AVE Trends in Intelligent Applied Sciences

Synthesis and Characterization of Polyaniline–Ce (IV) Tungstomolybdate Hybrid Nanocomposite for Cation Exchange and Dye Removal Applications

N. Kohila[1,*], P. Subbulakshmi[2]

[1,2]Department of Chemistry, Aditanar College of Arts and Science, Affiliated to Manonmaniam Sundaranar University, Tirunelveli, Tamil Nadu, India.
nkohila302@gmail.com[1], subbulakshmimuthukumar1991@gmail.com[2]

*Corresponding author

Abstract: A novel organic–inorganic nanocomposite cation exchanger, polyaniline cerium (IV) tungstomolybdate (PANI/Ce (IV)TM), was synthesised via sole-gel mixing of an organic polyaniline polymer into an inorganic cerium (IV) tungstomolybdate framework. Polyaniline was prepared through oxidative coupling using K2S2O8 in an acidic medium, with binding driven by ionic interactions between the polyaniline radical cations and the anionic groups of the inorganic matrix. FT-IR and UV-V spectroscopy confirmed successful composite formation, while XRD verified its crystalline nature with an average particle size of 8.7 nm. SEM imaging revealed distinct surface-morphology alterations post-incorporation. Compared to its precursors, PANI/Ce (IV)TM demonstrated an enhanced ion-exchange capacity, reaching 3.0 meq/g for K+ and 2.1 meq/g for Ba2+. Column dynamic trials revealed a selective affinity sequence (K+ > Na+ and Ba2+ > Sr2+ > Ca2+) governed by hydrated ionic radii. The hybrid exhibited remarkable chemical stability in organic solvents and concentrated acids (up to 7N), though it underwent alkaline hydrolysis. Crucially, the nanocomposite displayed highly efficient adsorption toward methyl violet dye. With excellent granulometric properties and reproducibility, PANI/Ce (IV)TM is a highly promising, sustainable adsorbent for industrial wastewater treatment and selective heavy-metal recovery.

Keywords: Organic–Inorganic Hybrid; Organic Polyaniline Polymer; Cation Exchanger; Polyaniline and Cerium (IV) Tungstomolybdate; Wastewater Remediation; Dye Adsorption; Cation Exchange.

Cite as: N. Kohila and P. Subbulakshmi, "Synthesis and Characterization of Polyaniline–Ce (IV) Tungstomolybdate Hybrid Nanocomposite for Cation Exchange and Dye Removal Applications," *AVE Trends in Intelligent Applied Sciences*, vol. 2, no. 1, pp. 45–58, 2026.

Journal Homepage: https://www.avepubs.com/user/journals/details/ATIAS

Received on: 24/12/2024, **Revised on:** 15/02/2025, **Accepted on:** 28/04/2025, **Published on:** 03/03/2026

DOI: https://doi.org/10.64091/ATIAS.2026.000295

1. Introduction

Conducting polymers are organic polymers that conduct electricity; such compounds may be true metallic conductors or semiconductors [2]. It is generally accepted that metals conduct electricity well and that organic compounds are insulating, but this class of materials combines the properties of both. Extensive delocalisation of electrons in the polymer backbone is necessary for a polymer to behave as an electrical conductor [1]. This delocalisation of electrons may occur through the interaction of π -bonded electrons in a highly conjugated chain or by a similar interaction of π-electrons with non-bonded

electrons of electron-rich hetero atoms (S, N, etc) in the backbone. Polyaniline is one of the most intensively investigated polymers during the last decade [3].

Aniline polymers have been of particular interest because of their environmental stability, controllable electrical conductivity, and redox properties associated with chain nitrogens [4]. The aniline polymers also exhibit crystallinity. Furthermore, the electrical properties of the aniline polymer can be substantially improved through secondary doping [5]. The excellent processability, together with the presence of multiple intrinsic redox states, has substantially enhanced the potential applications of aniline polymers in practical devices [6]. Insoluble salts of heteropolyacids with polyvalent metals are preferred over other ion exchangers because they exhibit selective ion-exchange behaviour. Islam and Patel [18] have studied tin (IV) vanadophosphate, tin (IV) vanadotungstate Qureshi and Kaushik [9], and tin (IV) phosphotungstate. Studies on Ce(IV) arsenite [11] and Ce(IV) vanadate [12] have already been reported. Heteropolyacid exchangers based on cerium (IV) have not been studied in detail [7]. Ion exchange materials have found extensive application in analytical and industrial chemistry due to their unique properties, including insoluble matrices, stoichiometric exchange, and good selectivity and specificity, as well as their applicability to column operations [8].

The important inorganic ion exchangers, tetravalent metal acid salts, are promising materials, as they possess robust properties, good ion-exchange characteristics, thermal stability, and chemical resistance [13]. The interest in using organic ion exchangers with rare-earth ions stems from their ability to increase the number of acid sites in the material's structure, thereby improving adsorption [9]. Among tetravalent metal acid salt mixed materials containing a cation and two different anions, those that show improved ion exchange properties and selectivity for a particular metal ion compared to their single salt counterparts. Separation involves both classical and modern techniques [10]. Examples of classical methods include precipitation and distillation. The general methods of separation include distillation, extraction, precipitation, crystallisation, dialysis, and diffusion [11]. The most modern and versatile techniques used for separations are chromatography, electrophoresis, and ion-exchange chromatography. Ion exchange chromatography has emerged as a versatile and standard analytical tool. Heteropolyacid salt can be used as an inorganic ion exchanger. The exchangers of this type are stable in moderately concentrated acid [12]. However, they dissolve in an alkali solution [13].

Heteropolyacid salt mixed materials containing a cation and two different anions show improved ion exchange properties and selectivity for a particular metal ion compared to their single salt counterparts [14]. The heteropolyacid exhibits a high affinity for heavy alkali metals, thorium, and silver. The size of univalent ions of these elements is suitable for their retention in the crystal lattice of heteropolyacids. They are more thermally and chemically stable; secondly, they are selective, and their ion-exchange capacities are higher than those of their simple salts. The main advantages of synthetic organic ion exchange resins are their high capacity, wide applicability, versatility, and low cost relative to some synthetic inorganic materials [15]. The main limitations are their limited radiation and thermal stability. At a total absorbed radiation dose of 10^9 to 10^{10} rads, most organic resins will exhibit a severe reduction in their ion exchange capacity. A composite ion exchanger consists of one or more ion exchangers combined with another material, which may be inorganic or organic and may itself be an ion exchanger [16]. The organic – inorganic hybrid materials prepared via the sol-gel technique have attracted significant attention in the literature. The combination of organic and inorganic precursors yields hybrid materials with mechanical properties not found in either precursor. Organic-inorganic composite ion-exchange materials exhibit improved granulometric properties, making them more suitable for column operation [17].

The binding of an organic polymer also improves the mechanical properties of the end product, i.e., composite ion exchange materials [19]. Inorganic ion-exchangers based on a polymer matrix are an interesting material, as they should possess mechanical stability due to the presence of organic polymeric species and the basic characteristics of an inorganic ion-exchanger, including selectivity towards specific metal ions. It was therefore considered to synthesise a hybrid ion-exchanger with a high ion-exchange capacity, good stability, reproducibility, and selectivity for heavy metal ions, indicating its environmental applications. Swain et al. [16] reported that the framework polyacrylamide with thorium (IV) phosphate was synthesised by the co-precipitation method. The practical applicability of this study was demonstrated by its use in removing lead ions. Soldatov et al. [17] reported that among the various methods adopted for the removal of different pollutants, the ion exchange method has attracted researchers because it exhibits high sorption efficiency in both gaseous and liquid media. Islam and Patel [18] reported that polyacrylamide thorium (IV) phosphate is an important lead-selective fibrous ion exchanger. Ray et al. [4] reported that synthetic inorganic ion exchangers based on tetravalent ions have been the subject of considerable study in recent years due to their selectivity and intercalation properties [20].

Shady [19] reported that Zr (IV) molybdate, one of the members of insoluble salts of polyvalent metals, was particularly selected to overcome the limitations associated with inorganic ion exchangers by creating a composite cation exchanger [21]. Qureshi et al. [8] reported that polyaniline Zr (IV) tungstomolybdate has a high ion-exchange capacity, high stability, and good selectivity for toxic metals [22]. The objective of the present work is to synthesise and characterise an organic-inorganic hybrid cation-exchanger by incorporating the organic polymer polyaniline into the inorganic ion-exchanger cerium (IV)

tungstomolybdate. It is also interesting to study the ion – exchange capacities of polyaniline-Ce (IV) tungstomolybdate cation-exchanger using an ion-exchange chromatography column. The effect of size and charge of metal ion on the IEC of polyaniline-Ce (IV) tungstomolybdate cation-exchanger was also studied by the column method. The physico-chemical characteristics of the hybrid cation-exchanger, polyaniline-Ce (IV) tungstomolybdate, were determined by FT-IR, UV-visible, XRD, and SEM studies. The particle size and morphology of the composite cation exchanger were also analysed using XRD and SEM. The sorption behaviour of cationic dye, crystal violet, towards the composite material has been studied [23].

2. Experimental Section

2.1. Chemicals

Polyaniline- [Sigma-Aldrich. CHEM Pvt. Ltd (AR)], potassium perdisulphate (KPS)- [Sigma-Aldrich. CHEM Pvt. Ltd (AR)], ceric ammonium nitrate- [HIMEDIA. CHEM Ltd (AR), sodium molybdate- [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], calcium chloride-[S.R & CHEM Pvt. Ltd], acetone, hydrochloric acid, ethanol, nitric acid, N-methyl pyrrolidone (NMP), and methyl violet are the chemicals used in this work without any purification. But aniline was purified by zinc dust distillation.

2.2. Preparation of Reagent Solutions

0.1M solutions of potassium perdisulphate and aniline were prepared in de-mineralised water and 1M HCl, respectively. A 0.1 M solution of sodium tungstate, sodium molybdate, and ceric ammonium nitrate was prepared in deionised water.

2.3. Synthesis of Polyaniline – Hydrochloric Acid Salt

Polyaniline emeraldine salt was easily synthesised by the oxidative polymerisation of aniline in aqueous acidic media by using KPS as an oxidising agent. The organic polymer, polyaniline, is prepared by mixing a 0.1M solution of KPS with a 0.1M aniline in 1M hydrochloric acid with continuous stirring by a magnetic stirrer for 30 minutes to form an emulsion of PANI/HCl; a green coloured precipitate was obtained, and it was kept for 24 hours at 0 ^{o}C in the refrigerator. The emeraldine salt was washed with organic solvents, including methanol and acetone, to remove oligomers. The polyaniline salt is dried under vacuum for 24 hours to obtain green-black powder of PANI-HCl emeraldine salt.

2.4. Synthesis of Cerium (IV) Tungstomolybdate Ion-Exchanger

Cerium (IV) tungstomolybdate was synthesised by mixing equimolar solutions of ceric ammonium nitrate (0.1), sodium tungstate (0.1M), and sodium molybdate (0.1M) in the volume ratio 1:1:2 with slow and continuous stirring at a pH of 2. Nitric acid was added to the precipitates to achieve the desired pH. The resulting yellow precipitate was allowed to stand in the mother liquor for 24 hours and then filtered. After filtration, the precipitate was continuously washed with distilled water to remove excess acid, then dried at room temperature.

2.5. Synthesis of Polyaniline-Ce (IV) Tungstomolybdate Hybrid Ion- Exchanger

The hybrid cation-exchanger was prepared by sol-gel mixing polyaniline, an organic conducting polymer, with the inorganic precipitate of cerium (IV) tungstomolybdate. In the synthesis of polyaniline Ce (IV) tungstomolybdate, when the gels of polyaniline were added to the yellow precipitate of Ce (IV) tungstomolybdate, with constant stirring for 7 hours. The resulting mixture was slowly turned into greenish-black coloured slurries and kept for 24 hours at 0 °C. Now, the polyaniline-based composite gels were filtered off and washed thoroughly with deionised water to remove excess acid and adhering traces of KPS. The dried product was washed with ethanol and acetone to remove oligomers. The dried product was ground into small granules and converted to the H+ form by placing it in 1 M HNO_3 for 24 hours with occasional shaking at room temperature. The excess acid was removed after several washings with DMW, and the sample was finally dried.

3. Results and Discussion

3.1. FT-IR Characterisation of the Material

An FT–IR study of the sample was performed to identify various functional groups and structural features in the material. The FT-IR spectra of polyaniline (PANI), Ce (IV) tungstomolybodate, polyaniline-Ce(IV) tungstomolybodate, and the H^+ form of polyaniline-Ce (IV) in the original form dried at 50 ^{o}C over were taken by the KBr disc method at room temperature.

3.1.1. FT-IR Characterisation of Polyaniline – HCl Salt

FTIR spectrum shows the presence of characteristic functional groups in the synthesised aromatic boron-containing compound. The observed characteristic absorption bands corresponding to N–H, aromatic C–H, N–B- N and C-N vibrations and the aromatic ring deformation modes support the successful formation of the proposed molecular structure (Table 1).

Table 1: Assignments for FT-IR absorption bands of PANI-HCl salt

Frequency (cm^{-1})	Assignment
3434.6	NH stretching vibrations
2922.5	Aromatic C-H stretching vibration
1460.3	stretching N-B-N
1398.3	C-N stretching in QB, Q
1013.4	C-H bending vibrations
735.71	C-H out-of- plane bending of 1, 4 rings
592, 535	Aromatic ring deformation

The FT-IR spectrum of PANI doped with HCl is shown in Figure 1. A broad, strong band at 3434 cm-1 is assigned to -NH stretching mode vibrations.

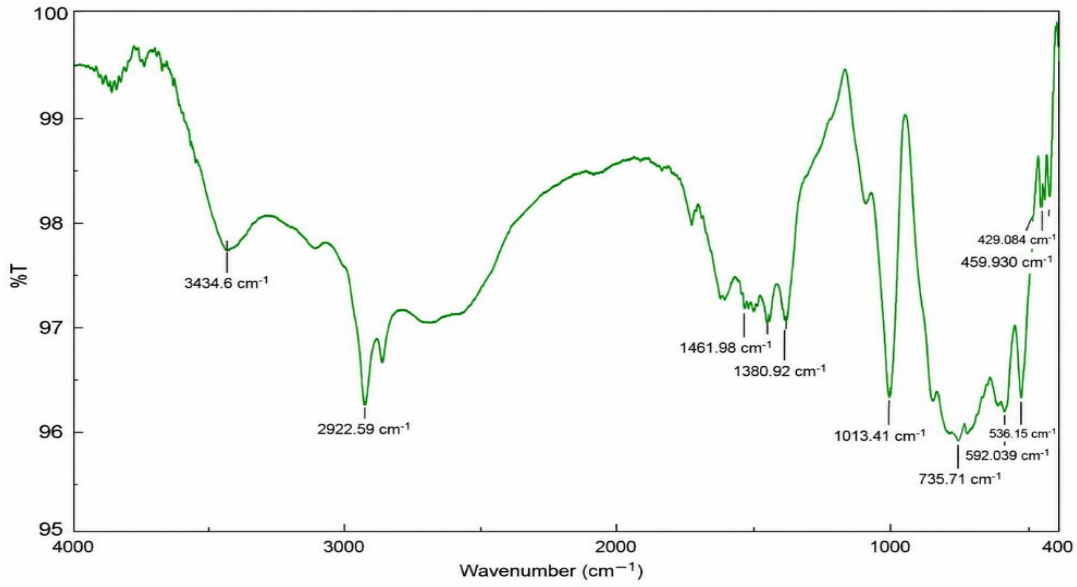

Figure 1: FT– IR spectrum of PANI – HCl salt

The polymer shows an absorption band at 2922 cm-1, attributed to aromatic C-H stretching vibrations. The weak intense bands at around 1550 cm^{-1} and 1460 cm-1 have been assigned, respectively, to the ring-stretching modes of the quinoid and benzenoid rings. The peaks at 1464 cm^{-1} confirm the presence of a protonated imine function.

3.1.2. FT-IR Characterisation of Ce (IV) Tungstomolybdate Ion-Exchanger

The FTIR analysis confirms the successful synthesis of the material, with characteristic bands for hydroxyl groups, water molecules, molybdate ions, and Ce-O bonds. The observed bands suggest the presence of hydration and the formation of a stable metal oxide framework (Table 2).

Table 2: Assignments for FT – IR absorption bands of Ce (IV) tungstomolybdate

Frequency (cm^{-1})	Assignment
3397.96	Presence of an interstitial water molecule and a hydroxyl group
1614.13	Due to the H–bonded OH group.
1382.62	Deformation vibrations of interstitial water

946.877	Presence of Ce-OH group
901.55	Presence of molybdate ion
536.1 & 419	M-O stretching vibrations (Ce-O)

In the FT-IR spectrum of cerium (IV) tungstomolybdate ion-exchanger, the broad band at 3397 cm^{-1} may be assigned to OH stretching vibrations [20]. The bands at 1618 cm-1 indicate the presence of an external water molecule. The peak around 1382 cm^{-1} is assigned to the deformation vibration of interstitial water [21]. A sharp peak at 946 cm^{-1} is attributed to the presence of the Ce-O-H group. The peaks at 901 cm^{-1} are due to the presence of the molybdate anion. The absorption band further confirms the presence of the tungstate group at 536 cm^{-1} (W-O stretching). An assembly of peaks in the region 700-419 cm^{-1} is attributed to metal oxygen stretching vibrations (Figure 2).

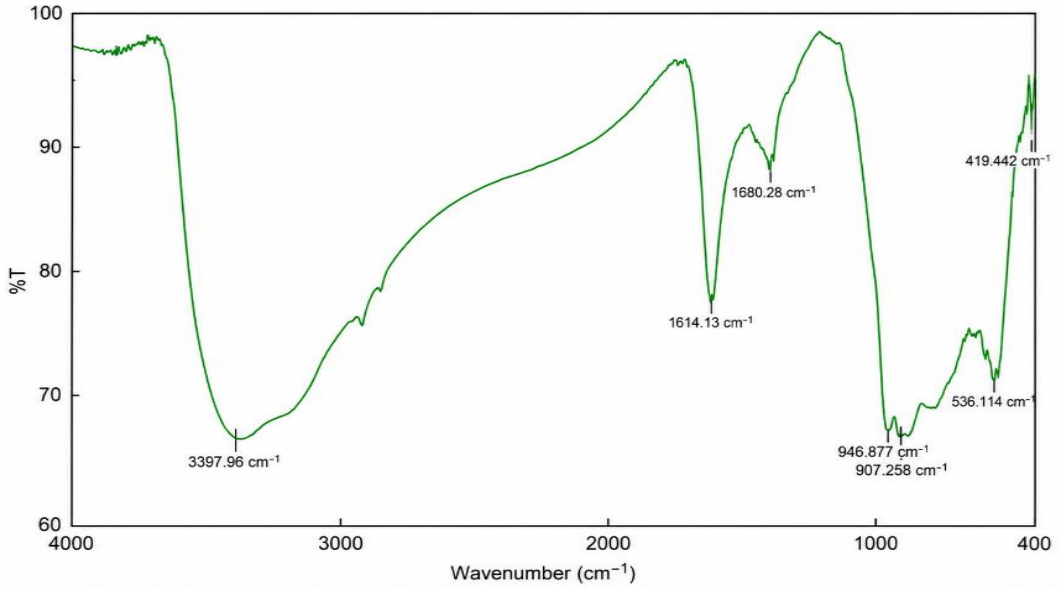

Figure 2: FT- IR spectrum of cerium (IV) tungstomolybdate

3.1.3. FT-IR Characterisation of Polyaniline-Ce (IV) Tungstomolybdate Ion – Exchanger

The characteristic functional groups and the metal-oxygen bonds in the FTIR spectrum confirmed the successful formation of the synthesised composite. Absorption bands are assigned to N-H, aromatic C-H, C-N, N═Q═N, N-B-N, Mo-O-Ce and M-O vibrations, indicating the presence of aromatic, boron-containing and metal oxide components in the composite structure (Table 3).

Table 3: Assignments for FT–IR absorption bands of polyaniline-Ce (IV) tungstomolybdate nanocomposite ion-exchanger

Frequency (cm^{-1})	Assignment
3418.21	NH stretching vibrations
2923.56	Armatic C-H stretching vibrations.
1563.99	Stretching of N=Q=N
1471.42	Stretching of N-B-N
1296.89	C-N stretching of primary amines
1118.51	Due to C-H bending vibrations
799.35	Due to the presence of the Mo-O-Ce linkage
501.4 & 410	Aromatic ring deformation, as well as the presence of M-O Stretching vibrations

The FT-IR spectrum of the PANI-Ce (IV) tungstomolybdate cation exchanger is shown in Figure 3. The vibration bands at 3418 cm-1, 2923 cm-1, 1563 cm-1, 1471 cm-1, and 1296 cm-1 are the characteristic peaks of polyaniline. In this spectrum, strong absorption peaks at 1563 cm^{-1} and 1471 cm^{-1} are assigned to the ring stretching mode of quinoid and benzenoid ring, respectively. The peak at 799 cm^{-1} may be due to the Mo-O stretching vibration. An assembly of peaks in the region 799 cm^{-1} – 410 cm^{-1} shows the M-O stretching vibrations. It is confirmed from the FT-IR spectrum of the composite that both organic polymer and inorganic ion–exchanger are present in PANI-Ce (IV) tungstomolybdate nanocomposite.

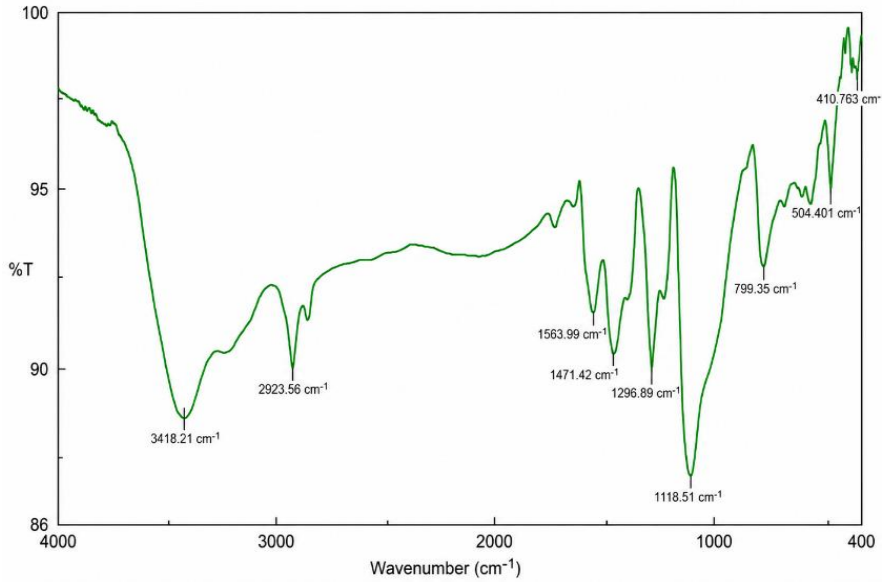

Figure 3: FT-IR spectrum of polyaniline-Ce (IV) tungstomolybdate ion – exchanger

3.1.4. FT-IR Characterisation of H^+ Form of Polyaniline-Ce (IV) Tungstomolybdate Ion – Exchanger

From the FT-IR spectrum of H^+ form of PANI-Ce (IV) tungstomolybdate, the principal characteristic peaks of quinoid, benzenoid N moieties, NH stretching, and C-N stretching vibrations are reported to occur at 1576 cm^{-1}, 1486 cm^{-1}, 3202 $cm^{-1,}$ and 1383 $cm^{-1,}$ respectively, implying the presence of polyaniline in the nanocomposite ion-exchanger. Still, they are modified both in intensity and peak position when polymers are incorporated into the inorganic matrix of Ce (IV) tungstomolybdate (Figure 4).

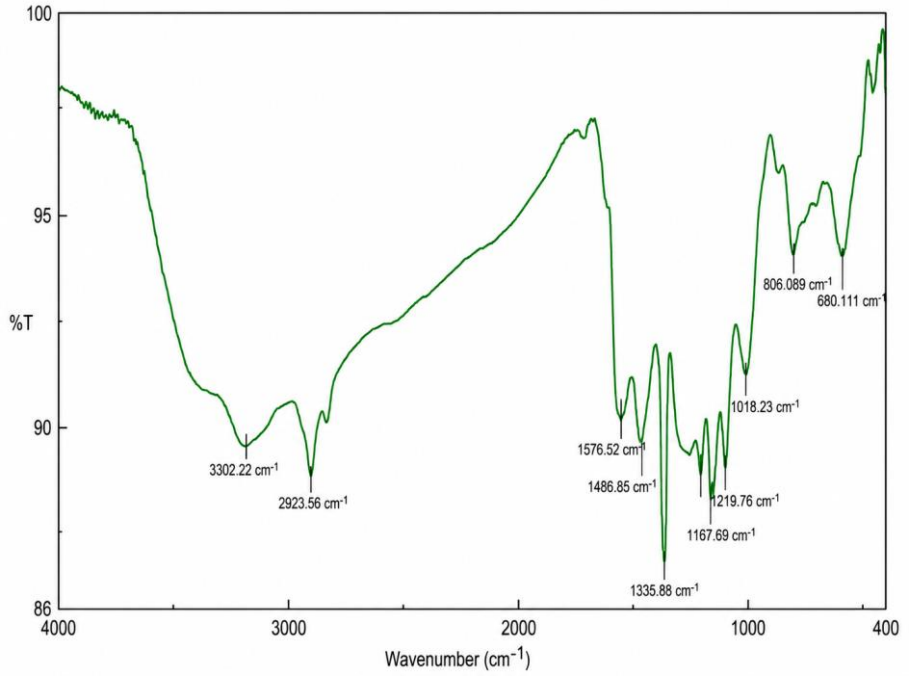

Figure 4: FT -IR spectrum of H^+ form of polyaniline-Ce (IV) tungstomolybdate ion- exchanger

An absorption peak at 1018.23 cm^{-1} is attributed to the presence of the Ce-OH group, and the peak around 806.09 cm^{-1} is due to the presence of Mo-O-Ce linkage, which is also present in the nanocomposite, indicating the binding of inorganic ion-exchanger with organic polymer and formation of organic-inorganic hybrid 'PANI/Ce (IV) tungstomolybdate (Table 4).

Table 4: Assignments for FT-IR absorption bands of H^+ form of polyaniline-Ce (IV) tungstomolybdate ion – exchanger

Frequency (cm^{-1})	Assignment
3202.22	NH stretching vibration
2923.56	Aromatic C-H stretching vibrations
1576.52	Stretching of N=Q=N
1486.85	Stretching of N-B-N
1383.68	C-N stretching vibration
1219.76	C-N stretching vibration of primary amine
1167.69	C-H in-plane bending of the 1,2,4 ring
1018.23	The presence of the Ce-O-H group
806	The presence of the Mo-O-Ce linkage
509.11	Aromatic ring deformation as well as M-O stretching vibrations

3.2. UV-Visible Characterisation of the Material

UV-visible absorption spectra of chemically synthesised polyaniline emeraldine salt and PANI-Ce (IV)tungstomolybdate in N-Methyl 2-Pyrrolidine as a solvent, and the spectra are represented in Figures 5 and 6. From the UV-visible spectrum of freshly prepared PANI in NMP solution, the broad band at around 620 nm is due to n-π $*$transition of quinine-imine groups. From the UV-visible spectrum of PANI-Ce (IV) tungstomolybdate ion-exchanger, the spectrum shows two absorption bands.

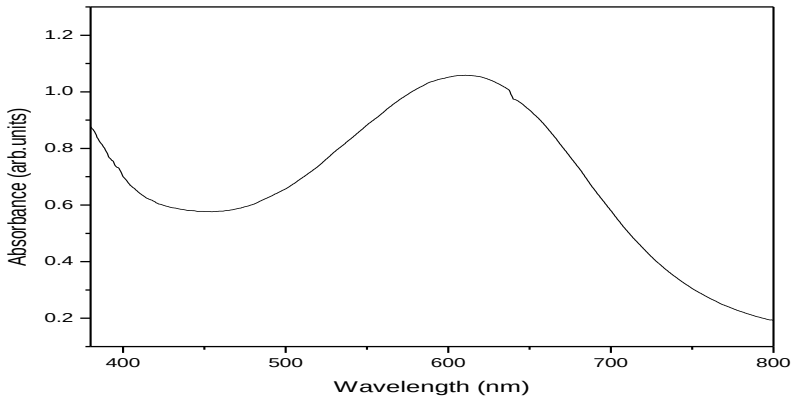

Figure 5: UV-visible spectrum of PANI-HCl emeraldine salt

The first absorption band is located at ~ 420nm, and another at 580nm, which has been assigned to a π-$\pi*$ transition, and the other is associated with the transition of benzenoid rings into quinoid rings.

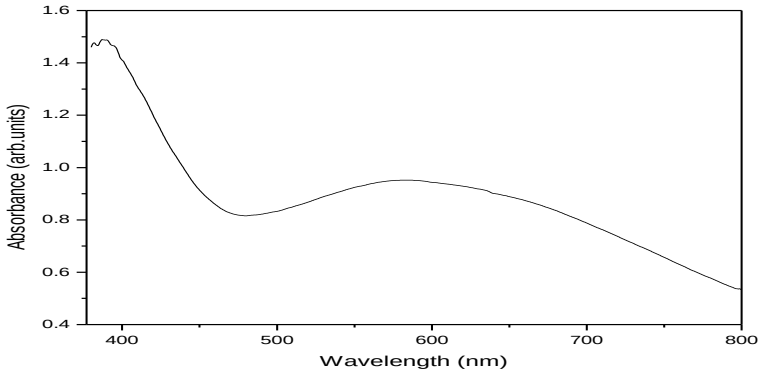

Figure 6: UV-visible spectrum of PANI-Ce (IV) tungstomolybdate ion-exchanger

Comparing with the UV-visible spectrum of PANI, the absorption peak due to quinoid ring transition of the curve appears at a shorter wavelength (i.e., 580nm suggesting that there may be an interaction between Ce (IV) tungstomolybdate and the PANI chain. This interaction increases the energy of the quinoid ring transition, thereby shifting it to a shorter wavelength.

3.3. XRD Characterisation of the Material

The powder X-ray diffraction technique has been employed to identify the crystalline phases of the present sample. X-ray diffraction patterns were recorded from 20 ˚ to 90 ˚ on a PANalytical diffractometer using CuKα (1.54056 Å) radiation at an accelerating voltage of 40 kV. Data were collected at a counting rate of 1/min, and the Kα doublets were well resolved. From XRD, the particle size can be found by using Scherrer's formula:

$$D = \frac{0.96\lambda}{\beta \, Cos\theta} \qquad (1)$$

D – Particle size of the sample (nm)
λ – Wavelength of X-ray (1.54056 Aº)
B – Full maxima half width (rad)
θ – Diffraction angle between the incident and diffraction beam (°)

The PANI diffraction pattern shows a broad peak at about 2θ = 28.1°, a characteristic PANI peak. XRD pattern of PANI – HCl is presented in Figure 7. Broad peaks were obtained, indicating the sample was poorly crystalline. The average crystalline size of PANI calculated is 37 nm.

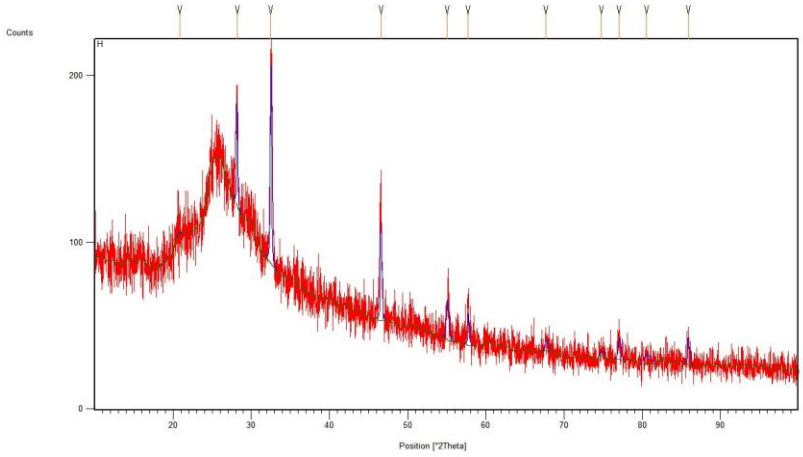

Figure 7: XRD pattern of PANI – HCl emeraldine salt

The X-ray analysis of the Ce (IV) tungstomolybdate ion-exchanger (Figure 8) showed that there are no sharp peaks. It was revealed that the material is amorphous.

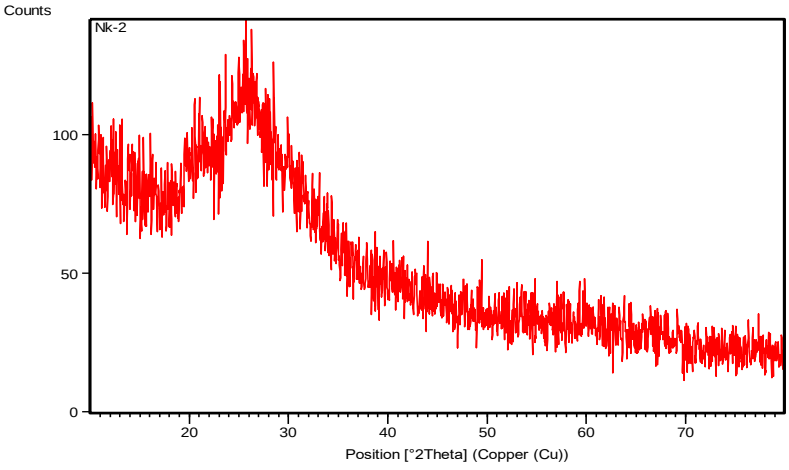

Figure 8: XRD pattern of Ce (IV) tungstomolybdate ion-exchanger

X–ray diffraction of the composite ion-exchanger PANI-Ce (IV) tungstomolybdate. Figure 9 showed a broad peak at 2θ = 25.0° rather than sharp peaks, indicating that the sample was poorly crystalline. The average crystalline size of PANI-Ce (IV) tungstomolybdate composite cation- exchangers was found to be in the range of 8.7 nm. Thus, XRD confirmed that the composite particle size falls within the nanoscale range.

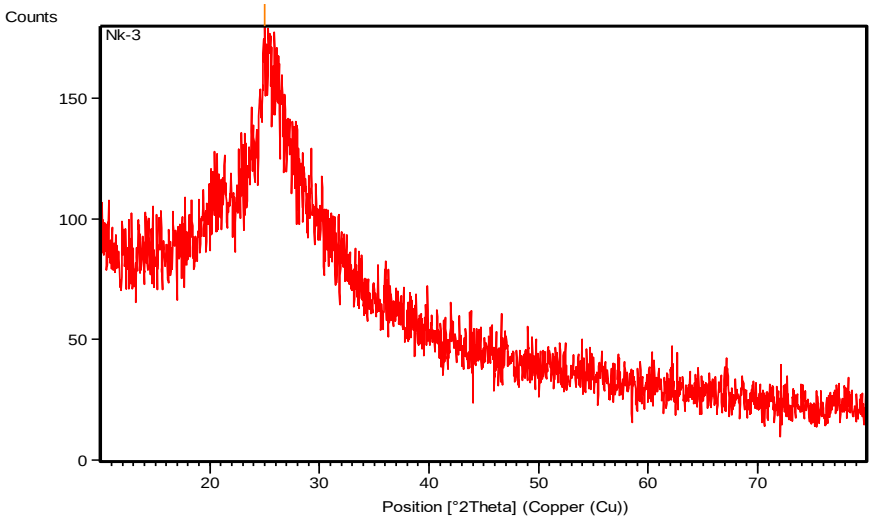

Figure 9: XRD pattern of PANI/Ce (IV) tungstomolybdate ion- exchanger

3.4. Scanning Electron Microscopy Studies

SEM was performed on ground materials by an electron microscope at various magnifications. Microphotographs of the original form of polyaniline, organic - inorganic hybrid ion- exchange materials, polyaniline-Ce (IV)tungstomolybdate, were obtained by scanning electron microscopy at various magnifications. SEM images showed differences in the surface morphology of the organic polymer and the composite. It has been revealed that, upon binding of PANI to Ce (IV) tungstomolybdate, the morphology changes (Figure 10).

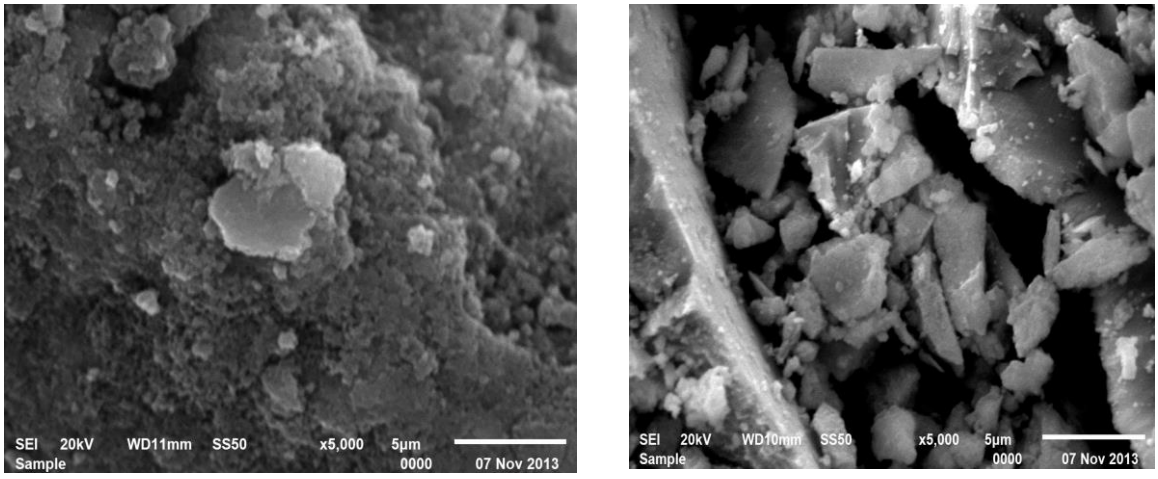

Figure 10: SEM photographs of (a) polyaniline, (b) PANI-Ce (IV) tungstomolybdate

3.5. Determination of Ion-Exchange Capacity (IEC) by Column Method

The IEC of the material was determined by the column method. 0.25 g of dry mass of PANI/Ce (IV) tungstomolybdate in the H+ form was packed into a glass column with a glass wool support at the base. An equimolar solution of alkali and alkaline earth metal chlorides was slowly passed through the column, with the effluent rate adjusted to 9-10 drops per minute. The

effluent was carefully collected in a 250 mL conical flask. The collected effluent was titrated against a standard sodium hydroxide solution to determine the total H^+ ions released.

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

The IEC of the polyaniline-Ce (IV) tungstomolybdate was also determined by the column process for different alkali and alkaline earth metals. Five equal parts of 0.25 g each of the cation-exchanger were packed in five different columns, and then some distilled water was passed through the column to wash and settle the granules to make a bed.

Table 5: IEC of PANI-Ce (IV) tungstomolybdate for various cations

Exchanging Cation	Salt Used	Ionic Radii (A°)	Hydrated Ionic Radii (A°)	IEC (meq. /g)
Na^+	NaCl	0.93	2.69	2.4
K^+	KCl	1.33	2.42	3.0
Ca^{2+}	$CaCl_2$	1.14	6.01	1.6
Sr^{2+}	$SrCl_2$	1.18		2.0
Ba^{2+}	$BaCl_2$	1.40	5.21	2.1

IEC – Ion Exchange Capacity

Five different metal ion solutions of equimolar concentration (0.4 M) were prepared. Each column was treated with a specific salt solution to induce ion exchange. The effluents were collected and titrated separately against a standard NaOH solution to determine the hydrogen ion concentration (Figure 11).

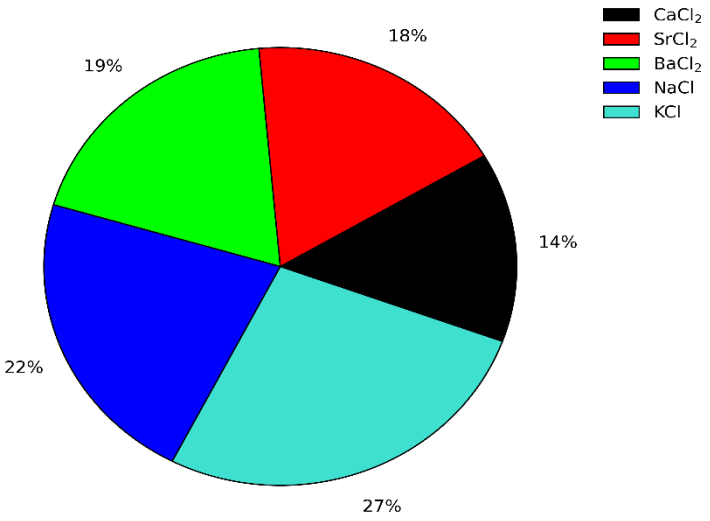

Figure 11: IEC of PANI / Ce (IV)tungstomolybdate for various cations

The effect of the size and charge of the exchanging ion on the ion exchange capacity was also observed for this hybrid material. Table 5 shows the IECs for alkali and alkaline-earth metal ions. The ion exchange capacity of hybrid cation-exchanger, polyaniline-Ce (IV) tungstomolbdate for alkali and alkaline earth metal ions increases according to a decrease in the hydrated ionic radii. Ions with smaller hydrated radii readily enter the pores of the composite cation-exchanger, leading to higher adsorption. The maximum ion-exchange capacity sequence for alkali metal ions is K+ > Na+, whereas for alkaline earth metals, the order is Ba2+ > Sr^{2+} > Ca^{2+}. The size and charge of the exchanging ion affect the IEC of polyaniline-Ce(IV) tungstomolybdate composite cation-exchanger.

3.5.2. Effect of Eluent Concentration on IEC

The magnitude of elution depends on the eluent concentration. To find out the optimum concentration of eluent for complete elution of H^+ ions, a fixed volume of NaCl solution of varying concentration was passed through a column containing 0.25g of the exchanger in H^+ form with a flow rate of 0.5ml min^{-1}. The effluent was titrated against a standard solution of NaOH to determine the H^+ ions eluted (Table 6).

Table 6: Effect of eluent concentration on IEC polyaniline-Ce (IV) tungstomolybdate cation-exchanger

Concentration of Eluent, NaCl (M)	IEC for Na^+ ion (meq. /g)
0.05	2.5
0.1	2.7
0.15	3.0
0.2	3.2
0.25	3.5
0.3	3.8
0.35	4.3
0.4	5.2
0.45	5.2
0.5	5.2
0.55	5.2

IEC-Ion Exchange Capacity

The optimal eluent concentration for complete elution of H+ ions was found to be 0.4 M NaCl. A maximum elution was observed with the concentration of 1M NaCl, as indicated in Figure 12.

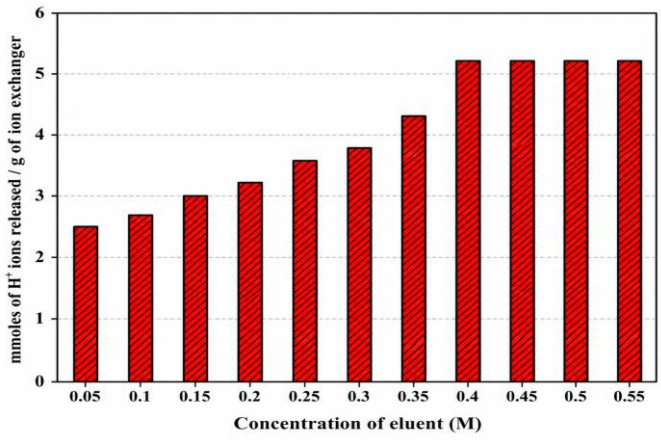

Figure 12: Concentration plot of polyaniline- Ce (IV) tungstomolybdate cation- exchanger

3.5.3. Elution Behaviour

For this study, a 0.4M NaCl solution of optimum concentration was passed for complete elution of H^+ ions through a column containing 1g of the polyaniline-Ce (IV) tungstomolybdate composite cation-exchanger H^+ form with a flow rate of 0.5 mL min^{-1} (Figure 13).

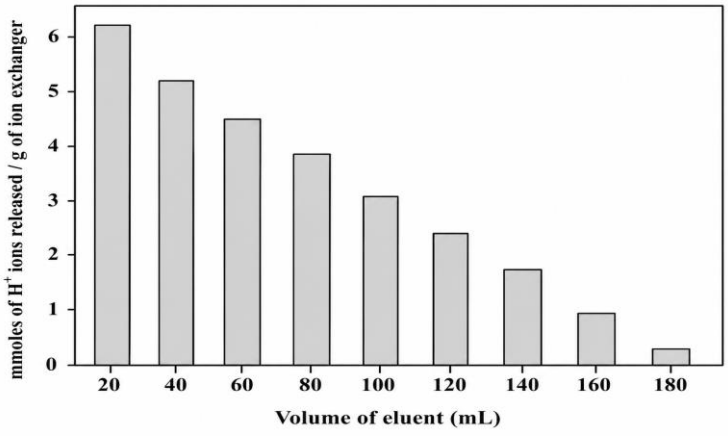

Figure 13: Elution behaviour of polyaniline-Ce (IV) tungstomolybdate cation-exchanger

The effluent was collected in 10 mL fractions, and each fraction was titrated against a standard alkali solution to determine the H^+ ions eluted. This experiment was conducted to determine the minimum volume required for complete elution of H+ ions, which determines the column's exchange efficiency. The elution behaviour of polyaniline-Ce (IV) tungstomolybdate composite cation-exchanger indicated that the exchange is quite fast because only 160 ml of NaCl solution (0.4M) is enough to release the H^+ from 1g of PANI-Ce(IV) tungstomolybdate cation-exchange material.

3.5.4. Effect of Time on IEC

The optimal shaking time for the ion exchanger with a NaCl solution for complete elution of H^+ ions was determined. 0.25g of ion exchanger was shaken with 25ml of NaCl solution, and the amount of liberated H^+ ions was titrated against the standard NaOH solution at different time intervals (Figure 14).

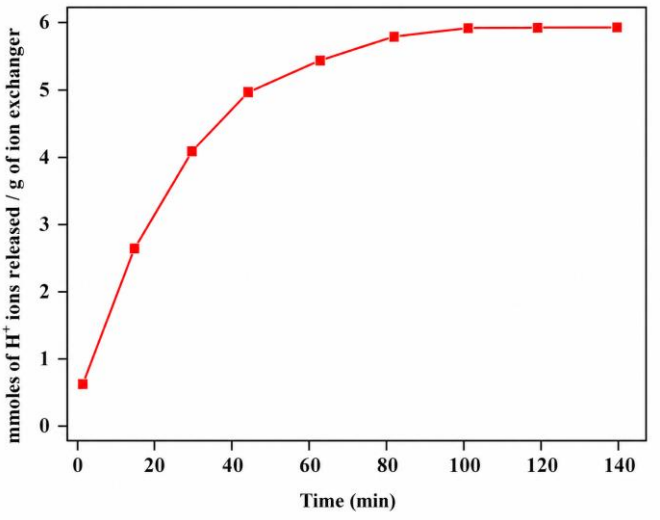

Figure 14: Effect of equilibrium time on IEC of polyaniline-Ce (IV) tungstomolybdate cation-exchanger

The effect of time on the exchange capacity of PANI-Ce (IV) tungstomolybdate cation exchanger shows a constant capacity only after 5 hours of equilibrium.

3.6. Chemical Stability Studies

To determine the extent of dissolution of the material in different chemical solvents, viz., de-mineralised water, solutions of metal chlorides, different concentrations of HCl, HNO_3, H_2SO_4, NaOH, KOH, organic solvents like acetone and ethanol, 0.1g of material was equilibrated with 25 ml of the solution of interest, and then the mixture was left as such for 24 hours at room temperature. If any material remains in solution, decant it and wash with DMW to remove excess acids and bases. The change in colour and weight was noted. This method was used to find the stability of the composite cation exchanger towards different solutions. Chemical stability studies showed that the material was stable in DMW, solutions of metal chlorides (MCl2), NaCl, and KCl, acid media (7N H2SO4, HCl, HNO3), and organic solvents (acetone, ethanol), as evidenced by no change in colour, form, or weight of the sample. It was, however, unstable in bases like NaOH and KOH. The material changed in alkaline media due to the exchanger's hydrolysis at higher p^H values.

3.7. Adsorption of Dyes

Aqueous solution of methyl violet (20 ml, $3x10^{-6}$ M) was equilibrated separately with 500 mg of polyaniline-Ce (IV) tungstomolybdate for 24 hours. The sample solution was then filtered and centrifuged to remove the adsorbent before analysis. Absorbances were recorded before and after equilibration with a UV-Visible “Elico Model SL 164” double beam spectrophotometer at the absorption maxima of the methyl violet dye (around 425 nm). UV-visible absorption spectrum of methyl violet dye before and after equilibration is shown in Figure 15. The absorption intensity of the peak at 425 nm for methyl violet showed a drastic decrease after equilibration with PANI-Ce(IV) tungstomolybdate cation exchanger. The decrease in intensity of absorption after equilibration indicates that the dye MV exhibits good sorption towards, which could be attributed to both the cation exchange nature of the sorbent and the cationic nature of the dyes. The dyes could bind to the sorbent via hydrogen bonds or weak van der Waals forces. The efficiency of the PANI/Ce(IV) tungstomolybdate cation exchanger for the removal of MV from aqueous solution indicates its promising use in wastewater containing dyes.

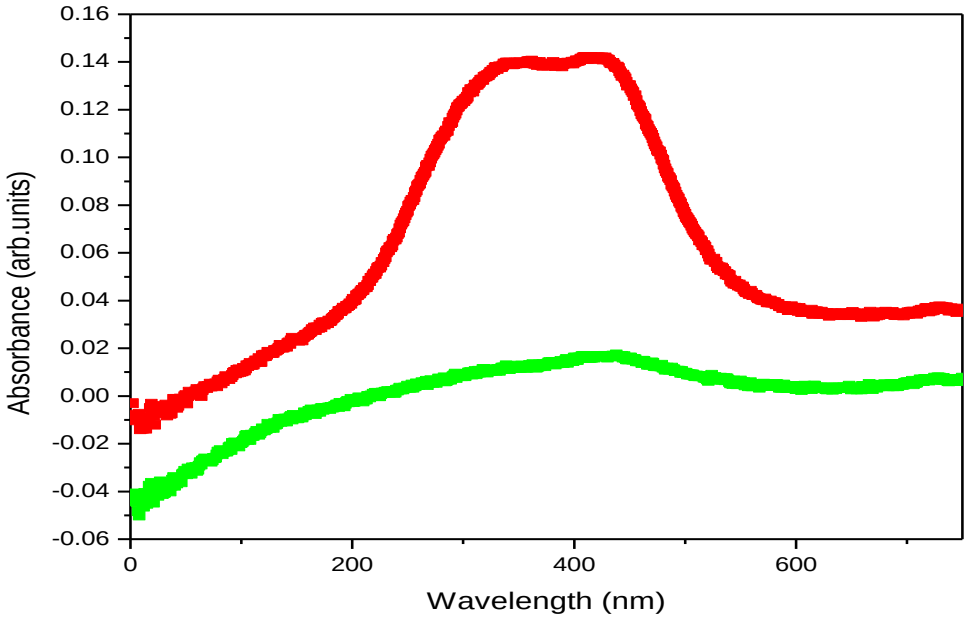

Figure 15: UV-visible absorption spectra for methyl violet

4. Conclusion

In the present study, a novel organic–inorganic nanocomposite cation exchanger, polyaniline-cerium (IV) tungstomolybdate, was successfully synthesised via a sol–gel mixing method. The fabrication relied on favourable ionic interactions between the oxidatively coupled polyaniline radical cations and the anionic framework of the inorganic matrix. Structural and morphological characterisations via FT-IR, UV-Vis, XRD, and SEM confirmed the successful integration of the polymer into the inorganic matrix, revealing a crystalline nanocomposite with an average particle size of 8.7 nm and a distinctly modified surface morphology. The hybrid material demonstrated superior performance and properties critical for environmental and industrial applications. The nanocomposite exhibited a significantly higher ion-exchange capacity than its individual components, achieving a maximum capacity of 3.0 meq/g for K^+ and 2.1 meq/g for Ba^{2+}. The exchange capacity was heavily influenced by the size and charge of the exchanging ions, inversely correlating with their hydrated radii (K^+ > Na+ and Ba2+ > Sr2+ > Ca2+), as smaller hydrated ions more readily accessed the material's nanopores. Column elution studies using NaCl showed rapid exchange kinetics, requiring a minimum eluent concentration of 0.4 M, with complete H^+ ion recovery achieved within 160 mL of effluent and a stable equilibration capacity reached at 5 hours. The material possessed excellent granulometric properties for column operations. It maintained robust chemical stability across neutral, organic, and highly acidic media (up to 7N HCl, HNO3, and 5M H2SO4), though it remained susceptible to alkaline hydrolysis. Concurrently, the nanocomposite displayed remarkable adsorption efficiency for the cationic dye, methyl violet. Combining high ion-exchange capacity, mechanical reproducibility, structural stability, and dye-adsorption capabilities, PANI- cerium (IV) tungstomolybdate emerges as a highly promising and effective hybrid adsorbent for industrial wastewater treatment and the selective removal of heavy metal ions.

Acknowledgement: The authors would like to express their sincere gratitude to Aditanar College of Arts and Science for its continuous support and encouragement throughout this research.

Data Availability Statement: Data supporting the findings are available from the corresponding author upon request.

Funding Statement: No financial support or funding was received for conducting this research or for the preparation of this manuscript.

Conflicts of Interest Statement: The authors declare that they have no conflicts of interest concerning this study. All information utilised in the research has been properly acknowledged through relevant citations and references.

Ethics and Consent Statement: Ethical guidelines were followed throughout the study. Approval was obtained from the concerned organisation, and informed consent was secured from all participants involved in the data collection process. Ethical clearance and participant consent were duly received before conducting the research.

References

1. H. Shirakawa and S.Ikeda, "Infrared spectra of poly(acetylene)," *Polym. J.*, vol. 2, no. 3, pp. 231-244, 1971.
2. D. MacInnes Jr and B. L. Funt, "Poly-o-methoxyaniline: A new soluble conducting polymer," *Synthetic Metals*, vol. 25, no. 3, pp. 235–242, 1988.
3. K. Amano, H. Ishikawa, A. Kobayashi, M. Satoh, and E. Hasegawa, "Thermal-stability of chemically synthesized polyaniline," *Synthetic Metals*, vol. 62, no. 3, pp. 229–232, 1994.
4. A. Ray, G. E. Asturias, D. L. Kershner, A. F. Richter, A. G. MacDiarmid, and A. J. Epstein, "Polyaniline: Doping, structure and derivatives," *Synthetic Metals*, vol. 29, no. 1, pp. 141–150, 1989.
5. E. T. Kang, K. G. Neoh, and K. L. Tan, "Protonation and deprotonation of polyaniline films and powders revisited," *Synthetic Metals*, vol. 68, no. 2, pp. 141–144, 1995.
6. J. P. Pouget, M. E. Jozefowicz, A. J. Epstein, X. Tang, and A. G. MacDiarmid, "X-ray structure of polyaniline," *Macromolecules*, vol. 24, no. 3, pp. 779–789, 1991.
7. A. G. MacDiarmid, L. S. Yang, W. S. Huang, and B. D. Humphrey, "Polyaniline: Electrochemistry and application to rechargeable batteries," *Synthetic Metals*, vol. 18, no. 1-3, pp. 393–398, 1987.
8. M. Qureshi, K. G. Varshney, and S. K. Kabiruddin, "Synthesis and Ion Exchange Properties of Thermally Stable Titanium (IV) Vanadate: Separation of Sr2+ from Ca2+, Ba2+, and Mg2+," *Canadian Journal of Chemistry*, vol. 50, no. 13, pp. 2071-2078, 1972.
9. M. Qureshi and R. C. Kaushik, "Synthesis and analytical applications of stannic vanadotungstate," *Separation Science and Technology*, vol. 17, no. 5, pp. 739–744, 1982.
10. M. Qureshi, R. Kumar, and R. C. Kaushik, "Synthesis and Ion-Exchange Properties of Reproducible Stannic Molybdoarsenate. Separations of Ba2+–La3+, Mg2+–La3+, Sr2+–Y3+, and Sr2+–La3+," *Separation Science and Technology*, vol. 13, no. 2, pp. 185-192, 1978.
11. C. Janardanan, S. M. Nair, and C. P. Savariar, "Studies on inorganic ion exchangers. Part 1. Preparation, properties and application of cerium (IV) arsenite," *Analyst*, vol. 113, no. 7, pp. 1141–1142, 1988.
12. C. Janardanan, S. M. K. Nair, and C. P. Savariar, "Studies on inorganic ion-exchangers: Part 3—Preparation, properties and applications of cerium (IV) vanadate," *Indian Journal of Chemistry*, vol. 28A, no. 8, pp. 693–695, 1989.
13. G. Alberti, A. Conte, and E. Torraca, "Influence of thermal treatment on the rate of ion exchange of zirconium phosphate," *Journal of Inorganic and Nuclear Chemistry*, vol. 28, no. 1, pp. 225–231, 1966.
14. Z. G. Yan and C. H. Yan, "Controlled synthesis of rare earth nanostructures," *Journal of Materials Chemistry*, vol. 18, no. 42, pp. 5056–5059, 2008.
15. R. Thakkar and U. Chudasama, "Synthesis, characterization and proton transport property of crystalline - zirconium titanium phosphate, a tetravalent bimetallic acid salt," *Journal of Scientific & Industrial Research*, vol. 68, no. 4, 312–318, 2009.
16. S. K. Swain, R. K. Dey, M. Islam, R. Patel, U. Jha, T. Patnaik, and C. Airoldi, "Removal of fluoride from aqueous solution using aluminum-impregnated chitosan biopolymer," *Separation Science and Technology*, vol. 44, no. 9, pp. 8–17, 2009.
17. V. S. Soldatov, A. A. Shunkevich, and G. I. Sergeev, "Synthesis, structure and properties of new fibrous ion exchangers," *Reactive Polymers*, vol. 7, no. 2-3, pp. 159–172, 1988.
18. M. Islam and R. Patel, "Polyacrylamide thorium (IV) phosphate as an important lead selective fibrous ion exchanger: Synthesis, characterization and removal study," *Journal of Hazardous Materials*, vol. 156, no. 1–3, pp. 509–520, 2008.
19. S. A. Shady, "Selectivity of cesium from fission radionuclides using resorcinol–formaldehyde and zirconyl-molybdopyrophosphate as ion-exchangers," *J. Hazard. Mater.*, vol. 167, no. 1-3, pp. 947-952, 2009.
20. K. Nakamoto, "Infrared Spectra of inorganic and coordination compounds," *Wiley-Interscience*, New York, United States of America, 1970.
21. M. Davies, "Infrared spectroscopy and Molecular structure: An Outline of the Principles," *Elsevier publishing co.*, Amsterdam, New York, United States of America, 1963.
22. S. A. Nabi, A. H. Shalla, A. M. Khan, and S. A. Ganie, "Synthesis, characterization and analytical applications of titanium (IV) molybdosilicate: A cation ion-exchanger," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 302, no. 1–3, pp. 241–250, 2007.
23. A. Nilchi, B. Maalek, A. Khanchi, M. G. Maragheh, and A. Bagheri, "Cerium(IV) molybdate cation exchanger: Synthesis, properties and ion separation capabilities," *Radiation Physics and Chemistry*, vol. 75, no. 2, pp. 301–308, 2006.