bi(III) phosphotungstate cation-exchanger in N-Methyl-2-pyrrolidone as a solvent are represented in Figures 7 and 8. The broad band at 615 nm observed in the UV-visible spectrum of freshly prepared POT (Figure 7) in NMP solution is due to an n- π^* transition of quinone-imine groups.

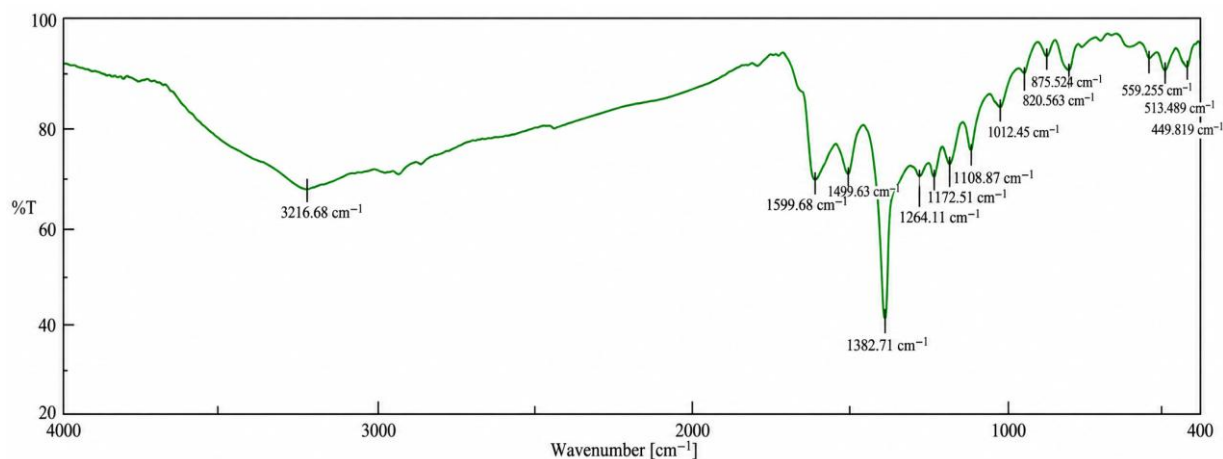


Figure 6: FT-IR spectrum of H⁺ form of POT/Bi(III) phosphotungstate nanocomposite

The UV-visible spectrum of the POT/Bi(III) phosphotungstate nano-composite ion exchanger shows two absorption bands. Absorption bands at ~420 nm and 550 nm have been assigned to the pi- pi* transition and the transition of benzenoid rings into quinoid rings, respectively.

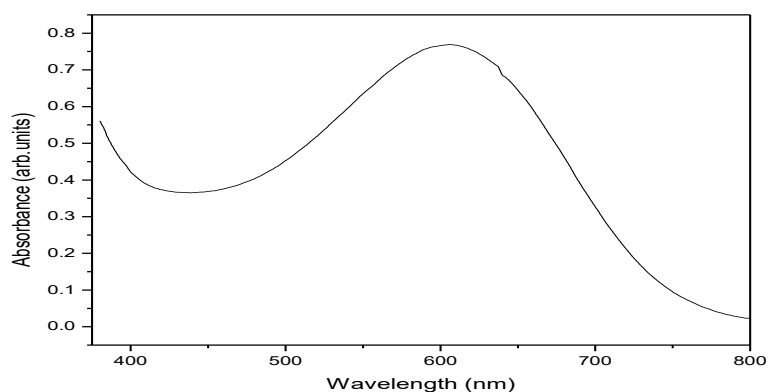


Figure 7: UV-visible spectrum of POT-H₂SO₄ emeraldine salt

Regarding the UV-Visible spectrum of POT, the absorption peak associated with the quinoid ring transition of the curve appears at the shorter wavelength (i.e., 550 nm indicating that there could be interaction between Bi(III) phosphotungstate and the POT chain. This interaction raises the quinoid-ring energy, shifting the transition to a shorter wavelength (Figure 8).

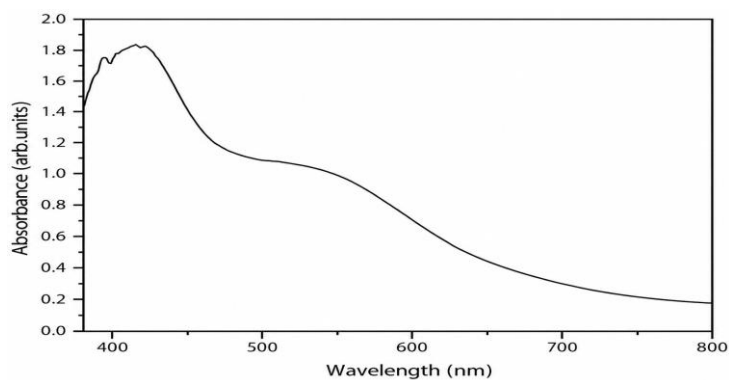


Figure 8: UV-visible spectrum of POT/Bi(III) phosphotungstate nano-composite

The crystalline phases in the sample were identified using powder X-ray diffraction. X-ray diffraction of the as-milled powder sample was carried out on the XRD diffractometer. X-ray diffraction patterns were recorded from 20 to 90 with a PANalytical

system diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) with an accelerating voltage of 40 kV. Data were collected at a counting rate of 1/min. The $\text{K}\alpha$ doublets were resolved well. Particle size can be calculated from XRD by using Scherrer's formula: $D = 0.96\lambda / \beta \cos \theta$. Where,

D = Particle size of the sample (nm)

λ = Wavelength of X-ray ($1.54056 \text{ \AA}$)

β = Full width at half maximum

θ = Diffraction angle between the incident and diffraction beam ($^\circ$)

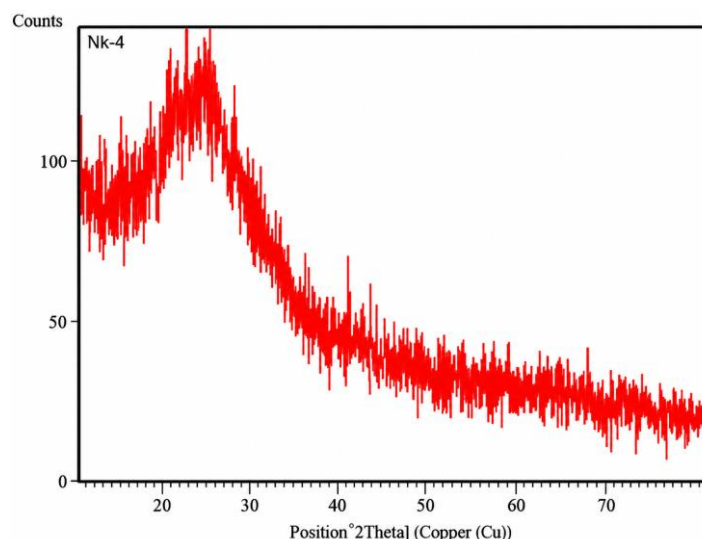


Figure 9: XRD pattern for POT-H₂SO₄ emeraldine salt

The diffraction pattern of POT shows a broad peak at about $2\theta = 24.8^\circ$, a characteristic POT peak. XRD pattern of POT is represented in Figure 9. The broad peaks indicate the material's amorphous nature. The calculated POT has an average particle size of 51.9 nm.

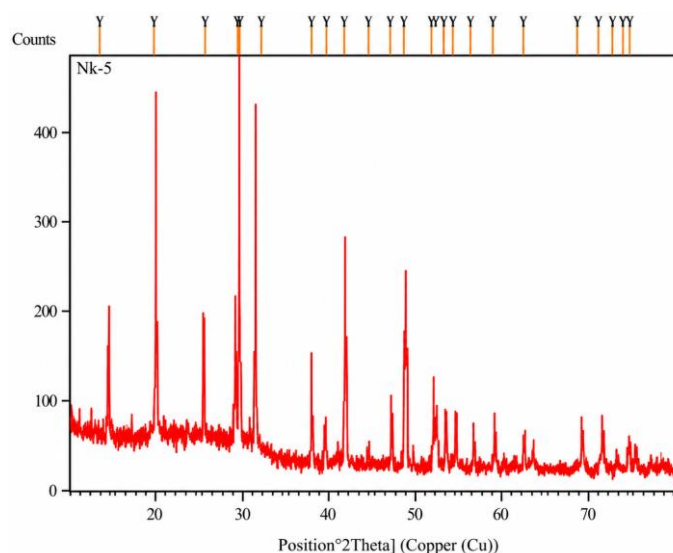


Figure 10: XRD pattern of Bi (III) phosphotungstate

The X-ray diffraction pattern of the ion-exchanger, Bi(III) phosphotungstate (Figure 10), shows several sharp peaks at 2θ values of 10.19° , 20.09° , 25.52° , 29.05° , 29.54° , 37.88° , 41.89° , 47.21° , and 48.75° , indicating some degree of crystallinity in the material. The average crystallite size of the Bi (III) phosphotungstate was calculated using Debye-Scherrer's equation from the full width at half maximum of the peak and found to be 69.6 nm.

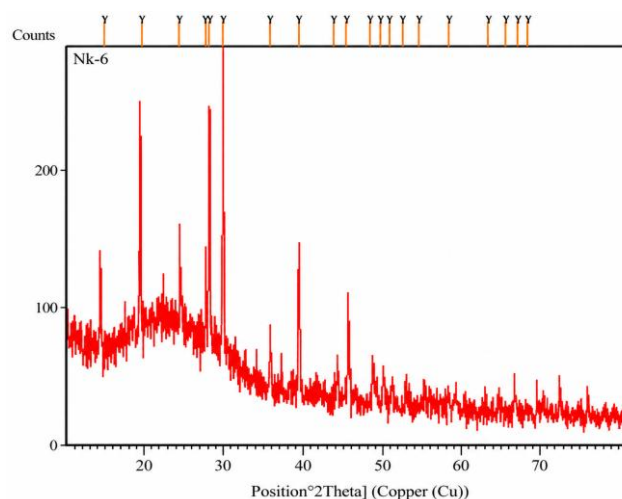


Figure 11: XRD pattern of POT/Bi(III) phosphotungstate nano-composite ion-exchanger

The X-ray diffractogram of Bi(III) phosphotungstate confirmed the presence of nanocrystallites.

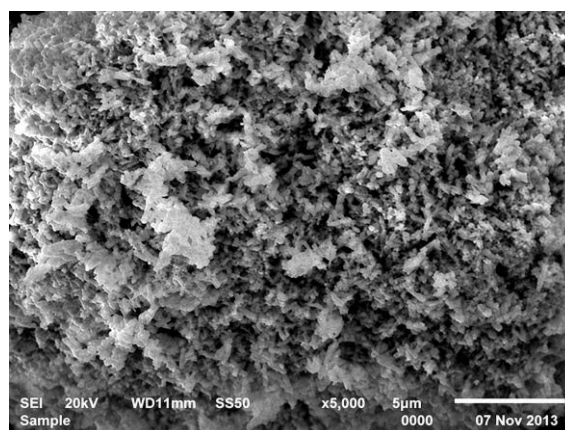


Figure 12: SEM photographs of poly-O-toluidine

X-ray diffraction of the POT/Bi (III) phosphotungstate ion-exchanger (Figure 11) exhibited a broad peak at $2\theta = 25.5^\circ$ and several sharp peaks, indicating the sample was crystalline.

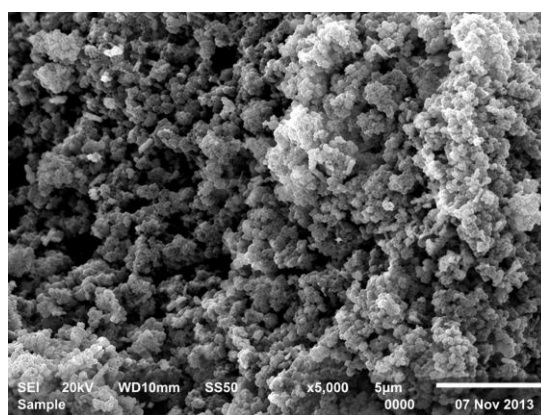


Figure 13: SEM photographs of POT/Bi(III) phosphotungstate

The average crystalline size of the POT/Bi(III) phosphotungstate composite cation exchanger was found to be in the range of 49 nm. XRD confirms that the composite material's particle size is in the nano range. SEM was performed on the ground

materials using an electron microscope. SEM photographs of the poly-O-toluidine (Figure 12) POT/ Bi(III) phosphotungstate nano-composite (Figure 13), obtained at a magnification of $\times 5000$, show the adhesion between the two phases (inorganic ion-exchange material and organic polymer (poly-O-toluidine)). SEM images show differences in the surface morphology of the organic polymer and the composite material. The images show that after poly-O-toluidine was bound to POT/Bi(III) phosphotungstate, the morphology changed. The nano-composite cation exchange materials have a polycrystalline structure. The effect of size and charge of the exchanging ion on the ion-exchange capacity was also observed for this nano-composite material.

Table 5: Effect of size and charge of metal ion on IEC

Exchanging Cation	Salt Used	Ionic Radii ($\text{\AA}$)	Hydrated Ionic Radii ($\text{\AA}$)	IEC (meq/g)
Na^+	NaCl	1.02	2.76	6.5
K^+	KCl	1.38	2.32	6.8
Ba^{2+}	BaCl_2	1.35	5.21	5.3
Sr^{2+}	SrCl_2	1.18	5.80	5.0

Table 5 shows that IEC for alkali and alkaline earth metal ions increases as the hydrated ionic radii decrease. Ions with smaller hydrated radii enter the pores of the composite cation exchanger more easily, resulting in higher adsorption (Figure 14).

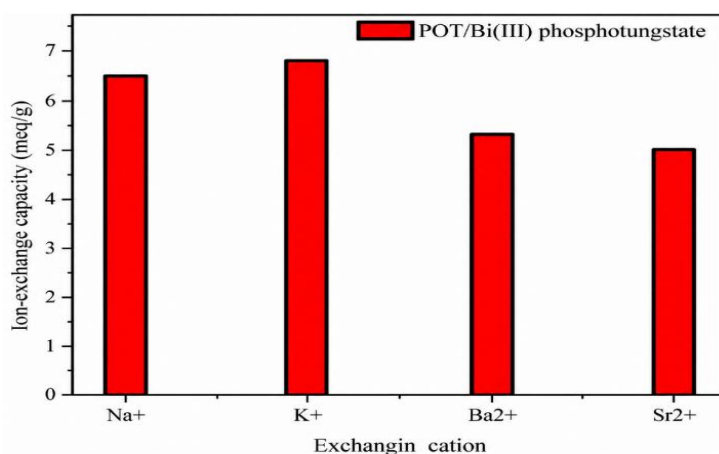


Figure 14: IEC of POT/ Bi (III) phosphotungstate for various cations

The order of maximum ion exchange capacity of alkali metal ions is $\text{K}^+ > \text{Na}^+$, and for alkaline earth metals, $\text{Ba}^{2+} > \text{Sr}^{2+}$. The ion-exchange capacity of poly-O-toluidine-Bi(III) phosphotungstate nano-composite cation exchanger depends on the size and charge of the ion exchanged (Table 6).

Table 6: Effect of eluent concentration on IEC of poly-O-toluidine-Bi (III) phosphotungstate cation exchanger

Concentration of eluent (M)	IEC for Na^+ ion (meq/g)
0.05	3.7
0.10	4.0
0.15	4.6
0.20	5.0
0.25	5.4
0.30	6.2
0.35	6.5
0.45	7.1
0.40	7.1
0.50	7.1
0.55	7.1

The optimum eluent concentration for complete elution of H^+ ions was 0.4 M NaCl. The maximum elution with a concentration of 0.4 M NaCl was observed, as indicated in Figure 15.

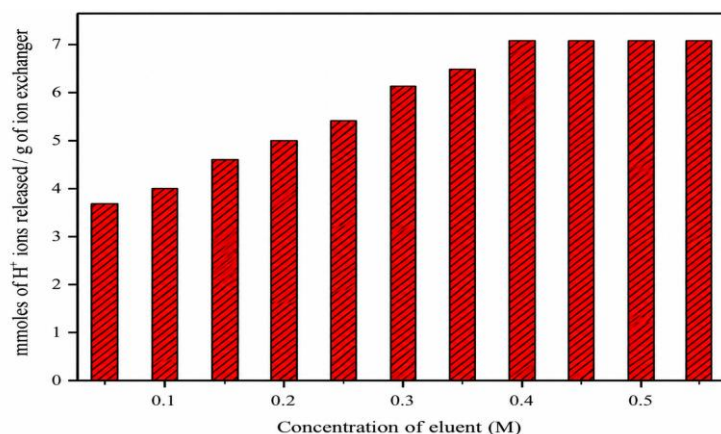


Figure 15: Concentration plot of POT/Bi(III) phosphotungstate cation-exchanger

The elution behavior of the poly-O-toluidine-Bi(III) phosphotungstate composite cation-exchanger (Figure 16) indicates that the exchange is fairly quick, as 160 mL of NaCl solution (1 M) is enough to release the H⁺ from 1 g of POT/Bi(III) phosphotungstate cation exchange material.

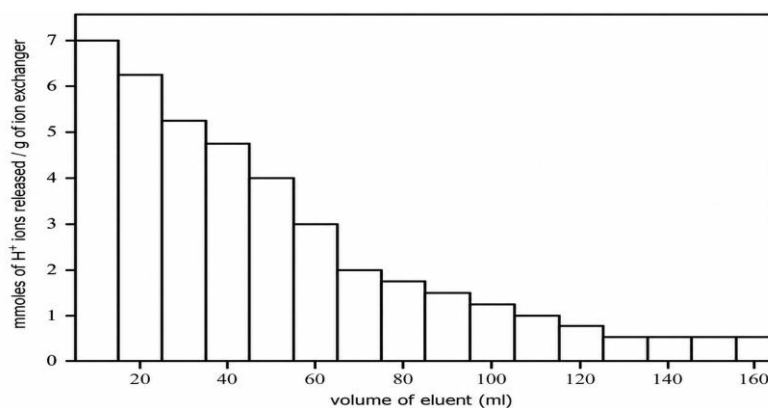


Figure 16: Elution behavior of poly-O-toluidine-Bi(III) phosphotungstate cation-exchanger

The effect of time on the exchange capacity of POT/Bismuth(III) phosphotungstate cation-exchanger (Figure 17) shows constant capacity only after 5 h of equilibrium.

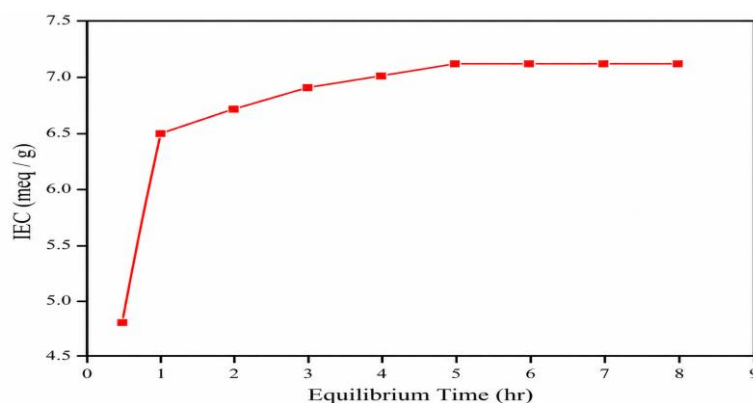


Figure 17: Effect of equilibrium time on IEC of POT/ Bi(III) phosphotungstate cation-exchanger

The chemical stability of the material was determined in demineralised water, metal chloride solutions (NaCl, KCl), acid media (H₂SO₄, HCl), and organic solvents such as acetone and methanol. The results showed that the material was stable in these media, as evidenced by no change in the sample's color, form or weight. However, it was unstable to bases such as NaOH and

KOH. In alkaline media, the material became colorless due to hydrolysis of the exchanger at higher pH values. The mechanism for the formation of the organic-inorganic nano-composite cation exchanger is (Figure 18):

- Poly-O-toluidine was prepared by oxidative coupling using K₂S₂O₈ in an acidic medium.

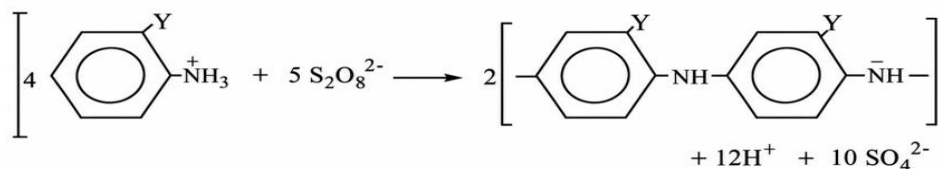


Figure 18: Schematic representation of the oxidative polymerization of substituted aniline

The ionic interaction between the radical cation of poly-O-toluidine and anionic groups of Bi (III)phosphotungstate makes possible the incorporation of polyaniline into the matrix of Bi(III)phosphotungstate (Figure 19).

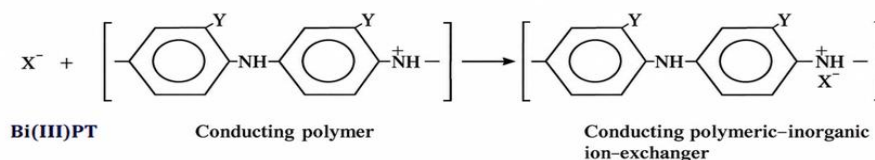


Figure 19: Schematic representation of the formation of the conducting polymeric-inorganic ion exchanger

Where,

Y- CH₃ – O-toluidine

X⁻ – Bi(III)PT

4. Conclusion

In this study, researchers successfully synthesized a novel organic-inorganic hybrid nano-composite cation exchanger, poly-O-toluidine-bismuth(III) phosphotungstate (POT/Bi(III)PT), via a facile sol-gel mixing method. Structural and morphological characterizations confirmed the successful integration of the organic polymer into the inorganic matrix. Fourier-transform infrared (FT-IR) spectroscopy demonstrated significant modifications in the characteristic quinoid, benzenoid, and C-N stretching modes (observed at 1588 cm⁻¹, 1492 cm⁻¹, and 1382 cm⁻¹, respectively), indicating a strong electrostatic and ionic interaction between the radical cations of poly-O-toluidine and the anionic groups of the bismuth(III) phosphotungstate matrix. X-ray diffraction (XRD) studies validated the nanomaterial profile of the hybrid exchanger, revealing a controlled crystalline particle size of 49.6 nm. Furthermore, scanning electron microscopy (SEM) images highlighted a distinctly transformed, heterogeneous surface morphology upon composite formation compared to the native polymer. The synthesized POT/Bi(III)PT nano-composite exhibited a superior ion-exchange capacity (IEC) relative to its individual organic and inorganic components. Evaluated parameters indicated that the material's IEC is strongly governed by both the size and charge of the exchanging ions.

For both alkali and alkaline earth metal ions, adsorption affinity inversely correlated with hydrated ionic radii (K⁺ > Na⁺ and Ba²⁺ > Sr²⁺), suggesting that ions with smaller hydration shells navigate the composite's porous architecture more easily. Chromatographic and elution performance tests showed highly efficient ion-exchange kinetics; complete elution of exchangeable H⁺ ions from 1 g of the material was achieved within the initial 160 mL of a 0.4 M NaCl eluent, while optimal equilibrium was achieved at a contact time of 5 hours. The hybrid material exhibited outstanding chemical stability and structural durability across diverse environments—including distilled water, neutral metal chlorides (NaCl, KCl), organic solvents (acetone, methanol), and highly concentrated mineral acids (7N HCl, 5 M H₂SO₄). Although it is susceptible to hydrolytic degradation at elevated alkaline values (NaOH, KOH), its overall robustness in harsh chemical environments, combined with enhanced granulometric stability, reinforces its adaptability for rigorous column operations. Collectively, the high selectivity for heavy metal ions, excellent reproducibility, and enhanced mechanical properties position the POT/Bi(III)PT nano-composite as a highly promising and sustainable candidate for targeted environmental remediation and wastewater treatment applications.

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Ethics and Consent Statement: This research adheres to ethical guidelines and obtains informed consent from all participants. Confidentiality measures were implemented to safeguard participant privacy.

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