ORIGINAL RESEARCH PAPER

Poly(O-Toluidine)/Zirconium-based nanocomposite ion-exchangers for Water treatment and environmental remediation

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ABSTRACT

A three-component nanocomposite Poly(O-Toluidine) Zr(IV) based ion exchangers are synthesized by the sol-gel method and characterized by Fourier transform infrared spectra, X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, ion exchange studies, conductivity, and antimicrobial studies. The organic polymeric part of the composites provides mechanical and chemical stability whereas the inorganic part supports the ion-exchange behavior, thermal stability and also increases the electrical conductivity due to the good ion-exchange behavior of Zirconium (IV) molybdophosphate and Zirconium(IV) iodovanadate. The nanocomposite of POT/ Zr(IV) Zirconium(IV) iodovanadate exhibited an excellent ion exchange capacity value for Na⁺ is 4.84meq g ⁻¹ and POT/Zr(IV molybdophosphate ionexchanger has the value 4.84meq/g. While compared to other nanocomposite ion-exchangers both the ion -exchangers have significant and effective ion-exchange behavior. From the sorption studies and the distribution coefficient values, both the composite ion exchangers show maximum selectivity towards Pb2+. They can conjugate the mechanical properties of the organic polymers with intrinsic properties of the inorganic ion exchangers creating a new class of organic-inorganic nanocomposite materials with improvement in thermal stability and good electrical conductivity, ion - exchange capacity and showed higher antimicrobial activity against Gram-positive and Gram-negative bacteria like Escherichia coli, $Pseudomonas\, and\, Staphylococcus\, saprophitocus, which leads to their usage for environmental remediation$ like water purification. POT/Zr(IV) molybdophosphate and POT/Zr(IV) iodovanadate nanocomposite ion exchangers were used as promising ion exchangers and applied as an electrochemically switchable ion exchanger for water treatment, especially water softening.

Keywords: Zr(IV) molybdo phosphate, Zr(IV) iodovanadate, Conducting nanocomposites, Cation-exchanger, Sol-gel method, Polymer-matrix composites

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INTRODUCTION

There is considerable interest in the treatment of water generated by an industrial process containing heavy metals. These metals when present in water more than the permitted limit which is injurious to our health. Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes. Removal of heavy metals from industrial wastewaters can be accomplished through various treatment options, including such unit

operations as chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electro-deposition, cementation, and membrane operations. Factors that may limit the applicability and effectiveness of the chemical process are high content of clay/silt, humic, calcite, Fe & Ca, heavy metals, anions, or high buffering capacity. Ion exchange can attract soluble ions from the liquid phase to the solid phase, which is the most widely

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used method in the water treatment industry. As a cost-effective point of view, the ion exchange process normally involves low-cost materials and convenient operations and it has been proved to be very effective for the removal of heavy metals from water [1]. In this process cations or anions containing special ion-exchanger are used to remove metal ions in the solution. Commonly used ion exchangers are synthetic organic ion exchange resins. But this method is highly sensitive to the pH of the aqueous phase. Ion exchange resins are water-insoluble solid substances that can absorb positively or negatively charged ions from an electrolyte solution and release other ions with the same charges into the solution in an equivalent amount. The positively charged ions in cationic resins such as hydrogen and sodium ions are exchanged with positively charged ions, such as nickel, copper, and zinc ions, in the solutions. Similarly, the negative ions in the resins such as hydroxyl and chloride ions can be replaced by the negatively charged ions such as chromate, sulfate, nitrate, cyanide and dissolved organic carbon (DOC Ion exchange materials have been proved more suitable for various environmental problems[2-4] One of the several limitations of the organic resins is their poor thermal stability. Since these are unstable at high temperatures and affected by strong radiation. Inorganic ion exchangers are not suitable for column operation because of their non-granulometric nature. To overcome the above limitations, many investigators have introduced various organicinorganic composite ion exchangers.[5-7].Most composites have been synthesized to improve the combination of mechanical characteristics such as stiffness, toughness and high- temperature [8-10] Therefore the synthesis of polymeric -inorganic composite ion -exchangers has received a great deal of attention because of their special mechanical, chemical, electrochemical and optical as well as magnetic properties[11].

Qureshi et al.,[12] reported that synthetic inorganic ion-exchangers based on tetravalent metals have been studied in recent years because of their good selectivity and intercalation properties. Zirconium based ion exchangers have received attention more because of their excellent ion exchange behavior and specific applications in the field of the ion-exchange, ion-exchange membrane as well as in solid-state electrochemistry.

Among the various methods adopted for the removal of different pollutants, the ion-exchange method has drawn the attention of researchers because it exhibits a high efficiency of sorption for the gaseous liquid media.[13] A literature survey also reveals that many hybrid types of fibrous ion-exchange materials have been synthesized in recent years by the combination of polymeric species and inorganic groups[14]. These materials have many industrial and environmental applications including purification of water in the atomic power plants under high temperature and pressure, Mohamudurislam *et al.* 15] reported that polyacrylamide-Thorium(IV) phosphate is an important lead selective fibrous ion-exchanger.

The major objective is to select a suitable support polymeric material for the immobilization of inorganic ion-exchanger. Recently, biopolymers have large attention due to their cheap cost and easiness of their preparation. Alginate, agar, and carrageenan are known as the major binding biopolymers. PVA also refers to various advantages over the conventional immobilization methods, such as low cost, high durability, and chemical stability, Intrinsically conducting polymers(ICP's) have recently used in the field of ion exchange. ICP's include polythiophene, polyacetylene, polyaniline, and its derivatives. Addition of dopant to these ICP's changes their magnitude of conductivity, from insulator to metal like conducting behavior. Among these, Polyaniline[PANI] has been at the center of investigations due to the unique electrochemical, optical properties, and stability. This system can be obtained by both electrochemical and chemical oxidative polymerization of aniline in aqueous and nonaqueous media. Poly(O-toluidine) [POT] is a derivative of polyaniline, which contains the methyl group in its ortho position. Recently, POT was also found to have an additional advantage concerning PANI due to its faster switching time between the reduced and oxidized states and also its good solubility [16].

While considering the inorganic ion exchangers, Zirconium vanadate behaves as a monofunctional ion-exchanger [17]. The presence of the host polymer mixture (PVA & alginate) decline the thermal stability of Zirconium vanadate composite [18].

A new and novel electrically conducting fibrous type polymeric-inorganic composite material; Polypyrrole Th(IV)Phosphate cation-exchanger is having good ion-exchange capacity, higher stability, reproducibility, and selectivity for heavy metals[19]. This electroactive material also showed DC electrical conductivity in the range of 10^{-6} to 10^{-4} Scm⁻¹.

Inamuddin et al. [20], reported that the organic polymer nylon-6,6 framework with Zr(IV)

Phosphate an inorganic ion-exchanger was found to be highly selective for Hg(II) a highly toxic environmental pollutant. This was helpful to decrease environmental pollution.

WeqarA.Siddiqui *et al.* [21] reported that incorporation of polymer material into an inorganic ion-exchanger provides a new class of hybrid ion exchangers with good ion exchange capacity, high stability, and highly selective for heavy metals. A novel organic-inorganic hybrid cation exchanger which is poly (Methyl methacrylate) Zr(IV) Phosphate used for the removal of heavy metals.

Organic-inorganic hybrid cation exchange membranes based on poly(vinylidene fluoride)-SiO₂ nanoparticles were prepared by blending method and cation exchange groups in the membrane matrix were introduced by the reaction of epoxy groups with fuming sulfuric acid at 25° C various membranes were prepared with different content of SiO₂ nanoparticles [22]

Asif Ali Khan *et al.* [23] reported that the ion-exchanger 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 common ion-selective electrodes. By using poly (O-toluidine) Th(IV) Phosphate, a nanocomposite cation-exchanger as an electroactive material for the determination of Hg (II) ion present in a sample solution. F. Bucatriu *et al.* 24] reported that the synthesis and characterization of novel organic-inorganic hybrid material with short peptide brushes generated on the surface.

A.A.Khan *et al.* [25] reported that the ion-selective electrode based potentiometry has become a well-established electroanalytical technique. Using this approach the applicability of the potentiometric method has been greatly extended enabling the sample and accurate determination of many heavy metals ions and has led to the preparation of sensitive and selective ion-sensors. Chemical sensors or more commonly ion-selective electrodes with Hg(II) sensitive polyanilineSn(IV) phosphate composite cation-exchange material is used in the determination of Hg⁺ from aqueous solutions.

The main objective of this present work is to synthesize and characterize conducting polymeric – inorganic hybrid cation – exchanger by the incorporation of organic conductive polymer, i.e., poly(O-toluidine), into matrices of the inorganic ion exchangers, 'Zirconium(IV) molybdophosphate' and Zirconium(IV) iodovanadate. To overcome the limitations of organic resins and inorganic

adsorbents, we wanted to carry out the synthesis of the above conducting polymeric – inorganic nanocomposite ion- exchangers. In addition to this, we are interested to study the ion – exchange capacities of conducting polymeric – inorganic hybrid cation exchanger using the ion-exchange chromatography column. Electrically conducting polymeric-inorganic composites is an advanced class of materials used as cationic exchangers [26-28] with various possible applications such as in making ion-selective membrane electrode, separation of heavy metals from wastewater and as electrochemically switchable ion – exchanger [229-32] for water treatment.

MATERIALS AND METHODS

Reagents and instruments

The chemicals used for the synthesis of study materials are mainly O-Toluidine (S.D. Fine Chem. Ltd), ammonium molybdate, Potassium iodate (Sigma Aldrich), Zirconium oxychloride (E-Merck), sodium meta vanadate (E-Merck) and Orthophosphoric acid (Sigma Aldrich). All other chemicals and reagents used were of analytical reagent grade.

FT-IR spectrometer (4100 typeA), double beam UV-VIS spectrophotometer (Jasco V-530), scanning electron microscope (JOEL Model JSM-6390 LV), impedance analyzer (IM6 ZAHNER) and CH instrument (CHI 680 Amp) were used for characterization.

Preparation of the reagent solutions

(0.1M) solution of Zirconium oxychloride (ZrOCl₂.8H₂O) and 0.1 M solution of phosphoric acid were prepared in 0.1M HCl and demineralized water respectively. 0.1 M solution of sodium metavanadate(NaVO₃) was prepared using hot water. A solution of 0.2 M was prepared in 1M HCl.1M solutions of potassium perdisulphate and nitric acid was prepared in demineralized water. 1M solution of ammonium hydroxide and potassium iodate was prepared in demineralized water.

Synthesis of poly(o-Toluidine)- hydrochloric acid emeraldine salt

Poly(O-toluidine) emeraldine salt can easily be synthesized by the oxidative polymerization of O-toluidine in aqueous acidic media by using potassium per disuphate (KPS) as an oxidizing agent. The organic polymer, Poly(O-toluidine) is prepared by mixing 5.4062 g of potassium per disuphate (KPS)(0.2M) to 0.2 M O-toluidine in

1M HCl with continuous stirring by a magnetic stirrer for 20 minutes to form an emulsion of POT/Hydrochloric acid, a green-colored precipitate was obtained and it was washed with organic solvents(methanol& acetone) to remove oligomers. The POT -Cl- Emeraldine salt is dried under vacuum for 24 hrs to obtain a green-black powder of POT-Hydrochloric acid emeraldine salt.

Synthesis of Zr(IV) molybdophosphate ion-exchanger

The aqueous solutions of $0.1\,\mathrm{M}$ orthophosphoric acid and $0.1\mathrm{M}$ ammonium molybdate into $0.1\,\mathrm{M}$ Zr(IV) oxychloride solution gradually with continuous shaking of the mixture in 2:1:1 volume ratio. The pH variation was adjusted by adding $1\,\mathrm{M}$ nitric acid solution to maintain the desired pH. The gelatinous precipitate so formed, was allowed to stand for $24\,\mathrm{hrs}$ in the mothor liquor for digestion. The supernatant liquid was removed and the precipitates were washed with demineralized water several times to remove excess reagents. The product was dried at $40\pm2^{\circ}\mathrm{C}$ in an oven.

Synthesis of Zr(IV) iodovanadate ion-exchanger

The material was synthesized by adding a mixture of 0.1 M potassium iodate and 0.1M sodium meta vanadate solution to 0.1 M zirconium oxychloride solution in the volume ratio 2:2:1 with continuous stirring to obtain a gel. The desired pH was adjusted by adding dilute HCl (or) NH $_3$ solutions. The gel was aged in the mother liquor for 24 hrs at room temperature and filtered under suction. The excess acid was removed by washing with demineralized water (DMW) and it was kept in an air oven at $40\pm1^{\circ}\mathrm{C}$ for drying.

Synthesis of poly(o-Toluidine)-inorganic ion exchanger Poly(o-Toluidine /Zr(IV) molybdophosphate and Poly(o-Toluidine/Zr(IV) iodovanadate ion-exchangers

The composite cation exchangers were prepared by the sol-gel mixing of Poly(O-toluidine), an organic conducting polymer, into the yellow-colored inorganic precipitate of Zirconium(IV) molybdophosphate or light green inorganic precipitate of Zirconium (IV) iodovanadate to get the appropriate nanocomposite ion -exchangers. In this process, when the gels of Poly(O-toluidine) were added to the inorganic precipitate of Zirconium (IV) molybdo phosphate/ Zirconium (IV) iodovanadate with constant stirring for 5 hrs. The resultant mixture was turned slowly into greenish-black colored slurries. The resultant greenish black-colored slurries were kept for 24 hrs at room temperature. Now the

poly(O-toluidine) based composite gels were filtered off, washed thoroughly with DMW to remove the excess acid and any adhering trace of KPS. The product was dried in an air oven. The dried product was washed with acetone to remove the oligomers present in the material. H⁺ form by treating with 1M HNO3 for 7 hrs shaking and kept for 24 hrs. at room temperature. The excess acid was removed after several washes with DMW and finally dried.

CHARACTERIZATION AND PHYSICO-CHEMICAL PROPERTIES

FT-IR studies

FT-IR spectra can yield valuable evidence concerning the electronic structures of various composites. FT-IR - the spectrum is used to characterize the molecular structures of organicinorganic hybrid ion-exchanger. FT-IR spectrum of conducting organic polymer, inorganic ionexchanger, conducting polymeric-inorganic hybrid ion-exchanger in the original form dried at 50° C was taken by KBr disc method at room temperature performed on NEXUS-670 FT-Infrared Spectrophotometer. The FT-IR spectrum is mostly used to identify the functional group present in the compounds and the structures of composite ionexchangers are also confirmed by FT-IR spectral data.

X-ray diffraction study

The powder X-ray diffraction technique has been employed to identify the crystalline phases of the present sample using monochromatized Cu K α (1.5056 A°). The particle size was measured form X-ray broadening employed the well-known Scherrer equation as

D=0.96
$$\lambda/\beta$$
 Cosθ (1)

Where,

 β - The width of the XRD pattern line at half peak-height(Rad) λ - The wavelength of the X-ray (1.5056A°) θ - The angle between the incident and diffraction beam(°) D - The particle size of the sample (nm)

Scanning electron microscopy (SEM) studies

SEM was performed on ground polymericinorganic composite ion-exchange materials by an electron microscope at various magnifications. Microphotographs of the original form of polymericinorganic composite materials were obtained by the scanning electron microscope at various magnifications by a microscope JEOL Model JSM- 6390 LV.

Thermo Gravimetric Analysis

Simultaneous studies of the composite cation-exchange material in the original form were carried out by an automatic thermal balance on heating the material from 10° C to 1000° C at a constant rate (10°C min⁻¹) in the air atmosphere with Perkin Elmer instrument.

Electrical conductivity measurements Sample (pellet) preparation

The sample material was dried completely at 45°C - 50°C in an oven. Then 200mg material was finely grounded in a mortar pestle and pellets were made at room temperature with the help of a hydraulic pressure instrument at 25 KN pressure for 20 minutes. DC electrical conductivity studies were performed on pressed material by using a two- probe method. AC electrical conductivity studies were performed on pressed material by using an electrical conductivity measuring instrument Digital LCR meter (Pacific, model: PL CR 8C).

Ion exchange studies Ion exchange capacity

The ion exchange capacity(IEC), which is generally taken as a measure of hydrogen ion liberated by neutral salt to flow through the composite ion-exchanger was determined by a standard column process. 1g of dry cation exchanger in the H⁺ form was taken into a glass column. 1M alkali metal chlorides(LiCl, NaCl, and KCl) as eluents were used to elute the H⁺ ions completely from the cation-exchange column maintaining a very slow flow rate (0.5ml min⁻¹). The effluent was titrated against a standard NaOH solution for the total ions liberated from the solution using phenolphthalein indicator. Effect of eluent concentration on ion -exchange capacity

The magnitude of elution depends on the concentration of eluent. To find out the optimum concentration of eluent for the complete elution of H⁺ ions, a fixed volume (250ml) of LiCl, NaCl, KCl solutions of varying concentration (0.2-2.0M) were passed through a column containing 1g of the exchanger in H⁺ form with a flow rate of 0.5ml/ min. The effluent was titrated against a standard alkali solution of 0.1M NaOH for the H⁺ ions eluted out using phenolphthalein as an indicator.

Elution behavior onion- exchange capacity

Since, with the optimum concentration for complete elution, was observed for POT/Zr(IV)

molybdophosphate and POT /Zr(IV) iodovanadate nanocomposite ion exchangers, a column containing 1g of exchanger in H $^+$ form was eluted with 1.4M LiCl, 1.4M NaCl and 1.6M KCl solutions of concentration in different 10ml fractions with minimum flow rate if 0.5ml min $^-$ 1 and each fraction of 10ml effluent were titrated against a standard alkali solution for the H $^+$ 1 ions eluted out. This experiment was conducted to find out the minimum volume of eluent necessary for the complete elution of H $^+$ 1 ions which determines the exchange efficiency of the column

Effect of time on ion-exchange capacity

The optimum equilibration time of POT/Zr(IV) molybdophosphate and POT /Zr(IV) iodovanadate nanocomposite ion exchangers with LiCl, NaCl, and KCl solutions for the complete elution of H⁺ ions were determined. 0.25g of ion exchanger was shaken with 25ml of LiCl, NaCl, and KCl, and the amount of liberated H⁺ ions was titrated against the standard NaOH solution after every half an hour interval.

pH titrations

pH titration studies of POT/ Zr(IV) molybdophosphate and POT /Zr(IV) iodovanadate was performed by the method of Topp and pepper [33]. 200mg portions of the cation – exchanger in the H+ form were placed in each of several 250ml conical flasks followed by the addition of alkali metal chlorides (LiCl, NaCl, and KCl) and their corresponding hydroxides in different volume ratio, the final volume was kept 50ml to maintain the ionic strength constant. The pH of the solution was recorded every 24hr until equilibrium was attained and which needed ~5 days and also pH at equilibrium was plotted against the mill moles of OH- ions added.

Selectivity (or) sorption studies

The distribution behavior of metal ions plays an important role in the determination of the selectivity of the ion-exchange material. In certain practical applications, equilibrium is most conveniently expressed in terms of distribution co-efficient of the counter ions.

The distribution coefficient (K_d values) of various metal ions POT/ Zr(IV) molybdodophosphate and POT /Zr(IV) iodovanadate nanocomposite ion-exchangers were determined by the batch method in various solvent systems. Each200mg of the composite nanocomposite ion-exchanger in the H⁺ form were taken in flasks with 20ml Pb(NO₃)₂, Co(NO₃)₂ and Cu(NO₃)₂, in the required medium and kept for 24 hours with continuous shaking. The metal ions in the

solution before and after equilibrium were determined by titrating against a standard 0.2M solution of EDTA. The distribution coefficient is given by the ratio of the amount of metal ion in the exchanger phase and the solution phase. In other words, the distribution coefficient is the measure of a fractional uptake of metal ions competing for H⁺ ions from a solution by an ion-exchange material and hence mathematically can be calculated using the formula given as,

$$K_d = \frac{mmoles\ of\ metal\ ions\ /\ gram\ ion - exchanger}{mmoles\ of\ metal\ ions\ /\ mL\ solution} \qquad \left(mL\ g^{-1}\right) \qquad (2)$$

$$K_{d} = \frac{(I - F)}{F} \times \frac{V}{M} \qquad (mL g^{-1})$$
 (3)

Where,

I= Initial amount of metal ion in the aqueous phase

F= Final amount of metal ion in the aqueous phase V= Volume of the metal ion (ml)

M= The amount of cation exchanger (g)

RESULTS AND DISCUSSION

In the present study, new and novel organicinorganic electrically conducting nanocomposite cation exchanger was chemically prepared by solgel mixing of organic conducting polymer like poly(O-toluidine) into the matrix of inorganic ionexchangers, i.e) Zr(IV) molybdo phosphate and Zr (IV) iodo vanadate.

- 1) The mechanism for the formation of conducting polymeric-inorganic nanocomposite cation exchangers is given below
- a) Poly(O-toluidine)-Cl $^-$ emeraldine salt was prepared by oxidation coupling using $K_2S_2O_8$ in acidic medium.

b) The binding of Poly(O-toluidine) into the matrix of Zr(IV) molybdo phosphate is possible is due to ionic interaction between the radical cation of Poly(O-toluidine) and anionic groups of Zr(IV) molybdo phosphate or Zr(IV) iodovanadate inorganic ion-exchangers.

The conducting polymeric-inorganic nanocomposite ion exchanger i.e. POT/Zr(IV) molybdophosphate and POT/Zr(IV) iodovanadate are prepared to have good ion-exchange capacity values compared to that of individual ionexchangers like Zr(IV) molybdophosphate and Zr(IV) iodovanadate, which has an ion exchange capacity 1.96 & 2.24meq/g respectively.

The ion – exchange capacity of the POT/ Zr(IV) molybdo phosphate nanocomposite ion-exchanger in meq/g for different metal ions are Li⁺-3.28; Na⁺-4.60; K⁺-5.34 meq/g respectively.

The ion-exchange capacity of POT/Zr(IV) iodovanadate ion-exchanger in meq/g for different metal ions are Li⁺ -3.48; Na⁺-4.84; K⁺-5.64 meq/g respectively. The IEC of the hybrid ion exchanger for alkali ion increased according to the decrease in the hydrated ionic radii.

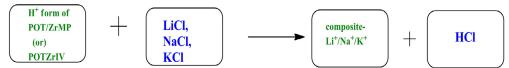
Conducting Polymer

Conducting Polymeric-inorganic ion-exchanger

$$Y = CH_3 \rightarrow O$$
-toluidine

X = Zr(IV) molybdophosphate or Zr(IV) iodovanadate

Scheme:1 Mechanism for the formation of POT/Zr(IV) molybdodophosphate and POT/Zr(IV) iodovanadate cation exchangers



Scheme 2: Scheme for the ion exchange in Conducting polymeric-inorganic Ion-Exchanger

Composite ion Exchangers	IEC (meq/g)	References	
PolyanilineZr(IV) silicophosphate	1.05	[34]	
PolyanilineTh(IV) tungstomolybdophosphate	1.07	[35]	
Polyaniline zirconium(IV) selenotungsto-phosphate	1.20	[36]	
PolyanilineSn(IV) tungstoarsenate	1.67	[37]	
PolyanilineSn(IV) tungstomolybdate	1.77	[38]	
PolyanilineSn(IV) tungstophosphate	1.10	[39]	
PolyanilineTi(IV) phosphate	2.59	[40]	
PolyanilineTi(IV) molybdophosphate	2.46	[41]	
PolyanilineZr(IV) tungstophosphate	1.54	[42]	
Polyaniline Ti(IV)arsenophosphate	1.13	[43]	
PolyanilineZr(IV) tungstoiodophosphate	2.86	[44]	
PolyanilineZr(IV) molybdophosphate	2.50	[45]	
PolyanilineZr(IV) titanium phosphate	4.52	[46]	
PolyanilineZr(IV) sulphosalicylate	1.80	[47]	
PolyanilineSn(IV) iodophosphate	1.20	[48]	
poly-o-toluidine Zr(IV) tungstate	1.98	[49]	
poly-o-toluidine Sn(IV) tungstate	2.50	[50]	
Poly-o-toluidine(POT)/multiwalled carbon	1.05	[61]	
nanotubes(MWCNTs)/Sn(IV) tungstate	1.05	[51]	
poly-o-toluidine Th(IV) phosphate	1.90	[52]	
Polyaniline Zr(IV) molybdophosphate	2.05	[53]	
POT/Zr(IV) molybdophosphate	4.60	In present study	
POT/Zr(IV) iodovanadate	4.84	In present study	

 $\label{eq:continuous_poly} \begin{tabular}{l} Table 2. IEC of various exchanging ions on poly (O-toluidine) / Zr(IV) molybdophosphatenanocomposite ion - exchanger using KPS oxidant. \\ \end{tabular}$

Exchanging ions	pH of the metal solution	Ionic radii (A ⁰)	Hydrated ionic radii (A ⁰)	Ion exchange capacity (meq/g)
Li ⁺	3.3	0.68	3.40	3.28
Na^+	4.99	0.97	2.76	4.6
K^{+}	6.8	1.33	2.32	5.34

Table 3. IEC of various exchanging ions on poly(O-toluidine) Zr(IV)/ iodovanadatenanocomposite ion – exchanger using KPS oxidant.

Exchanging ions	pH of the metal solution	Ionic radii (A ⁰)	Hydrated ionic radii (A ⁰)	lii Ion exchange capacity (meq/g)	
Li ⁺	3.3	0.68	3.40	3.48	
Na^+	4.99	0.97	2.76	4.84	
K ⁺	6.8	1.33	2.32	5.64	

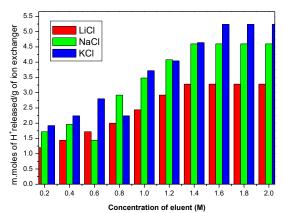


Fig. 1. Effect of concentration of eluent on IEC of nanocomposite ion- exchanger POT/Zr(IV) molybdophosphate

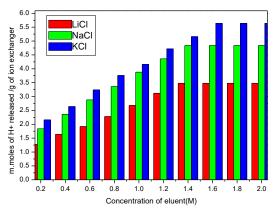


Fig. 2. Effect of concentration of eluent on IEC of nanocomposite ion-exchanger POT/ Zr(IV) iodovanadate

While comparing with other nanocomposite ion-exchangers [34-53] as well as POT/Zr(IV) molybdophosphate, POT/Zr(IV) iodovanadate nanocomposite ion-exchanger has an excellent ion-exchange capacity as shown in Tables 1, 2 and 3

The rate of elution is governed by the concentration of eluent. The minimum molar concentration of LiCl, NaCl, KCl as eluents for Poly(O-toluidine)/Zr(IV) molybdo phosphate and Poly(O-toluidine)/Zr(IV) iodovanadate was found 1.4 M, 1.4M and 1.6M for the maximum release of $\rm H^+$ ions from 1 g of ion exchanger as shown in Fig. 1 and 2

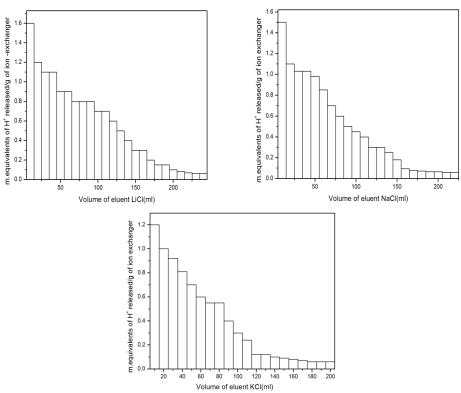
From Fig. 3 for Poly(O-toluidine)/Zr(IV) molybdophosphate nanocomposite ion-exchanger, the elution behavior of LiCl, NaCl, KCl indicates that the exchange is quite fast as at the beginning and all the exchangeable $\rm H^+$ ions are eluted out in 240ml,210ml, and 190ml. respectively Similarly Poly(O-toluidine)/Zr(IV) iodovanadate (Fig. 4) elution behavior of LiCl, NaCl, KCl indicates that the exchange is quite fast as at the beginning and all the

exchangeable H⁺ ions are eluted out in 220ml,210ml, and 170ml respectively.

The effect of equilibration time on ion exchange capacity of Poly(O-toluidine)/Zr(IV) molybdophosphate using LiCl, NaCl, KCl as eluents show a constant capacity only after 3.5, 3.5 and 3.0 hours equilibration respectively (Fig 5)

The effect of equilibration time on ion exchange capacity of Poly(O-toluidine)/Zr(IV) iodovanadate using LiCl, NaCl, KCl as eluents show a constant capacity only after 3.0, 3.0 and 2.5 hours equilibration respectively(Fig. 6)

The pH titration curves (Fig 7 and 8) show that increase in pH, when LiOH, NaOH, KOH were added to the nanocomposite ion exchanger. The pH titration curves for POT/Zr(IV) molybdo phosphate and POT/ Zr(IV) iodovanadate were obtained under equilibrium conditions with LiOH-LiCI, NaOH-NaCl and KOH- KCl systems indicating that bifunctional behavior of the ion-exchange materials. The rate of H⁺ - K⁺ exchange was faster than those



 $Fig.\ 3.\ Elution\ behaviour\ of\ POT/Zr(IV)\ molybdophosphate\ nanocomposite\ ion-exchanger$

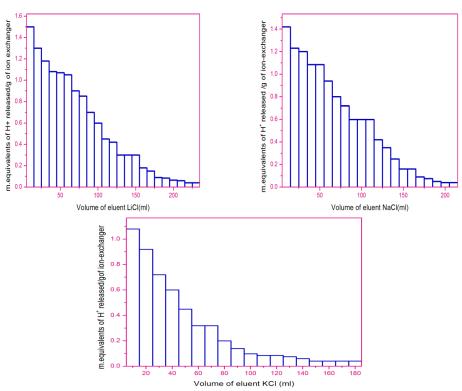


Fig. 4. Elution behaviour of POT/Zr(IV) iodovanadate nanocomposite ion- exchanger

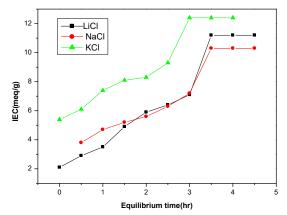


Fig. 5 . Effect of elution time on IEC of POT/Zr(IV) molybdophosphatenanocomposite ion- exchanger

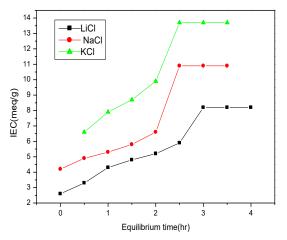
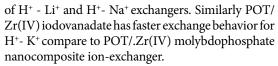


Fig. 6. Effect of elution time on IEC of POT/Zr(IV) iodovanadate nanocomposite ion-exchange material



The distribution studies for three metal ions was performed in four solvent system for both the nanocomposite ion-exchangers. The K_d values (or) the sorption studies show that (Table 4 and 5). The nanocomposite ion-exchangers have maximum selectivity towards Pb^{2+} because Pb^{2+} has highly adsorbed in all solvent media but other remaining metal ions were poorly adsorbed. Actually K_d values depend upon nature, composition, and tendency to complex formation of the solvent media.

From the FT-IR spectral data of Poly(Otoluidine) samples the principle characteristic peaks of quinoid – benzenoid N – moieties C-N stretching, C-H aromatic in-plane and out – plane

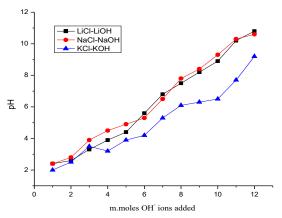


Fig. 7. pH titration curves for POT/Zr(IV) molybdophosphate nanocomposite ion-exchanger with various alkali metal hydroxides.

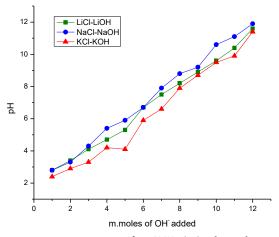


Fig. 8. pH titration curves for POT/ Zr(IV) iodovanadate nanocomposite ion-exchanger with various alkali metal hydroxides.

bending vibrations of Poly(O-toluidine)are reported to occur at about 1600, 1500, 1350, 1130 and 820 cm -1 respectively. In the present study, also all the peaks are observed in Poly(O-toluidine) / Zr/(IV) molybdophosphate and Poly(O-toluidine)/Zr(IV) iodovanadate nanocomposite ion-exchangers using KPS as the oxidant but there are modified both in intensity and peak position when Poly(Otoluidine) is incorporated into the inorganic matrices Zirconium(IV) molybdophosphate and Zirconium (IV) iodovanadate. In FT-IR spectrum of H⁺ form of Poly(O-toluidine) / Zr(IV) molybdophosphate (Fig. 9), a broad weak band at 3227.29 cm⁻¹ is assigned to N-H stretching mode. The peak at 2811.32 cm⁻¹ may be due to C-H stretching vibration. The vibration bands at 1576.52 and 1499.74 cm⁻¹ implies the presence of POT in the composite ion-exchangers. The band at 1092.25

 $\label{eq:continuous} \begin{array}{l} \text{Table 4. } K_d \text{values of some metal ions on POT/ } Zr(IV) \\ \text{molybdophosphate nanocomposite ion-exchanger in different} \\ \text{solvent systems} \end{array}$

Solvents	Pb ²⁺	Co ²⁺	Cu ²⁺
DMW	146	84	31
10% ethanol	112	58	41
10% acetone	140	43	46
1M H ₂ SO ₄	385	180	101

cm $^{-1}$ due to the presence of PO $_4^{3-}$, HPO $_4^{2-}$, H $_3$ PO $_4^{-1}$. The band at 805.135 cm $^{-1}$ due to the presence of molybdate and M-O bond.

From the FT-IR spectrum of H⁺ form of Poly(Otoluidine) / Zr(IV) iodovanadate nanocomposite ion-exchanger nanocomposite ion-exchanger(Fig. 9), a broad weak band at 3287.2cm⁻¹ due to N-H stretching mode. The peak at 2828.10 cm⁻¹ due to C-H stretching vibration. The vibration bands at 1247.96 and 1478.17 cm⁻¹ implies the presence of POT in the composite ion-exchangers. The spectrum also shows that a strong band in region 830-500 cm⁻¹ indicating the presence of iodate, vanadate, and metal oxide [54-56].

XRD pattern of these ion exchangers shows that the composite materials are in amorphous form as evidenced from Fig. 10. SEM photographs of POT/Zr(IV) molybdophosphate and POT/Zr(IV) iodovanadate nanocomposite ion-exchangers are obtained at different magnification (Fig. 11) indicate the adhesion between two phases i.e. inorganic ion-exchange material with organic polymer poly(O-toluidine). The SEM images have been revealed that after binding of POT with Zirconium (IV) molybdophosphate and Zirconium(IV)

Fig. 9. FT-IR spectra of a)POT-Cl⁻ Emeraldine salt b)H⁺ form of POT/Zr(IV) molybdophosphate nanocomposite ion–exchanger c) H⁺ form of POT/Zr(IV) iodovanadate nanocomposite ion–exchanger

Table 5. K_d values of some metal ions on POT/ Zr(IV) iodovanadate nanocomposite ion-exchanger in different solvent systems

Solvents	Pb ²⁺	Cu ²⁺	Co ²⁺
DMW	137	88	30
10% ethanol	105	63	39
10% acetone	134	46	51
1M H ₂ SO ₄	306	169	119

iodovanadate the morphology has been changed [57]. When the functionality and nature of the ion or conducting polymer are modified to include other interaction mechanisms (beyond Coulombic attraction), then further sensing opportunities arise. This is due to π -ion interactions between the ion of interest and the conjugated backbone of the conducting polymer. [58] The X-ray powder diffraction pattern of this ion exchanger exhibited no peak in the spectrum which suggests the amorphous nature of composite ion-exchange material. It is also reported that the X-ray diffraction pattern of cellulose acetate-Zr(IV) molybdophosphate also is amorphous [59].

TGA and DTG data of POT-Cl⁻ emeraldine salt, POT/Zr(IV) molybdophosphate, and POT/Zr(IV) iodovanadate nanocomposite ion-exchangers are given in Table 6. Zr(IV) molybdophosphate has high thermal stability, unlike the organic resins which have poor thermal stability.[59] The thermogravimetric analysis curve of the POT/Zr(IV) molybdo phosphate (Figs. 12 and 13) showed that continuous weight loss up to (about 6%) 100°C, which may be due to the removal of external water molecules [60]. Further weight loss between

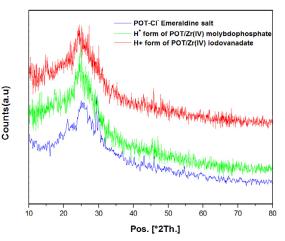


Fig. 10. XRD pattern of a)POT-Cl $^{+}$ Emeraldine salt b)H $^{+}$ form of POT/Zr(IV) molybdophosphate nanocomposite ion—exchanger c)H $^{+}$ form of POT/Zr(IV) iodovanadate nanocomposite ion—exchanger

100°C and 300°C may be due to the condensation of intramolecular hydroxyl groups or removal of dopant. A steep weight loss of mass was observed in the temperature range of 300°-500° C may be due to the conversion of the phosphate group to pyrophosphate. Slight decomposition of an organic part may be observed in the temperature range of 500°-650°C. At 650°C onwards, a smooth horizontal section represented the complete formation of the oxide form of the material.

As evident from the Figs. 12 and 13, the TGA of POT /Zr(IV) iodovanadate showed three main degradation steps. The first degradation step is associated with the removal of external water. and also interpreted that the second decomposition is due to the elimination of the dopant molecule. The third stage decomposition is obviously due to the complete degradation of the polymer chain. In this way, it was thought that the presence of the host polymer may contribute to declining the thermal stability of Zr(IV) in the composite. It is also reported that the thermogram of zirconium(IV) iodovanadate reveals that the derivative curve exhibits two peaks with temperature maxima at 90 and 515.82 °C. Corresponding to two distinct weight losses. The external water molecules are lost up to 145 °C which corresponds to weight loss of 10.71%. Further, loss in weight is observed from 145 to 491 °C which is attributed to the condensation of the IO $_3$ group into I $_2$ O $_5$ The corresponding weight loss is 4.60%. There is an abrupt weight loss from 491.08to 545.27 $^{\circ}$ C indicating the volatilization of ionogenic groups. Beyond 600 $^{\circ}$ C, the weight becomes constant owing to the formation of metal oxide[61].

Conclusively the TGA studies point out the inference that POT/Zr(IV) molybdo phosphate and POT/Zr(IV) iodovanadate ion exchangers are thermally more stable So they can be effectively used as ion exchangers in high-temperature conditions.

Conductivity for this organic-inorganic hybrid ion exchangers steadily increases with an increase in temperature up to 100° C and thereafter decreases which shows the semiconductor behavior of the ion exchange materials. The linear portion of the graph was fit to the Arrhenius type equation (1) and log σ Vs. 1/T plots were made for this ion-exchanger.

To determine the nature of the dependence of electrical conductivity on temperature plots of log σ versus 1000/T(K) were drawn and they followed the Arrhenius equation. It was also observed that the composite material showed enhanced electrical conductivity due to the charge transfer reaction between poly(O-toluidine) component of the composite and doping agent HCl and (or) Zr(IV) molybdophosphate/ Zr(IV) iodo vanadate. The energies of activation of electrical conduction for the

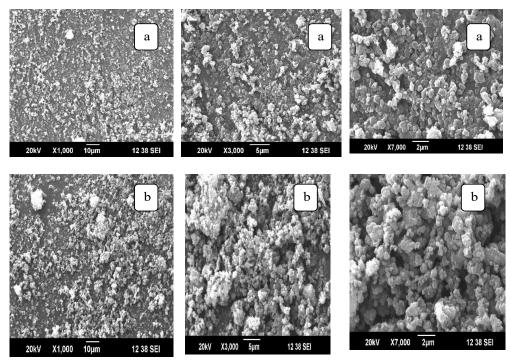


Fig. 11. SEM images of a) POT/Zr(IV) molybdophosphate b) POT/Zr(IV) iodovanadate nanocomposite ion-exchangers at different magnifications

Table 6. TGA and DTG data of POT/Zr(IV) molybdophosphate and POT/Zr(IV) iodovanadatenanocomposite ion-exchangers

Sample	Temperature Range	% of weight loss	% of residue	DTG peak position	Comments	
	50-100	6%			i)Removal of external water molecule	
POT emeraldine salt	100-300	15%	No residue	No residue	295.10	ii)Removal of dopant molecule
	300-1000	100%			iii)Complete decomposition of organic part	
					i)Removal of external water molecule	
	50-100	6%	5% residue	188.73 445.38	ii)Removal of dopant molecule or Condensation	
POT/Zr(IV) molybdo	100-300	20%			of hydroxyl groups	
phosphate					iii)Decomposition of organic part	
nanocomposite ion-exchanger	300-500	30%			iv) Formation of oxide of form of material.	
	>500	95%			Decomposition is completed by leaving 5% residue with two ininflection points	
					i)Removal of external water molecule	
	50-100	5%			ii) Elimination of dopant molecule	
POT/Zr(IV) iodovanadate	100-300	18%	5% residue	199.57	iii) Degradation of polymer chain	
nanocomposite	300-600	45%		458.6	, ,	
ion-exchanger	>600	95%			 iv) Formation of oxide form of material. Decomposition completed by leaving 5% residue with two inflection points 	

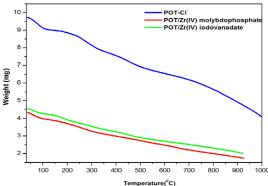


Fig. 12. TGA curve of POT/Zr(IV) molydophosphate and POT/Zr(IV)iodovanadate nanocomposite ion-exchanger

composite samples POT/Zr(IV) molybdophosphate and POT/Zr(IV) iodo vanadate were calculated from the slopes of the Arrhenius plot is 0.3543eV and 0.2970 eV respectively.

The room temperature conductivity of all the polymer composite ion exchanger samples is given in Table 7 and the plot depicted in Figs. 15 and 14 Conductivity steadily increases with an increase in temperature up to 100°C for this organic-inorganic hybrid ion exchange showing semiconductor behavior. The linear portion of the graph was fit to Arrhenius type equation (1) and log σ Vs 1/T plots were made for this ion- exchanger. Figs. 14 and 15 is the representative of such Plot.

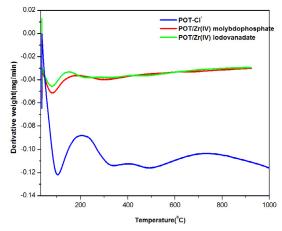


Fig. 13. DTG curves of POT/Zr(IV) molydophosphate and POT/Zr(IV)iodovanadate nanocomposite ion-exchanger

$$\sigma(T) = \sigma_0 \exp(-Eg/2KT) \tag{4}$$

Where, Eg, the activation energy of conductivity calculated from the slope. K is Boltzmann's constant the variation of conductivity (σ) as a function of 1/T at constant frequency is shown in Figs. 14 and 15 It is found that the value of $\sigma(T)$ is also strongly dependent on frequency. The activation energy of conductivity for these hybrid ion exchangers was found to be0.3769eV and 0.3022 eV. The followup Arrhenius behavior is regenerated as a good approximation to band theory.

To determine the conductivity parameters, the temperature dependence of conductivity (linear portion) is fit to the following equation.

$$\sigma(T) = \sigma_0 \exp(-To/T) \frac{1}{2}$$
 (5)

Further, the temperature dependence of conductivity, the follow-up Arrhenius behavior indicates that the conduction in poly (O-toluidine) composite ion – exchanger is predominantly performed by the variable range hopping process. An increase in the values of the AC electrical conductivity is driven by the mobility of free charges (i.e) Polarons and free ions as the temperature is increased.

The mobility of charge carriers under the influence of an external field up to $100\,^{\circ}$ C increases with the doping level. The value of activation energy is indicating that the charge carrier has to overcome the same energy barrier while conducting. Thus the polarons act as charge carrier hopping from state to state in all our polymer samples.

The proton-induced emeraldine salt form of POT using KPS oxidant has the electrical conductivity $2.106\times10^{-6}(\Omega m^{-1})$ which is having high electrical conductivity when compared with that of emeraldine base form of POT using KPS oxidant $7.91\times10^{-7}(\Omega m^{-1})$.

The incorporation of conducting organic polymer, i.e POT into the matrix of inorganic ion-exchanger Zr(IV) molybdophosphate and Zr(IV) iodovanadate leads to an increase in conductivity $(1.78\times10^{-3} \text{ and } 2.5159\times10^{-3} \text{ Scm}^{-1})$.

From the electrical conductivity studies, it is clear that both the organic-inorganic nanocomposite ion-exchangers are having good electrical conductivity compared to those of their corresponding organic polymer(POT). Although the presence of organic groups (-CH₃) in POT should decrease the electrical conductivity, if it is compared with polyaniline composites, the electrical conductivity of this material is not much affected. It may be due to the presence if Zirconium (IV) molybdophosphate and Zirconium(IV) iodovanadate which are good inorganic ion- exchangers.

The antimicrobial activity studies of POT/Zr(IV) molybdophosphate and POT/Zr(IV) iodovanadate nanocomposite ion exchangers were carried out against three bacteria namely *Escherichia coli. Staphylococcus saprophitocus* and *Pseudomonas*. The antimicrobial activity study results are summarized in Table 8. From the table, POT emeraldine salt, POT emeraldine base, and the conducting polymericinorganic nanocomposite ion-exchangers showed higher antimicrobial activity against Gram-positive

Table 7. Conductivity of various polymer sambles at room temperature

Sample	Capacitance	Dielectric loss D or tan δ	$\sigma_{a.c}(S \text{ cm}^{-1})$
POT emeraldine salt	5.39 (nf)	5.05	2.106x10 ⁻⁶
POT emeraldine base	12.4 (pf)	0.86	7.91x10 ⁻⁷
POT /Zr(IV) molybdo phosphate nanocomposite	62 (nf)	2.02	1.782x10 ⁻⁴
POT/Zr(IV)iodovanadatenanocomposite	56 (nf)	3.15	2.5159x10 ⁻⁴

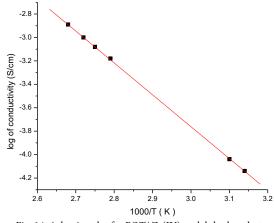


Fig. 14. Arhenius plot for POT/ Zr(IV) molybdophosphate nanocomposite ion-exchanger

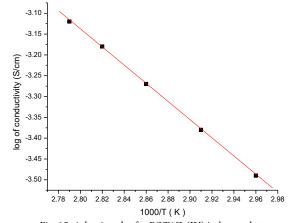


Fig. 15. Arhenius plot for POT/ Zr(IV) iodovanadate nanocomposite ion-exchanger

and Gram-negative bacteria like Escherichia coli, Pseudomonas and Staphylococcus saprophitocus and with very good inhibition zones due to their significant antimicrobial activity and they can rupture the cell wall of the bacteria and therefore they can be used to remove the pathogens effectively from aquatic systems (Figs.16) The mechanism responsible for the antimicrobial activity which involves the binding of conducting polymer or nanocomposite ion exchangers to the outer membrane of Gram-positive and Gram-negative bacteria and biological macromolecules causing the inhibition of active transport and retards the enzyme activity. The conducting polymer or nanocomposite ion exchangers release ions, which react with the thiol groups (-SH), present on the bacterial cell surface. Thus it deactivates the proteins, ruptures the cell membrane, and eventually causing cell death[62].

CONCLUSIONS

In the present paper, POT/Zr(IV) moly-bdophosphate and POT/Zr(IV) iodovanadate nanocomposite ion exchangers were used as

promising and powerful ion exchangers due to their enhanced ion exchange capacity compared to their inorganic counterparts and also other nanocomposite ion-exchangers. They can conjugate the mechanical properties of their corresponding organic polymers with intrinsic properties of the inorganic ion-exchangers and creating a new class of nanocomposite ion-exchange materials with very good improvement in their mechanical properties, thermal stability, electrical conductivity as well as ion - exchange capacity. They showed higher antimicrobial activity against Gram-positive and Gram-negative bacteria like Escherichia coli, Pseudomonas, and Staphylococcus saprophitocus, which leads to their effective usage for environmental remediation like water purification.

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 $\label{thm:condition} \begin{tabular}{ll} Table 8. Antimicrobial activity study results of POT/\ Zr(IV) molybdophosphate and \ POT/\ Zr(IV) iodovana date nanocomposite ion-exchangers \end{tabular}$

			Zone of inhibition in (mm)				
S.No Organism	Media	Control	POT	POT Base	POT/Zr(IV) molybdo Phosphate	POT/Zr(IV) iodo vanadate	
1	Escherichia coli	Muller Histon	17	22	20	19	20
2	Pseudomonous	Muller Histon	24	21	17	19	21
3	Staphylococcus saprophitocus	Muller Histon	18	19	11	14	18



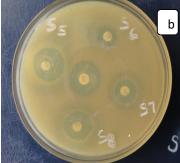




Fig. 16. The zone of inhibition against a)E.Coli b) Staphylococcus saprophitocus c) Pseudomonas (S_5) POT $-Cl^-$ emeraldine salt (S_6) POT emeraldine base (S_7) POT/Zr(IV) molybdophosphate and (S_8) POT/Zr(IV) iodovanadate

CONFLICT OF INTEREST STATEMENT

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sector preferences.

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