SYNTHESIS AND CHARACTERIZATION OF CELLULOSE ACETATE TITANIUM (IV) TUNGSTOMOLYBDATE NANOCOMPOSITE CATION EXCHANGER FOR REMOVAL OF SELECTED HEAVY METALS FROM AQUEOUS SOLUTION

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Synthesis and Characterization of Cellulose Acetate Titanium (IV) Tungstomolybdate Nanocomposite Cation Exchangers for the Removal of Selected Heavy Metals from Aqueous Solution

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I hereby certify that I have read and evaluated this Thesis entitled: “**Synthesis and Characterization of Cellulose acetate Titanium (IV) Tungstomolybdate Nanocomposite Cation Exchanger for the Removal of Selected Heavy Metals from Aqueous Solution**” prepared under my guidance by **Belay Minase**. I recommend that it be submitted as fulfilling the Thesis.

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DEDICATION

This thesis work is dedicated to my dearest mom, Genet G/Tsadik.

STATEMENT OF THE AUTHOR

By my signature below, I declare and affirm that this Thesis is my own work and I have followed all ethical and technical principles of scholarship in the preparation and complication of this thesis. Any scholarly matter that is included in the Thesis has been given recognition through citation.

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BIOGRAPHICAL SKETCH

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ACRONYMS AND ABBREVATIONS

AAS	Atomic Absorption Spectroscopy
BET	Bruanour -Emmet-Teller
CA	Cellulose Acetate
CATTM	Cellulose Acetate Titanium(IV) tungstomolybdate
CSIC	Catalysis and Petroleum Chemistry
DTA	Differential Thermal Analysis
DMF	Dimethyl Formamide
DDW	Double Distilled Water
DMSO	Dimethyl Sulfoxide
EDTA	Ethylene Diamine Tetra acetic Acid
FTIR	Fourier Transforms Infrared Spectroscopy
IEC	Ion Exchange Capacity
IIE	Inorganic Ion Exchanger
SEM	Scanning Electron Microscopy
TGA	Thermo Gravimetric Analysis
XRD	X-ray Diffraction
K_d	Distribution Coefficients
MHA	Muller Hinton Agar
PDA	Potato Dextrose Agar

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Synthesis and Characterization of Cellulose acetate titanium (IV) tungstomolybdate Nanocomposite Cation Exchanger for the Removal of Selected Heavy Metals from Aqueous Solution

ABSTRACT

Cellulose acetate titanium (IV) tungstomolybdate nanocomposite cation exchanger was synthesized by sol-gel method by incorporating cellulose acetate polymer into inorganic exchanger, titanium (IV) tungstomolybdate. Different techniques including FTIR, XRD, TGA SEM and BET were used to characterize the exchanger. The Cellulose acetate titanium (IV) tungstomolybdate (CATTM) behaved as a good cation exchanger with ion exchange capacity of 1.64 meq g^{-1} *for* Na^+ *ions. The sequence of ion exchange capacity for alkali metal ions was found to be* $K^+ > Na^+ > Li^+$ *and that for alkaline earth metal ions was* $Ba^{2+} > Ca^{2+} > Mg^{2+}$*These orders revealed that the ions with smaller hydrated radii acquired larger ion exchange capacity. The pH titration curve indicated that the material obtained as such is a bi functional strong cation exchanger as indicated by a low pH (~2.25) of the solution when no* OH^- *ion was added. Thermal analysis of the material showed that the material retained 55 % of its ion exchange capacity up to 600°C. Adsorption behavior of metal ions in different solvents with varying concentration has also been explored and the sorption studies revealed that the material was selective for Cr(III) and Pb(II) ions. The analytical utility of the material was investigated by performing binary separations of selected metal ions in a column based on the distribution coefficients of the metals. Cr(III) and Pb(II) were selectively removed from synthetic mixtures of Cr(III)-Co(II), Cr(III)-Cd(II), Pb(II)-Co(II) and Pb(II)-Cd(II). Antimicrobial activity of the synthesized titanium (IV) tungstomolybdate compound was evaluated and showed a considerable antibacterial activity against Staphylococcus aureus, Streptococcus agalactiae, Escherichia coli and Shigella flexneri. The inorganic counterpart has also exhibited a promising antifungal activity against Aspergillus niger and Fusarium oxysporum.*

Key Words: *Antimicrobial, Cellulose acetate, Cation exchanger, Nanocomposite, Sol-gel method*

1. INTRODUCTION

Heavy metals are unpleasantly affecting our ecosystem due to their toxicological and physiological effects in the environment. If these metals are present beyond a certain concentration it can be a serious health hazard which can lead to many disorders in normal functioning of human beings and animals (Nabi *et al*., 2011). Heavy metals are released into the environment from industrial applications, including mining, refining and production of textiles, paints and dyes. These pollutants greatly threaten the health of human populations and the natural ecosystems even at low concentration (Lenntech, 2004) as they do not degrade biologically like most of organic pollutants, their presence in drinking water or industrial effluents is a public health problem due to their absorption and therefore possible accumulation in organisms (Awual *et al.,* 2015). The toxic heavy metal ions released from industries and automobile exhausts have many adverse effects on both aquatic and terrestrial life. Therefore, heavy metal poisoning due to contamination of, surface water and soil has been a serious concern in many areas of the world (Wang *et al*., 2007).

Heavy metals are considered to be toxic because these ions are not biodegradable and tend to accumulate in living organisms. Mercury, cobalt, Zinc, copper, nickel, mercury, cadmium, lead and chromium are particular concern in the treatment of industrial waste waters (Alshehim *et al*., 2015 and Sahat *et al*., 2015). The removal of these toxic metal ions from industrial effluents, water supplies and mine waters are a major global challenge in the 21st century. An increased level of lead in blood leads to increase in blood pressure, fertility problems, nerve disorders, muscle and joint pain, irritability and memory or concentration problems. Nickel exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis (Bushra *et al*., 2017). It is very difficult for anyone to avoid exposure to any of the many harmful heavy metals that are so prevalent in our environment. So removal of toxic metals from the industrial effluents has special importance from the Eco toxicological point of view it is very difficult for anyone to avoid exposure to any of the many harmful heavy metals that are so prevalent in our environment. Despite rapid development in the detectability of instrumental methods for analysis, a direct determination of trace metal ions in the samples of complex matrices still remains a difficult task because of insufficient sensitivity and selectivity of the methods used and strong interference from the sample matrix (Bamlaku *et al*., 2016).

Several methods, such as chemical precipitation, electrolysis, membrane separation, and ion exchange are available to remove toxic metals from aqueous waste streams. Among the heavy metal removal processes, ion exchange process is very effective to remove various heavy metals and can be easily recovered and reused by regeneration operation. Thus, it is probably one of the most attractive processes and, consequently, the one commonly used in industry, because of its simple and efficient application as well as cost effectiveness (Bezabih *et al*., 2016).

The advantages of organic ion exchange are their high capacity, wide applicability, wide versatility and low cost relative to some synthetic inorganic materials. But they also have some limitations. The main limitations are their limited radiation and thermal stabilities. Most organic resins exhibit a severe reduction in their ion exchange capacity loss at higher temperature, due to physical degradation both at the molecular and macroscopic level. Polystyrene divinyl benzene, Phenolic Acrylic and etc. are classified under main groups of synthetic organic ion exchange resins (Naushad, 2009).

Inorganic ion exchangers (IIEs) are a vast field for study and materials of ever-higher selectivity's that are required to treat the large amounts of nuclear waste around the world. The IIEs normally present high capacity and fast speed exchange and are better than organic resins moreover they are chemical and radioactive steady. Inorganic ion exchangers are also classified as natural or synthetic (Naggar *et al*., 2007).

Materials such as clays, zeolites, wood carbon charcoals and ceramics are categorized under natural inorganic ion exchanger (Abdel-Galil, 2010***).*** The first inorganic ion exchangers successfully used for the large scale effluent treatment were the natural zeolites. Among the inorganic ion exchangers the alumino-silicates, both natural and synthetic, are suitable for technical purposes. One of the big potential advantages of natural materials is their relative cheapness, but if they need to be processed after mining, this advantage is reduced. Zeolites are naturally occurring cation exchangers and apatite is a naturally occurring anion exchanger (Cheruvalath, 2006).

There is currently high interest in engineering mixed materials (organic/inorganic) where features of the organic and inorganic components complement each other leading to the formation of new solid-state structures and materials with new composite properties. Some recent examples are inorganic solids with organic intercalates, zeolites and open framework host materials with organic guests and thin film hetero structures built up from alternating layers of organic poly electrolytes and colloidal inorganic poly ions (Chithra *et al.*, 2008)

Organic–inorganic composite materials are not simply physical mixtures. They can be broadly defined as composites with organic and inorganic components, intimately mixed. Indeed, hybrids are either homogeneous systems derived from monomers and miscible organic and inorganic components, or heterogeneous systems (nanocomposites) where at least one of the components' domains has a dimension ranging from some (A°) to several nanometers. It is obvious that properties of these materials are not only the sum of the individual contributions of both phases, but the role of the inner interfaces could be predominant. The nature of the interface has been used to grossly divide these materials into two distinct classes. In class I, organic and inorganic components are embedded and only weak bonds (hydrogen, van der Waals or ionic bonds) give the cohesion to the whole structure (Sanchez *et al.*, 2005).

A number of papers dealing with the synthesis and ion exchange properties of ion exchangers have been published today. There are many nanocomposites ion exchangers such as cellulose acetate- Sn(iv) phosphate (Gupta *et al.,* 2013), Cellulose acetate-Sn (IV) molybdate (Gupta *et al.,* 2014), Cellulose acetate Zr (IV) molydophosphate (Nabi *et al.,* 2007), polyortho-ansidne-Sn (IV) tungstate (Khan *et al.,* 2011), polyaniline-Sn (IV) tungstomolybdate (Rahman *et al.*, 2013)...etc.

Despite their advantages, inorganic ion exchangers are non-reproducible, expensive and are incompetent to treat large volume of waste effluent. On the other hand, the organic ion exchangers have less thermal and radiation stability (Bamlku *et al*., 2016).Recently, attempts have been made to develop organic–inorganic composite ion exchangers by incorporation of organic monomers in the inorganic matrix to obtain materials of extra ordinary electrical, magnetic, ion exchange and optical properties, which arise from the synergism between the properties of the organic–inorganic components. The combination of organic and inorganic precursors yields hybrid materials that have mechanical properties not present in the pure materials. The organic group can be reactive which implies that it is able to form an organic network as well as inorganic network (Khan *et al*., 2005; Nabi and Naushad, 2008).

In our research group, we reported a novel organic-inorganic composite exchanger, polyanilne tin (IV) molybdophosphate with demonstrated selectivity for Cu(II) and Pb(IV) ions from aqueous solution (Bamlaku *et al*., 2016). Recently, we have also synthesized a new inorganic exchanger, nano-titanium(IV)tungstomolybdate with promising separation potential towards metal ions such as Pb(IV), and Cr(III) and a redionucleotide UO_2^{2+} (uranyl ions) from a given mixture of toxic heavy metal ions (Bezabih *et al*., 2016).

These findings inspired us to work more on novel exchanger's particularly hybrid exchangers. No work has been done so far by supporting the inorganic exchanger we reported previously with organic matrices such as polyaniline, cellulose acetate and others. The present work is therefore aimed at evaluating the ion exchange and antimicrobial activity of new exchanger cellulose acetate tin (IV) tungstomolybdate ion exchanger.

Objectives of the Study

General Objective

- To assess the ion exchange and antimicrobial potential of new exchanger, cellulose acetate Titanium (IV) tungstomolybdate composite cation exchanger.

Specific Objectives were to:

- Synthesize inorganic Titanium (IV) tungstomolybdate and composite cellulose acetate titanium (IV) tungstomolybdate cation exchangers.
- Characterize the as-synthesized exchangers using modern analytical techniques such as FTIR, BET, XRD, TGA and SEM-EDX
- Investigate the thermal and chemical stability of the as- synthesized nanocomposite cation exchanger.
- Evaluate the ion exchange capacity of the as-synthesized nanocomposite cation exchanger.
- Evaluate the ability of cellulose acetate titanium (IV) tungstomolybdate composite cation exchanger for the separation of selected heavy metals from their binary mixtures
- Assess the antimicrobial activity of the as-synthesized nanocomposite exchanger on selected pathogenic microorganism using the Disc Diffusion Method.

2. LITRATURE REVIEW

2.1. Ion Exchange Theory

A description of Ion exchange process can be cited in the most ancient literature following A paragraph written in 'Holy Bible'. In the Old Testament scribes which says "Moses succeeded in preparing drinking water from brackish water by an ion exchange method" (Naushad, 2009). Now-a-days the ion exchange has come to be recognized as an extremely valuable technique. Ion exchange is a process in which "an insoluble (or immiscible) material, when come in contact with an electrolyte solution takes up stoichiometrically ions of positive or negative charge and release other ions of like charge from the exchanger phase into the solution phase". Carriers of these exchangeable ions are called "Ion exchangers" (Chand *et al*., 2011).

Ion exchange was originally discovered in naturally occurring materials such as soils, clays and zeolites. These materials found application as water softeners, but the first commercially available ion exchangers were amorphous aluminum silicate gels. In spite of their low cost but their industrial use was often difficult (impurities, bad physical properties for packed bed operations) and they sometimes need a chemical or thermal pretreatment. This is by its rule makes a need for alternatives, which led to development and synthesis of organic ion exchanger resins in 1930's. However, extensive studies on the synthetic inorganic ion exchangers have proved their potential in solving diverse problems of environmental and analytical chemistries (AbdEl-Latif and El-Kady, 2008).

2.2. Ion Exchange Processes and Mechanism

Ion exchange, like any heterogeneous process, is accomplished by transfer of ions to and from the inter-phase boundary, i.e. the chemical reaction itself, diffusion inside the material, and diffusion in the surrounding solution should be taken into account. Besides the two major phases, the thin film of solution at surface of the exchanger should be accounted separately. The film properties differ from properties of the surrounding bulk solution. Formation of this film is unavoidable. Even a rigorous agitation (an intensive stirring in batch processes or turbulent hydrodynamic flow in flow in column systems) while being able to reduce the thickness of the inter-phase film – can never take it off completely (Khalil M, *et al*., 2012).

Figure 1. Shows the simplest illustration of the mass transfer at ion exchange. Ions B diffuse from the solution through the film into the beads and ions A diffuse out of the beads crossing the film into the solution. This inter-phase diffusion of counter ions is what is called ion exchange to complete the overall picture of the ion exchange mechanism. Thus, the mechanism of ion exchange can be presented by Figure.1. The first step is diffusion of the first ion from bulk of the solution towards the interphase. This step can be easily manipulated because the diffusion transport in the bulk solution can be assisted with agitation. If a column process is considered, turbulence of the local flows between the exchanger beads can assist the mass transfer (Khalil M, *et al*., 2012).

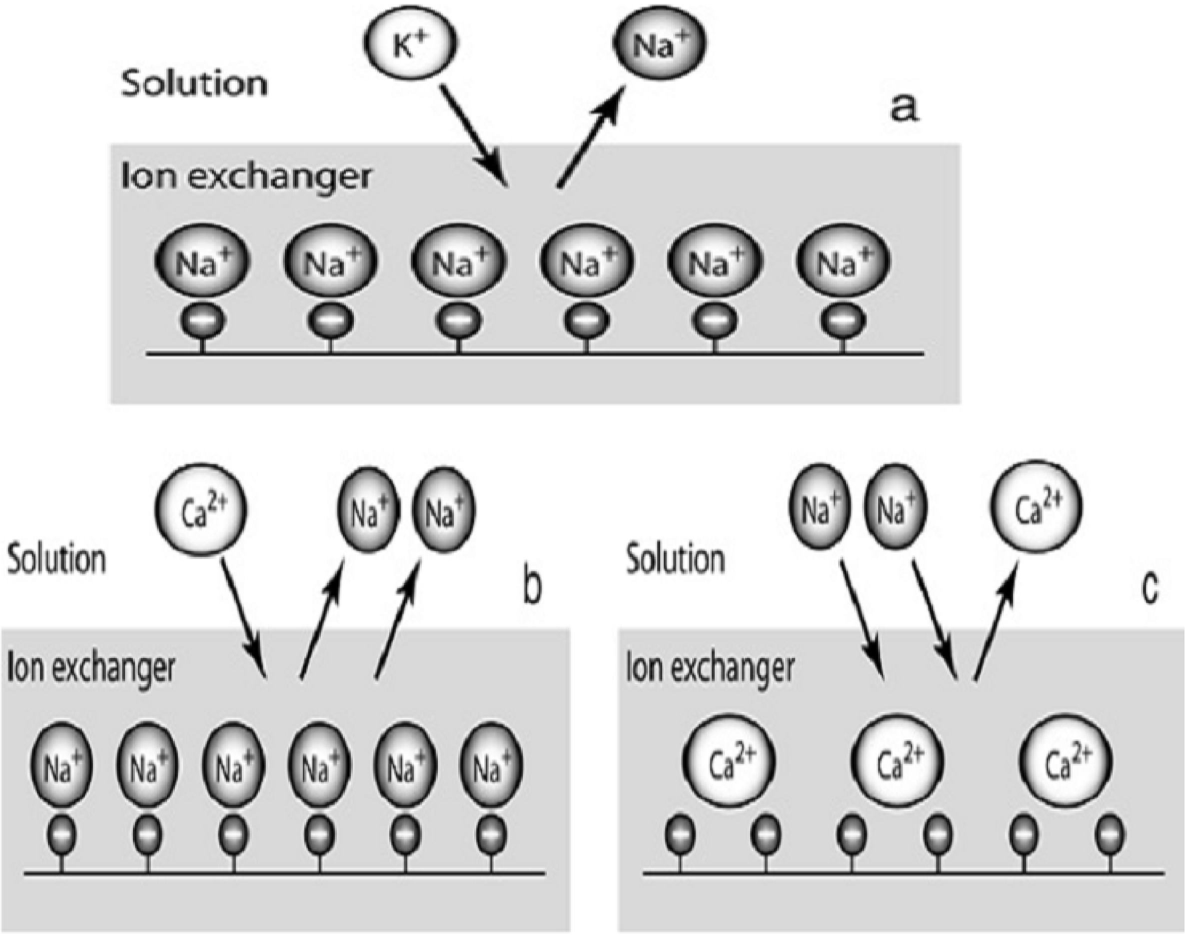


Figure 1. Mechanism of ion exchanger

If a column process is considered, turbulence of the local flows between the exchanger beads can assist the mass transfer An ion exchange reaction may be defined as the reversible interchange of ions between a solid phase (the ion exchanger) and a solution phase, the ion exchanger being insoluble in the medium in which the exchange is carried out. Although ion exchangers comprise a very heterogeneous group of materials, their general structure has one common feature a frame work with surplus electric charge which can bind oppositely charged ions, as well as mobile (charge compensating) counter-ions which can be exchanged for a stoichiometric amount of similarly charged ions. Exchangers carrying exchangeable cations (mobile) are called cation exchangers, while carriers of exchangeable anions are referred to as anion exchangers. Certain materials possess the ability to exchange both cations and anions and these are called amphoteric ion exchangers (Hendricks, 2005).

If an ion exchanger M^-A^+, carrying cations A^+ as the exchanger ions, is placed in an aqueous solution phase containing B^+ cations, an ion exchange reaction takes place which may be represented by equation.

$$\underset{\text{Solid}}{\overset{-}{M}\,\overset{+}{B}} + \underset{\text{Solution}}{\overset{+}{A}} \rightleftharpoons \underset{\text{Solid}}{\overset{-}{M}\,\overset{+}{A}} + \underset{\text{Solution}}{\overset{+}{B}}$$

The equilibrium represented by the above equation is an example of cation exchange, where M^- is the insoluble fixed anionic complement of the ion exchanger M^-A^+, often called simply the fixed anion. The cations A^+ and B^+ are referred to as counter-ions, when ions in the solution which bear the same charge as the fixed anion of the exchanger are called co-ions. In much the same way, anions can be exchanged provided that an anion-receptive medium is employed. An analogous representation of an anion exchange reaction may be written (Dorfner, 1991).

$$\underset{\text{Solid}}{\overset{-}{M}\,\overset{+}{A}} + \underset{\text{Solution}}{\overset{+}{B}} \rightleftharpoons \underset{\text{Solid}}{\overset{-}{M}\,\overset{+}{B}} + \underset{\text{Solution}}{\overset{+}{A}}$$

Solution; A; schematic representation of the process of ion exchange. A cation exchanger in the form of ‘A’ is placed in a solution of electrolyte ‘B’.

‘A’ migrates from the exchanger into the solution, while counter ions ‘B’ migrate from the solution into the ion exchanger. Within a certain time span, ion exchange equilibrium is attained, which both the ion exchanger as well as the solution contains both counter-ions pieces ‘A’ and ‘B’. However, the pores of the ion exchanger are occupied not only by charge compensating ions (counter-ions), but also by solvent and ions (solutes) which may enter the pores when the ion exchanger is in contact with the solution.

A cation exchanger containing counter ions ‘A’ is placed in a solution containing counter-ions ‘B’ (left).The counter ions are re distributed by diffusion until equilibrium is attained (right) (Helfferrich,1962). The unique characteristic properties of ion exchangers can be attributed to a distinctive feature in their structure. They consist of a frame work, held together by chemical bonds or lattice energy and the framework carries a positive or negative electric surplus charge, which is compensated by ions of opposite sign, also referred to as counter-ions. The counter-ions are mobile thus able to move within the framework and can be replaced by other ions of the same sign. However, electro-neutrality must be preserved, i.e. the electric surplus charge of the ion exchanger must be compensated at any time by a stoichiometric ally equivalent number of counter-ions within the pores. A counter-ion can subsequently leave the framework, only when, simultaneously, another ion enters and takes over the task of contributing its share to the compensation of the framework charge (Helfferrich,1962; Hendricks, 2005).

The process of ion exchange can be carried out in a variety of ways with different main objectives (Hendricks, 2005):

- **Substitution:** A valuable ion can be recovered from solution and replaced by a valueless one. Similarly, a toxic ion (*e.g.*, mercury) can be removed from solution and replaced by a nontoxic ion.
- **Separation:** A solution containing a number of different ions passes through a column with beads of ion exchange resin. The ions are separated and emerge in order of increasing affinity for the resin.

- **Removal:** By using a combination of cation (in the H^+ form) and anion resin (in the OH^- form), all ions are removed and replaced by H^+ and OH^- ions, the solution is thus demineralized.

2.3. Ion Exchange Materials

By definition, ion exchangers are insoluble solid materials carrying exchangeable cations or anions, which can be exchanged for a stoichiometric ally equivalent amount of other ions of the same sign when the ion exchanger is in contact with an electrolyte solution (Hendricks, 2005). An ion exchanger can be considered as a “reservoir” of exchangeable mobile ions (also referred to as functional groups/ion genic groups, or exchangeable cations) and these ions are utilized in ion-exchange operations and hence, the number of ion genic groups/exchangeable ions per specified amount of ion exchanger is one of the most important characteristics of an ion exchanger (Helfferrich, 1962).

Although ion exchangers comprise a very heterogeneous group of materials, their general structure all have one common feature framework with electric surplus charge which can bind oppositely charged ions, as well as mobile (charge compensating) counter-ions which can be exchanged for a stoichiometric amount of similarly charged ions. Exchangers carrying exchangeable cations (mobile) are called cation exchangers, while carriers of exchangeable anions are referred to as anion exchangers. Certain materials possess the ability to exchange both cations and anions and these are called amphoteric ion exchangers (Hendricks, 2005).

The ability of ion exchange materials to remove trace ions from solution and the concentration which may be achieved on elution with suitable solutions have been used in the treatment of wastes and in processes for recovery of metals from very dilute solutions. Ion exchangers have been used extensively in treating rinse water wastes in plating industry for example, where valuable metals are recovered at costs comparable to or less than conventional chemical treatment, with appreciable saving in space for treatment plant (Nilchi *et al*., 2005).

2.3.1. Organic Ion-exchange Materials

The largest group of ion exchangers available today are synthetic organic resins in a powdered (5–150 μm) form. The framework, or matrix, of the resins is a flexible random network of hydrocarbon chains. This matrix carries fixed ionic charges at various locations. The resins are made insoluble by cross-linking the various hydrocarbon chains. The degree of cross-linking determines the mesh width of the matrix, swelling ability, and movement of mobile ions, hardness and mechanical durability (IAEA, 2002). The main advantages of synthetic organic ion-exchange resins are their high capacity, wide applicability, wide versatility and low cost relative to some synthetic inorganic media. The main limitations are their limited radiation and thermal stabilities (Khan *et al.,* 2012).

2.3.2. Inorganic Ion Exchange Materials

The last fifty years or so has seen a great upsurge in the researches on synthetic inorganic ion exchangers, the reason being probably due to some important characteristics of inorganic ion exchangers such as resistance to temperatures, oxidizing radiation and strongly oxidizing solutions, the main emphasis being development of new materials possessing thermal stability, chemical stability reproducibility in ion exchange behavior and selectivity for certain metal ions important from analytical and environmental point of view. Important classes of inorganic ion exchangers are clay minerals, zeolites, heteropolyacid salts, oxides/hydrous oxides, hexacyno-ferrates and tetravalent metal acid salts. Inorganic ion exchangers possess several characteristic features which have led to their numerous applications in diverse fields. The most important property of inorganic ion exchangers is their stability at elevated temperatures and resistance to high radiation fields. Due to their rigid structure, the inorganic ion exchangers possess specific and unusual selectivity, and they do not undergo appreciable dimensional change during the ion exchange process (Singh *et al*., 2017).

2.3.3. Organic-Inorganic Composite Ion-Exchange Materials

The combination of organic and inorganic precursors yields hybrid materials that have mechanical properties not present in the pure materials. Organic- inorganic composite ion exchange materials show the improvement in its granulometric properties that makes them more suitable for the application in column operations. The binding of organic polymer also introduces the better mechanical properties in the end product, i.e. composite ion exchange materials (Khan *et al*., 2012).

2.3.4. Ion Exchangers as Supports

Ion exchangers are now extensively used in heterogeneous photo catalysis. Thus, in order to obtain associated organic and inorganic materials as ion-exchangers support, attempts have been made to develop a new class of composite ion exchangers by the incorporation of electrically conducting organic polymers (polyaniline, cellulose acetate polypyrrole, polythiophene, poly-otoluidine, poly-oanisidine) into the matrices of inorganic precipitates of multivalent metal acid salts (Siddiqui and Valaski*et al.,* 2006). Composite exchangers have more advantages over organic and inorganic ion-exchangers as they overcome two major drawbacks from which the latter suffers like thermal and chemical stability as well as reproducibility. Due to these advantageous composite ion exchange materials have been extensively used in environmental remediation, analytical and the electro analytical processes such as waste water (Dhanitha and Janardanan, 2015).

2.4. Synthesis Methods of Nano size Ion Exchanger Materials

To obtain Nano-crystalline powders with high homogeneity and uniform structure, many Techniques have been provided (Rashad *et al.,* 2009). There are many kinds of processes related to soft solution processing and the important ones are sol-gel precipitation and co-precipitation (Byrappa and Yoshimura, 2001). Generally, there are others but the above two including Hydrothermal were most frequently used for preparation of Nano materials (Abd El-latif and El-Kady, 2011).

2.4.1. Sol –gel Precipitation

The sol-gel technique is one of the fastest growing fields of contemporary chemistry. Sol-gel processing is a wet chemical synthesis approach that can be used to generate nano particles by gelation, precipitation, and hydrothermal treatment (Kung and Ko, 1996). For sol–gel growth generally the required sol is prepared and the template is put into the sol for a required period (e.g. 0.5–1 h). After removing the membrane from the sol it is dried and then annealed at higher temperature before the required phase is formed. The sol is prepared by dissolving a stoichiometric ratio of precursor materials in an equal amount of water and Adding ethylene glycol. The mixture is then heated on a hot plate till a sol of desired viscosity formed (Rao *et al.,* 2004).

2.4.2. Co-Precipitation (Homogenous Precipitation)

The chemical co precipitation method ensures proper distribution of the various metals ions resul ting to stoichiometric and smaller particles size product, compared to some of the other procedur es In co-precipitation processes, the metal precursors (salts like chlorides) are dissolved in an appropriate solvent and a precipitating agent (e.g.NH_4OH) is added to form Nano particles (Kooti and Matturi, 2011). The co-precipitation method requires that all the components have roughly the same solubility. Otherwise, when the precipitating agent is added, the less soluble components will precipitate out as a separate phase (Lalena *et al.,* 2008). The main drawback is that this process is difficult to control and the particle size is not, relatively, small and mono dispersed enough for specific applications like recording media applications (Rashad *et al., 2009).*

2.4.3. Hydrothermal Technique

The term hydrothermal usually refers to any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and Recrystallize (recover) materials that are relatively insoluble under ordinary conditions (Byrappa and Yoshimura, 2001). In practice, hydrothermal synthesis is conducted in an autoclave. Thus, it is an environmentally friendly process as it is carried out in a closed system. The various components to be assembled are mixed with a diluent (generally H_2O). An acidic or basic catalyst is required. Additives which are not involved directly in the composition of the material are introduced in order to control the sizes of cavities and the crystalline type of the final product. This mixture is heated at temperatures from 100^oC up to several hundred ^0C (Corriu and Anh, 2009).

2.5. Nanomaterial

The term Nano scale refers to the size of the particles, with at least one dimension range from approximately 1nm to 100 nm. The term ‘nanomaterial’ is now frequently used for a variety of materials. It usually refers to materials with any external dimensions, or an internal structure, in the Nano scale or having internal structure or surface structure in the Nano scale that exhibit additional or different properties and behavior as compared to the other materials with similar chemical composition (Lövestam *et al*., 2010).

Intense research activity is seen in recent years in advancing the synthesis and functionalization of various sizes and shapes of semiconductor and metal nano particles. The most fundamentally important theme of this field is that the Nano scale building blocks, because of their sizes below about 100 nm, impart to the nano structures created from them new and improved properties and functionalities unavailable in conventional materials and devices. The reason for this is that materials in this size range can exhibit fundamentally new behavior when their sizes fall below the critical length scale associated with any given property. Thus, essentially any material property can dramatically be changed and engineered through the controlled size-selective synthesis and assembly of Nano scale building blocks (Hu *et al*., 1999).

Research in nano structured materials is motivated by the belief that ability to control the building blocks or nano structure of the materials can result in enhanced properties at the macro scale: increased hardness, ductility, magnetic coupling, catalytic enhancement, selective absorption, or higher efficiency electronic or optical behavior (Kamat and Meisel, 2002). Every property has a critical length scale, and if a Nano scale building block is made smaller than that critical length scale, the fundamental physics of that property starts to change. By altering the sizes of those building blocks, controlling their internal and surface chemistry, and controlling their assembly, it is possible to engineer properties and functionalities in unprecedented ways (Hu *et al*., 1999).

2.6. Application of Ion Exchanger Material's

The ion-exchange composite materials are the materials that have vast applications around the world in various processes such as electro-dialysis, desalination, diffusion, electro-deionization, membrane electrolysis, electro chemical synthesis, fuel cells, and storage batteries and etc.There fore they are useful in pollution control, energy saving, power generation, resource recovery, etc (Gohil *et al*., 2006). Generally, Ion exchanger materials are used for the following process:

- Removal of heavy metals from electroplating waste waters and other industrial processes
- Polishing of waste water before discharging.
- Nitrogen control (removal of ammonium ion from waste waters).
- Removals of salt build up in close-loop utility water (e.g., removal of salts from cooling water blow down).
- Purification of acids and bases to reuse them.
- Removal of radioactive contaminants in the nuclear.

The inorganic–organic composite ion exchange materials demonstrates a large number of applications, which make them nice-looking to filtration tasks in the beverage and textile industry, medicine, pharmacy, chemical industry, waste water treatment and others. These applications are due to their high thermal resistance, chemical resistance and the mechanical strength (Mohammad *et al.,*2012). Successful commercial inorganic–organic hybrids have been part of manufacturing technology since the 1950s. Ion-exchange is a well-established technique for performing chemical separations and purification. Major commercial applications include water softening and purification, decontamination and re-cooperation of waste streams, and recovery and purification in hydrometallurgy, pharmaceuticals, and the food industry. Ion-exchange materials have been fabricated into a variety of inert porous media that allows use for specific ion transport such as sodium ions in chlor-alkali electrolyzers or protons in low temperature hydrogen fuel cells. Since the advent of the nuclear age, ion-exchange materials have been used in the separation and purification of radioactive materials as well as the decontamination of nuclear waste solutions (Taylor-Pashow *et al*., 2013).

In addition to the above application, Ion-exchange method may have the various advantages such as regeneration capability of ion-exchange materials, low cost, p_H independence, high selectivity, etc. when compared with other methods (Naushad *et al*., 2015). In designing composite materials scientists and engineers have ingeniously combined various metals, ceramics, and polymers to produce a new generation of extra ordinary materials that encompass a wide variety of applications. Most composites have been created to improve combination of mechanical characteristics such as stiffness, toughness, and ambient and high temperature strength. (Khan and Alami, 2003).

3. MATERIALS AND METHODS

3.1. Experimental Site

Synthesis of cellulose acetate Ti(IV) tungstomolybdate composite exchanger were carried out at Haramaya University, Chemistry Department Research Laboratory and the antimicrobial properties of the as-synthesized nanomaterial were conducted in the School of Plant Sciences. Characterizations of the as-synthesized composite using TGA-DTA, BET and SEM-EDX were carried out at the Institute of Catalysis and Petroleum Chemistry (CSIC), Madrid, Spain. On the other hand, FT-IR analysis and XRD patterns were carried out at Addis Ababa University, Chemistry Department.

3.2. Instruments and Apparatus

The instruments that were used in this study include the following: XRD (BRUCKER D8 Advanced AXS GmbH, Germany), FTIR spectrometer (SHIMADZU 1730, Japan), pH meter (METTLER TOLEDO, MP 220, Switzerland), powder X-ray diffraction (XRD) using X'Pert Pro PANalytical equipped with an X-ray source of a CuKa radiation (wavelength of 0.15406 nm) at step scan rate of 0.02 (step time: 1 s; 2θ range: 5.0–90.4^{o}),scanning electron microscopy (SEM) using a Hitachi TM1000 with EDX detector and the micropore surface areas were calculated by the Brunauer–Emmett–Teller (BET)method.thermogravimetric analysis (TGA) was performed on a thermo gravimetric analyzer PerkinElmer TGA7. Samples were heated at a rate of 20 °C min^{-1} to a maximum temperature of 700 °C in a flowing atmosphere of oxygen.

3.3. Chemicals

The main chemicals used for the synthesis of the exchangers were: (Cellulose acetate , BDH), (sodium molybdate, UK), (sodium tungstate, BLULUX), (formic acid, BLULUX), (isopropoxide, BLULUX) HCl (35.6%), H_2SO_4 (98%, laboratory reagent, LOBA, India), HNO_3 (69% LR, Brck land Scientific Supplies, U.K), DMF (98%), NaOH (97.5% BDH), KOH, NaCl, KCl,$BaCl_2$,$MgCl_2$, $CaCl_2$, $CaCO_3$,acetone phenolphthalein,Erochrome bluck T(Switzerland), diso diumsaltsof EDTA and adition nitrate/ sulfate /carbonate or chloride salts of Pb(II), Cd(III),Cu (II),Cd(II),Co(II), Cr(III), Ni(II) and Fe(III) were used for the preparation of standard and working solutions of the respective metal ions, and deionized water used to prepare solutions and double deionized water for washing the synthesized precipitates.

3.4. Preparation of Reagents

Solution of 0.1M sodium tungstatedehydrate ($Na_2WO_4.2H_2O$) and 0.1M sodium molybdate dehydrate ($Na_2MoO_4.2H_2O$) solution was prepared in demineralized water (DMW) (Bezabih *et al.,* 2017). And 0.1M solution of ti (IV) isopropoxide ($C_{12}H_{28}O_4Ti$) was prepared in ethanol, HCl and DMW (Karkare *et al*., 2014).

3.5. Preparation of Solution of Cellulose acetate

Solution of cellulose acetate was prepared in concentrated formic acid (Nabi and Naushad, 2008; Ahamad *et al*., 2015). This was done by dissolving cellulose acetate in concentrated formic acid (2 g of cellulose acetate powedr was dissolved in concentrated formic acid until gel like solution was formed).

3.6. Synthesis of Titanium (IV) Tungstomolybdate

The titanium precursor was prepared using sol-gel method as described by (karkare, 2014) with certain modification to suit our purpose. Accordingly, 6ml titanium (IV) isopropoxide (TTIP) was dissolved in 50 mL absolute ethanol and stirred for 30 min. A mixture of 2ml distilled water and 0.5 mL hydrochloric acid was added to the solution drop wise with constant stirring. A homogeneous solution was obtained after stirring vigorously for 2h. Then sol was formed and after aging for 24 h, the sol was transformed into gel. Upon the TiO_2 precursor formed, 0.1M sodium molybdate and 0.1M sodium tungstate were added and a homogeneous solution was obtained after stirring vigorously for 2h. After washing the sample twice with doubly distilled water to remove traces of chloride ions, and then dried at 50^oC for 24h. The powder obtained was immersed into 1M nitric acid for 24h with gentle stirring in order to transform the ion exchanger into its hydrogenated form. In order to determine the chemical and physical properties of the prepared samples, the one which showed the largest IEC for Na^+ ion was selected and characterized using physical and chemical characterization techniques (Bezabih *et al.,* 2016).

3.7. Synthesis of Cellulose Acetate Titanium (IV) Tungstomolybdate Nanocomposite Cation Exchanger

In order to get a stable product with good ion exchange properties, a number of samples of cellulose acetate-ti (IV) tungstomolybdate were synthesized by mixing a mixture of the aqueous solutions of 0.1M sodium tungstate and 0.1M sodium molybdate into the gel of ti (IV) tungstomolybdate solution gradually with continuous shaking of the mixture in varying mixing ratios. The pH variation was adjusted by adding 1M nitric acid or 1M ammonia solutions to maintain the desired pH. The gel of cellulose acetate which was prepared in concentrated formic acid was added into the inorganic precipitate of ti (IV) tungstomolybdate and mixed thoroughly with constant stirring for 1h.

The gelatinous precipitate so formed, was allowed to stand for 24 h in the mother liquor for digestion.The supernatant liquid was removed and the precipitate was washed with demineralize d water several times to remove excess reagents. The product was dried at 50°C in an oven. The dried product was then kept in demineralized water for cracking and to obtain the particle of the size of (~125 µm). then converted to H^+ form by placing it in 1M HNO_3 solution and was washed with demineralized water to remove excess acid and finally dried at 50^0C. Hence, a number of samples were prepared, and on the basis of ion exchange capacity and percentage yield, the proper sample was selected for detailed studies (Naushed *et al.*, 2007)

3.8. Evaluation and Chemical Characterization of the Synthesized Cellulose Acetate Titanium (IV) Tungstomolybdate Ion Exchanger

3.8.1. Ion-Exchange Capacity (IEC)

The ion exchange capacity, which is generally a measure of the hydrogen ion liberated by neutral salt to flow through the composite cation exchanger was determined by standard column process. 1.0 g (dry mass) of the composite ion exchange material in H^+ form was placed in a glass column with a glass wool support at the bottom. It was washed with demineralized water to remove any excess of acid remained sticking on the particles. The hydrogen ions were then eluted with 0.1 M solution of different alkali and alkaline earth salts. The collected effluent was titrated against a standard solution of sodium hydroxide using phenolphthalein as an indicator. The hydrogen ions released was then calculated.

$$\text{IEC} \quad = V_{\text{NaOH}} \frac{\text{CNaOH}}{\boldsymbol{W}}$$

where V_{NaOH}, C_{NaOH} and W are the volume of NaOH in milliliters, the concentration of NaOH in milli equivalents per milliliter and the weight of the dry exchanger sample in gram, respectively (Abd El-Latif and El Kady, 2011).

3.8.2. Thermal Effect on Ion Exchange Capacity

To determine the effect of heating temperature on ion exchange capacity of the material, 1.0 g sample of the cellulose acetate titaniumi (IV) tungstomlybdate in H^+ form was heated at different temperatures in a muffle furnace for 1h and Na^+ ion exchange capacity was determined after cooling them at room temperature by standard column process as described above.

3.8.3. pH-Titration

pH - titration studies of cellulose acetate ti (IV) tungstomolybdate composite cation-exchanger was performed by (Topp and Pepper, 1949) method. In this procedure a total of 500 mg portions of the cation-exchanger in the H^+ form was placed in each of several 250 mL conical flasks, followed by the addition of equimolar solutions of alkali metal chlorides and their hydroxides (NaCl-NaOH) in different volume ratios, the final volume being 50 mL to maintain the ionic strength constant. The pH of the solution was recorded every 24 h until equilibrium was attained which needed 5 days.

3.8.4. Chemical Stability

Each of 0.4 g portions of the composite cation exchange cellulose acetate Ti (IV) tungstomolybd ate) in H^+ form was treated separately with 50 mL of 0.1 M each of different reagent solutions such as: HNO_3, H_2SO4, NaOH, KOH and acetone, and finally with demineralized water (DMW) for 24 h with occasional shaking. After removal of excess reagent (liquid) the composite was dried in oven at 50^{o}C.The ion exchange capacity of the remaining material was determined by the batch method (Abd El-Latif and El-Kady, 2011; Chand *et al.*, 2011).

3.8.5. Distribution Studies

In order to get the idea of partition behavior of the exchanger towards the separation of metal ions of analytical interest, distribution coefficients (K_d) was determined in several solvents systems. A 0.4 g exchanger in H^+ form was treated with 40 mL solution of metal ions in required solvent medium in a 100 mL Erlenmeyer flask. The mixture was agitated for 6 h at 25^{0}C in a shaker. The amount of metal ions before and after adsorption was determined by titration against a standard solution of 0.01 M di-sodium salt of EDTA. The K_d values were expressed as follows,

$$K_d = \frac{\text{metal ions (mequiv.)/ion−exchanger (g)}}{\text{metal ions (mequiv.)/solution (mL)}}$$

$$K_d = \frac{I-F}{F} \times \frac{V}{M} \text{ mL g}^{-1}$$

Where I is the initial amount of metal ion in the aqueous phase, F the final amount of metal ion in the aqueous phase, V the volume of the solution (mL) and M the amount of cation- exchanger (g) (Nabi and Shalla, 2009; Chand *et al.*, 2011).

3.9. Quantitative Separation of Metal Ions in Binary Synthetic Mixtures

A quantitative separation of some important metal ions of analytical utility was achieved in a column filled with cellulose acetate ti (IV) tungstomolybdate. 1.5 g of exchanger in H^+ form was packed in a glass column of 0.9 cm internal diameter with a glass wool support at the end. The column was washed thoroughly with demineralized water and the mixture of two metal ions, having initial concentration 0.1M of each with different volume ratios, was loaded on it and allowed to pass through the column at a flow rate of 0.20 mL min−1 till the solution level was just above the surface of the material. The column was then rinsed with demineralized water so that the metal ions, which were not exchanged, could be removed. Individual metal ions adsorbed on the exchanger, was then eluted using the appropriate eluting reagents. The flow rate of the eluent was maintained at 0.5 mL min^{-1} throughout the elution process. The effluent was collected in 10 mL fractions and was titrated against the standard solution of 0.01 M di-sodium salt of EDTA.

3.10. Characterization of As-Synthesized Nanocomposites Exchangers

The as-synthesized nanocomposites exchangers were characterized using FTIR, BET, TGA, XRD, and SEM -EDX. The FTIR spectrum of cellulose acetate titanium (IV) tungstomolybdate in their original form dried at 40^{o}C was taken by KBr disc method at room temperature. Typically 10 mg of each was taken and thoroughly mixed with 100 mg of KBr, and the mixture was ground and pressed with a special press to give a disk of standard diameter. IR absorption spectrum was scanned and recorded in the region 4000–400 cm^{-1}.

X-ray diffraction is non-destructive analytical technique that can be applied for the identification of unknown specimens and for the determination of materials properties. It is the most important and beneficial technique in solid state chemistry and it has been applied for the fingerprint characterization of crystals and for the determination of their structures. XRD (X'Pert Pro PANalytical equipped with an X-ray source of a CuKa radiation (wavelength of 0.15406 nm) pattern was determined for all of the as-synthesized powders) instrumental techniques. Thermogravimetric analysis was performed on the thermo gravimetric analyzer Perkin Elmer TGA7. The sample was heated at rate of 10°C min^{-1} up to a maximum temperature of 1200^{0}C in a flowing atmosphere of oxygen.

SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography and composition. SEM was used to identify the surface quality and morphology/microphotographs of the synthesized composite material. Scanning electron microphotographs of the synthesized nano composite was recorded at different magnifications using scanning electron microscope.

The elemental composition of the nanocomposite ion exchanger was determined by energy dispersive X-ray coupled with scanning electron microscopy (SEM-EDX) (Rathore *et al*., 2014). The syntesied material of cellulose acetate Titanium (IV) tungstomolybdate and Ti(IV) tungstomolybdate was charecterized Brunauer Emmett Teller (BET) method in order to deterimane the surface area.

3.11. Anti-microbial Studies

The organic polymer, inorganic, and composite exchangers were tested for their effect on selected microbes using the paper disc diffusion method. Antibacterial studies were conducted against four important bacteria (*Escherichia coli and salmonella typhi* from Gram-negative) and, *staphylococcus aureus and strepto coccus from Gram-positive)* and two fungal species *Aspergillus niger and Fusarium* where they are using nutrient agar medium. *Chloramphenicol,* standard antibiotic drug, was used as reference in the antibactericidal studies and *Tilt* was the standard antibiotic drug used as reference in antifungal studies. The effectiveness of the compounds was determined by measuring the diameter of inhibition zones (Marinella *et al*., 2012). All the microbial species were obtained from Plant Pathology Laboratory of the School of Plant Science, Haramaya University.

3.11.1. Preparation of the Media

Bacteria *E. coli* and *Salmonella thype*, *Streptococcus* and *Staphylococcus aureus* and fungi *Aspergillius niger and Fusarium* were transferred from the culture and then streaked on Mueler Hinton agar (MHA) plate and incubated for 24 h at 37^0C. The bacteria were transferred to the autoclaved MHA plate and cooled at about 45^0C in water bath and mixed vigorous by swirling of flasks and fungus using (PDA) medium (Marinella *et al*., 2012). The media was transferred to sterilize petri-dishes. Finally, the media containing bacteria and fungus suspension were poured to sterilized plates and used for the antimicrobial tests. In this experiment piece of paper containing as synthesized nanocomposites, inorganic and organic polymer were placed on an agar plate where bacteria and fungi had been placed, and the plate was left to incubate for 24 h at 37^0C. Then, after, the inhibition zone of bacteria and fungi in each case was measured using ruler. The size of this zone depends on the effectiveness of nanocomposite at stopping the growth of the bacterium. Accordingly, the stronger antibiotic nanocomposite creates a larger zone (Marinella *et al*., 2012).

3.11.2. Preparation of Inoculums

The tested bacterial species were transferred from the stock cultures and streaked on Mueller Hinton (MHA) plates and incubated for 24 h. Well separated bacterial colonies were then used as inoculums. Bacteria were transferred using bacteriological loop to autoclaved MHA that was cooled to about 45^{0}C in water bath and mixed by gently swirling the flasks. The medium 22 was then poured to sterile Petri dish, allowed to solidify and used for the biotest. For test fungi, mycelia plugs from stock cultures were transferred to Potato Dextrose Agar (PDA) plates and incubated for 5 days. Then spores of *Aspergillus niger* were harvested by washing the surface of the colony using 10 ml sterile distilled water and transferred to 250 ml autoclaved PDA cooled to about 45 ^{0}C in water bath. Likewise, mycelium of *Aspergillus* fumigates were washed with 10 ml sterile distilled water, macerated in a blender and the mycelia suspension was transferred to 250 ml autoclaved PDA cooled to about 45 ^{0}C in water bath. The medium containing spore or mycelia suspension was poured to sterile; a plate allowed to solidify and was used for disk diffusion bioassay (Nwinyi *et al.*, 2009).

3.11.3. Preparation of test Solution

The nano of cellulose acetate polymer powder, titanium tungstomolybdate and nanocomposite were dissolved in Dimethyl salfoxide of 0.2 g respective in 2 ml concentrated Dimethyl salfoxide solvents, the three nanomaterial's 100% was used to test antimicrobial activities.

3.11.4. Testing for Antifungal Activity

Filter paper discs of 6 mm in diameter placed in beaker were sterilized in an oven at 180 ^{0}C for 1h. The organic polymer, synthesized inorganic and composite exchangers each of the concentration of the prepared materials were then pipetted to the sterile paper discs. 10 µL and 20 µL of the samples was pipette to the discs in three replications. The paper discs impregnated with the given nano solution were then transferred using sterile forceps to potato dextrose agar (PDA) seeded with spore suspension of test fungi as described under inoculums preparation above. The Petri dishes were incubated at 27^{0}C for 5 days. All the tests were performed in triplicate. The antifungal activity was evaluated by measuring the zone of inhibition against the tested organisms.

3.11.5. Testing for Antibacterial Activity

Sterilized paper discs were transferred to MHA plate's seeded with bacteria and incubated at 37 ^{0}C for 24 h. All the tests were performed in triplicate. The organic polymer, nano inorganic, nano composite materials were taken to test the sensitivity towards four bacteria.

4. RESULTS AND DISCUSSION

4.1. Synthesis of Titanium (IV) Tungstomolybdate

Titanium (IV) tungstomolybdate was prepared by sol-gel method with titanium isopropoxide as precursor of TiO_2. Aqueous solution with constant pH and peptizing the resultant suspension has been applied for preparation of the TiO_2 nano powder with narrow size distribution. The conditions used for the preparation have considerable effect on the degree of hydration and the composition of the exchanger. These two factors are responsible for the shape and size of cavities inside the ion exchanger and for other properties of the exchanger resulting in their unusual ion exchange behavior (Bezabih *et al*., 2017)

4.2. The Mixing Volume ratio of the Precursors

In order to determine the optimum mixing volume ratio of the precursors, different samples with varying mixing volume ratios were prepared keeping other parameters constant (Table 1). The mixing volume ratio of nano composite exchangers (2:1:2) in sodium molybdate dehydrate, sodium tungstate dehydrates, and titanium isopropoxide, respectively, resulted in stable and better yield of precipitate with relatively higher IEC (1.64 meq/g) and was selected as an optimum mixing volume ratio for the entire synthesis work.

4.3. Synthesis of Cellulose Acetate Titanium (IV) Tungstomolybdate Nano Composite

Cellulose acetate Titanium (IV) tungstomolybdate nanocomposite was synthesized under varying condition by sol-gel mixing of inorganic precipitate titanium (IV) tungstomolybdate and cellulose acetate gel. Cellulose acetate is a commercially available white crystalline powder, and titanium (IV) tungstomolybdate is a light-white precipitate. The final product obtained cellulose acetate titanium (IV) tungstomolybdate, after changed to H^+ form, dried and grained was found to be light yellow powder. The physical appearance of the material resembles more the organic resin cellulose acetate polymer with inorganic moiety titanium (IV) tungstomolybdate.

4.4. Characterization and Analytical Application of the Material

4.4.1. Ion exchange capacity

Table 1. Condition of synthesis of different samples of Titanium (IV) tungstomolybdate and cellulose acetate Titanium (IV) tungstomolybdate nanocomposite exchanger.

Sample No	Mixing Volume ratio						
	$Na_2WO_4.2H_2O$ (M)	$Na_2MO_4.2H_2O$ (M)	Isopropoxide (ml)	Cellulose acetate (g)	P^H	Yield (g)	IEC (meq/g)
BM-1	2	2	3	-	1	2.54	0.26±0.02
BM-2	2	1	2	-	1	2.01	0.42±0.06
BM-3	2	2	1	-	1	2.60	0.58±0.03
BM-4	1	1	1	-	1	0.87	0.73±0.09
BM-5	2	2	1	-	1	1.33	0.83±0.06
BM-6	1	1	4	-	1	1.84	0.96±0.02
BM-7	3	1	2	-	1	1.25	1.02±0.05
BM-8	1	2	2	-	1	1.29	1.09±0.23
BM-9	1	2	1	2.0	1	1.78	1.26±0.07
BM-10	1	1	3	1.5	1	2.56	1.38±0.01
BM-11	1	2	3	1.0	1	2.98	1.41±0.49
BM-12	3	2	2	0.5	1	3.27	1.56±0.09
BM-13	1	3	2	0.5	1	4.44	1.62±0.01
BM-14	1	2	2	0.5	1	5.91	1.64±0.02

Where BM = sample code, from BM - 1 up to BM - 8 is inorganic, from BM - 9 to BM-14 is nanocomposite.

Ion exchange capacity for sodium ion was a general parameter used as a measure for the ion exchange capacity of cation exchanger materials. The sodium ion exchange capacities of the newly synthesized composite cation exchange material are presented in Table 1. Among the as-synthesized samples BM-14 possessed relatively good yield (5.91g) and better ion exchange capacity 1.64 meq/g and was selected for further studies.

The composite cation-exchange material possessed a better Na^+ ion-exchange capacity (1.64 meq /g) as compared to inorganic counterpart, Titanium (IV) tungstomlybdate (1.09 meq/g). Cellulose acetate Titanium (IV) tungstomlybdate (BM-14) was found to exhibit comparable ion exchange capacity with composite exchangers where the organic moiety is cellulose acetate. However, better exchange capacity is also observed by composite exchangers where the organic counterpart is cellulose acetate. In general, the as-synthesized exchanger is considered to exhibit moderate exchange capacity.

Table 2. Sodium ion ($Na^{+)}$ exchange capacity in mill equivalent per gram of different composite cation exchanger materials.

No	**Exchange Material**	**Na^+ IEC(meq/g)**	**Reference**
1.	Cellulose acetate -Sn (IV) phosphate	1.48	Gupta *et al*., 2013
2.	Cellulose acetate Sn -(IV) molybdate	1.56	Gupta *et al*., 2014
3.	Cellulose acetate Zr (IV) molydophosphate	1.96	Nabi and Naushad, 2008
4.	Cellulose acetate Zr-(IV) phosphate	1.40	Gupta *et al*., 2013
5.	Poly ortho-ansidne-Sn -(IV) tungstate	2.25	Khan *et al.,* 2011
6.	Polyaniline Sn-(IV) molydophosphate	1.79	Bamlku *et al*., 2017
7	Polyaniline Sn-(IV) tungstomolybdate	1.77	Bushra *et al*., 2015
8.	Cellulose acetate Ti (IV) tungstomolybdate	1.64	Present work

Ion-exchange capacity of the cellulose acetate Titanium (IV) tungstomolybdate (BM-14) for alkali and alkaline earth metal ions are depicted in Table 3**.** As can be seen in Table 3, the affinity sequence for alkali metal ions was $K^+ > Na^+$ and for alkaline earth metal ions was $Ba^{2+} > Ca^{2+} > Mg^{2+}$, This sequence is in accordance with the hydrated ionic radii. The ion-exchange capacity should increase with decreasing hydrated radii. The ions with large ionic radii have smaller hydrated radii and easily enter the pores of exchanger resulting in higher adsorption (Bamlaku *et al*., 2017).

Table 3. Ion-exchange capacity of cellulose acetate Titanium (IV) tungstomolybdate for selected metal ions

Metal Ions	Salt concentration	Ionic radii (Å)	Hydrated ionic radii (Å)	IEC (meq/g)
Na^+	1M	0.97	7.90	1.64
K^+	1M	1.33	5.30	1.83
Mg^{2+}	1M	0.78	10.80	0.98
Ca^{2+}	1M	1.06	9.6	1.02
Ba^{2+}	1M	1.42	8.80	1.12

4.4.2. pH Titration Curve

The pH-titration curves obtained under equilibrium conditions for NaOH-NaCl and KOH-KCl systems is shown in Figure.2. The titration curve showed two inflection points. This indicates that cellulose acetate titanium (IV) tungstomolybdate has bi functional nature. (Appendix Table. 1) indicates that the synthesized nanocomposite appears to be strong cation exchanger as indicated by a low pH (~2.25) of the solution when no OH^- ion was added. As the volume of NaOH added to the system is increased, more OH ions are consumed suggesting in the increase of the rate of ion exchange in basic medium due to the removal of H^+ ions from the external solution, the rate of H^+–Na^+ exchange was faster than H^+–K^+ exchangers. This might be due to the displacing capacity of the metal towards H^+. As compared to K^+, Na^+ is at the bottom of the activity series, so that the ability of Na^+ to displace the H^+ is lower than K^+ i.e the pH of the solution increase since the hydrogen is kept with Na^+ and what is remaining is the $OH.^-$

The pH titration in the presence of cellulose acetate Titanium (IV) tungstomolybdate was performed for NaCl-NaOH and KCl-KOH system. The pH titration curves show that pH increases when NaOH and KOH were 5-15-mmol per 0.2 g of composite cation exchange material and relatively very slow steep increase when hydroxide were added 20-35 mmol per 0.2 g of the composite material. The material is an acid cation exchanger because the pH titration curves usually showed a step edge at 35 mmol for the same mass of the material that is the –H functional group on the hybrid cation exchanger which were depleted and replaced with Na^+ and K^+ at these points.

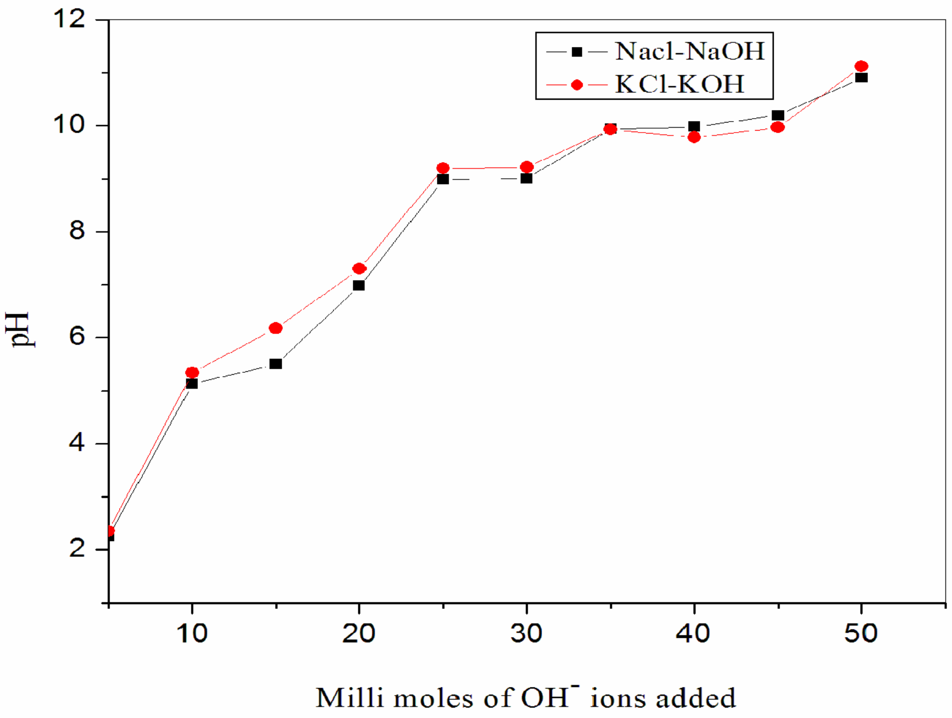


Figure 2. pH-titration curves for cellulose acetate Titanium (IV) tungstomolybdate composite

4.4.3. Chemical Stability

Chemical resistivity/stability of an ion exchanger in acids, bases and organic solvent media is important for its various applications in varied environments. The synthesized cellulose acetate titanium (IV) tungstomolybdate cation exchanger exhibit good chemical stability in some strong acids like, H_2SO_4 and also in some organic solvents. However, it shows low stability in strong base, like NaOH. The values of IEC of cellulose acetate Titanium (IV) tungstomolybdate nano composite in different solvents using titration of exchanger are given in Table 4. As synthesized nanocomposite has good chemical stability, as it was resistant to 10% ethanol and 0.1M M H_2SO_4. This chemical stability may be due to the presence of binding polymer, which can prevent the dissolution of hetero polyacid salt or leaching of any constituent elements into the solution.

The composite cation exchanger also exhibited moderate stability towards 0.1 M HCl, 0.1 M HNO_3, 0.1 M DMSO and 10% acetone. However, the material shows very high weight loss and extreme decrease in its IEC which shows high dissolution in basic medium. This may be related to the hydrolysis of exchanger beads or the high solubility of exchanger at higher pH.in 0.1M NaOH and 0.1M KOH poor stability of the nanocomposite is observed towards bases

Table 4. The chemical dissolution of Synthesized Nanocomposite under different solvents.

Chemical	**Wt. before treatment (g)**	**Wt. after treatments (g)**	**% retentions**	**IEC (meq/g) of retained exchanger**
0.1M HCl	0.2	0.136	68	0.66
0.1M H_2SO_4	0.2	0.165	82.5	1.67
0.1M HNO_3	0.2	0.138	69	0.46
0.1M NaOH	0.2	0.088	44	0.24
0.1M KOH	0.2	0.067	33.5	0.20
10% Acetone	0.2	0.154	77	0.62
10% Ethanol	0.2	0.134	89	1.41
0.1M DMSO	0.2	0.145	72.5	0.83
DMW	0.2	0.171	85.5	0.42

4.4.4. Thermal studies

The ion exchange capacity of the synthesized nanocomposite material was changed by heating in different temperatures for 1h. The mass, physical appearance and ion-exchange capacity of cellulose acetate Titanium (IV) tungstomolybdate was noted. The ion exchange capacity of the material decreased with increased heating temperature. The results revealed that the material is appreciably thermally stable since it retains about 55 % of its ion exchange capacity up to 600^0C. Effect of heating temperature on the ion exchange capacity of the material is indicated in Table 5. The thermal stability of the exchanger is comparable with previous reports such as cellulose acetate zirconium(IV) molybdophosphate that lost 58 % of its ion exchange capacity when heated to 600^0C (Nabi, and Naushad, 2008), polyaniline titanium (IV) tungstoarsenate which retained about 35 % its initial ion exchange capacity up to 600 ^{0}C (Khan and Alam, 2003). On the other hand, some literatures revealed organic-inorganic composite cation exchangers that possess high thermal stability. For example, acrylamide zirconium (IV) arsenate retains 84% of its ion-exchange capacity up to 600 ^{0}C (Nabi and Shalla, 2009). Comparison of our finding with literatures stated above implicates the moderate thermal stability of the as-synthesized exchanger.

Table 5. Thermal stability of synthesized cellulose acetate-titanium (IV) tungstomolybdate nano composite

Temp ^{0}C	WBH (g)	WAH (g)	AAH	% Retention	IEC (meq/g)
50	0.2	0.20	Gray	100	1.64
100	0.2	0.20	Gray	100	1.46
200	0.2	0.198	Gray	99	1.26
300	0.2	0.173	Light gray	86.5	1.02
400	0.2	0.16	Light gray	80	0.83
500	0.2	0.13	Deep gray	65	0.41
600	0.2	0.11	Deep gray	55	0.24

WBH = weight before heating,WAH = weght after heating, LIW = loss of weght, AAH = appreance of colur after heating.

4.5. Distribution Studies of Cellulose Acetate Titanium (IV) tungstomolybdate Nanocomposite

The distribution coefficient is the measure of the affinity of the cation exchanger towards different metal ions. Hence, the ion-exchange properties of the synthesized cation exchanger were studied by measuring the distribution coefficients (K_d) of common metal ions using column experiments in different solvent systems (Table 6). The Kd values of the metal ions were studied as a function of type and concentration of electrolyte solution and the results are presented in (Table 6). Measurement of distribution coefficient (Kd) of metal ions over a wide range of condition is a good way to avoid choosing eluting conditions for column separations by a strictly trial and error method. Although this distribution coefficient is measured on a batch basis, it can be used to predict elution behavior of metal ions eluted from an ion exchange column. To separate two substances, conditions should be selected such that the distribution coefficient of one of them is low so that its elution from the column will be rapid, while the distribution coefficient of the other substance under the same conditions should be as large as possible so that this substance will be tightly held by the resin (Shaha *et al.,* 2008).

In this work the distribution coefficient (Kd) values in different solvent systems were evaluated for eight metal ions towards cellulose acetate titanium (IV) tungstomolybdate by the batch equilibration method. The Kd values of the metal ions were studied as a function of type and concentration of electrolyte solution and the results are presented in Table 6. Effect of different concentrations of electrolyte on metal ion uptake by the synthesized cation exchange material was studied. In general, the Kd values are lower in high concentration of electrolyte and vice versa. It was observed that Kd values decreases with increase in the concentration of all acids. This may be due to slower release of H^+ ions from the exchange in strongly acidic medium so less adsorption of metal ions take place by the exchanger. Further, the Kd values in strong electrolyte media are lower as compared to weak electrolyte media as well as aqueous medium. This may be attributed to high competition amongst ions for exchange in strong electrolyte media. Kd values are higher for all metal ions in DMW than in electrolyte media. Smaller the size of the cation, greater is the tendency to be hydrated and greater the hydrated ionic radii. Larger ions being less hydrated, less energy is utilized for dehydration of the metal ions to occupy a site on the exchanger, which plays a prominent role in determining the selectivity of metal ions (Abou Mesalam, 2003).

The promising feature of the synthesized composite material is its selectivity for Cr(III) (Kd= 6405 mLg-1) and Pb(II) (Kd= 5098 mLg-1) ions, which are the most toxic and polluting metal ions in the environment. The high selectivity of Pb(II) as compared with other metal ions is also observed in other tetravalent metal acid (TMA) salts based composites, vis. polyaniline tin(IV) molydophosphate (8509), (Bamlku *et al*., 2017), Poly(methyl methacrylate) zirconium(IV) phosphate (5500) (Siddiqui *et al*., 2006), acrylamide zirconium(IV) arsenate retains (650) (Nabi and Shalla, 2009) and Poly-o-anisidine tin(IV) arsenophosphate (400) (Khan *et al*., 2009), values in parenthesis are distribution coefficients (*Kd)* of the respective ion exchange materials in mLg^{-1}. The high affinity of Cr(III) and Pb(II) towards cellulose acetate titanium(IV) tungstomolybdate in the present study suggests its possibility of separating these ions from other pollutants.

Table 6. Distribution coefficients (Kd) of different metal ions on cellulose acetate Titanium (IV) Tungstomlybdate in different solvent systems.

Metal ions	DMW	0.01M H_2SO_4	0.1M H_2SO_4	1M H_2SO_4	0.01M HCl	0.1M HCl	1M HCl	0.01M Formic acid	0.1M Formic acid	1M Formic acid
Cd(II)	766^{g}	627^{f}	544^{f}	456^{e}	361^{f}	363^{g}	301^{e}	477^{g}	420^{f}	226^{e}
Fe(II)	1804^{d}	1750^{c}	1342^{c}	1062^{b}	1765^{c}	1336^{c}	1065^{c}	1230^{b}	1020^{c}	963^{b}
Ni(II)	2402^{c}	855^{d}	728^{d}	476^{d}	976^{d}	584^{d}	321^{d}	963^{d}	722^{d}	584^{c}
Cr(III)	6405^{a}	5071^{a}	3803^{a}	3030^{a}	4074^{a}	2940^{a}	1995^{a}	3013^{a}	2027^{a}	959^{b}
Cu(II)	835^{e}	742^{e}	481^{g}	395^{f}	508^{fe}	432^{e}	321^{d}	664^{e}	548^{e}	433^{d}
Pb(II)	5085^{b}	5006^{b}	2848^{b}	1161^{b}	2994^{a}	1970^{b}	1995^{a}	2428^{b}	1765^{b}	1236^{a}
Co(II)	643^{h}	512^{h}	473^{g}	377^{g}	380^{fg}	255^{g}	144^{g}	516^{f}	405^{g}	222^{e}
Zn(II)	782^{f}	602^{g}	586^{e}	466^{ed}	545^{e}	434^{e}	264^{f}	483^{g}	339^{h}	197^{f}

Note: The values are the average of three replicate measurements.

a, b, c, d, e f, g, h, i, j : means values in the same row with the same letter are not significantly different at $P < 0.05$.

4.6. Separation of Metals Ions in Binary Mixtures

The separation capability of the material has been demonstrated by undertaking a number of binary separations of some important metal ions. Obviously, to achieve more clear separation of metal ions, large ΔKd values should be selected on the same experimental conditions. The sequential elution of ions through column depends upon the metal–ligand stability. The weakly retained metal ions eluted first and strongly retained at last (Nabi, and Naushad, 2008). The study of the distribution behavior of metal ions in aqueous as well as in various electrolyte media gives an indication of the possible binary metal ions separations as well as the eluents that could be used for separation. Kd values suggest the possibilities for many important binary separations. Based on separation factor α, binary separations have been carried out for four sets of metal ions: Cr(II)-Co(II), Cr(III)-Cd(II), Pb(II)-Co(II) and Pb(II)-Cd(II). The separation factors are guiding measures for separations. The details of these separation studies are presented in Table 7.

Table 6. Binary separation of metal ions achieved on synthesized nano composite in a column

Separation achieved	Separation factor (α)	Eluent used	Amount of metal ion used in (mg)		Percent of Recovery (%)
			Loaded	*Found*	
Cr(III)-Co(II)	9.99	1M FA Cr(III)	3.43	3.15	90.25
		1M HCl Co(II)	18.1	16.8	92.8
Cr(III)-Cd(II)	8.38	1M FA Cr(III)	20.11	18.96	94.28
		1M FA Cd(III)	5.24	4.69	89.5
Pb(II)-Co(II)	7.95	1M H_2SO_4 Pb(II)	7.56	6.18	81.7
		1M HCl Co(II)	4.91	3.85	78.4
Pb(II)-Cd(II)	6.67	1M H_2SO_4 Pb(II)	14.56	12.33	84.6
		1M FA Cd(III)	4.24	4.11	96.9

Note: $\alpha = Kd1/Kd2$, where $Kd1$ and $Kd2$ are Kd values of metal 1 and metal 2 in aqueous media.
% Recovery = (concentration of metal ion eluted/concentration of metal ion loaded) ×100.

To elute Cr(III) and Pb(II), 1M formic acid and 1M H_2SO_4 respectively was preferably used. This is due to the fact that low Kd values of these metals in1M formic acid and 1M H_2SO_4 enables quantitative elution. While for Cd(II) ,1M of Formic acid was used in Pb(II)- Cd(II) system and1M H_2SO_4 in Pd(II)- Cd(II) system, 1M HCl was employed to elute Co(II) from Cr(III)- Co(II) system and 1M H_2SO_4 was used to elute it from Pb(II)- Co(II) mixture. All selections of solvents were done based on the Kd values of both metal ions in the solvent. Cellulose acetate titanium (IV) tungstomolybdate exhibits a78.4%- 96.9% separation efficiency for these metal ions.

4.7. Physical Characterization of the Nanocomposite Ion Exchanger

4.7.1. FTIR analysis

The FTIR spectra of the synthesized cation exchanger Ti(IV) tungstomolybdate are presented in Figure 3. A broad band in the region 3600-2800 cm-1 is due to the O-H stretching vibration of the water bonded to TiO_2 (Bezabih *et al.,* 2016). A sharp peak around 1634 cm^{-1} corresponds to the deformation/bending vibration of water molecules (H-O-H). A band at around 1388cm-1 is also described to the presence of water bonded with TiO*2*. Finally, from the IR analysis it can be deduced that bands at around 906 $cm^{-1}$and 609 cm^{-1} and may be due to the presence of Ti-O, W-O and Mo-O stretching vibration mode, respectively (Bezabih *et al.,* 2016)

The FT-IR spectra of the synthesized nanocomposite exhibits the following absorption peaks. A strong and broad peak at 3352 cm^{-1} is attributed to –OH bond stretching vibration of water molecule, the peak at 2929 cm^{-1} is could be due to C−H stretch modes of the substituent methyl group. A peak at 1628 cm^{-1} may be due to deformation vibration of free water molecule, the absorption band around at 1735 cm^{-1} may be assigned to the C=O stretching of ester group in cellulose acetate ,the peak depicted at 1384 cm^{-1} may be due to -CH bands (Nabi *et al.,* 2007). A broad peak at around 820 cm^{-1} is due to the presence of molydate group and an assembly of sharp peaks in the region 500–550 cm^{-1} is due to the superposition of metal–oxygen stretching vibrations which shows the binding of inorganic precipitate with organic polymer and formation of ‘organic–inorganic’ hybrid (Nabi and Naushad, 2008). An assembly of bands in the region 400–800 cm^{-1} was due to the metal–oxygen stretching vibration.

Cellulose acetate spectrum shows a band at 1384 cm^{-1} can be assigned to stretching vibration of carbonyl group of cellulose acetate (Siddiqui & Khan, 2007; Nabi and Naushad, 2008). The peak ~964 cm^{-1} may be usually assigned to an out of plane bending vibration of C-H, bond of cellulose acetate (Khan and Baig, 2013). Also at 1752 cm^{-1} which are indicated as ester group, and a peak at 1035 cm^{-1} indicating the presence of acetyl =CO. The presence of acetyl C-O indicates that the OH group in cellulose molecules has been substitute by =CO group producing the cellulose acetate and the peak range from 906cm^{-1} -604 cm^{-1} for the metal-oxygen bond and sharp peak at 1638 cm-^{1}corresspondes to the deformation vibration of free water molecule in the organic polymer (Candido *et al.*, 2017).

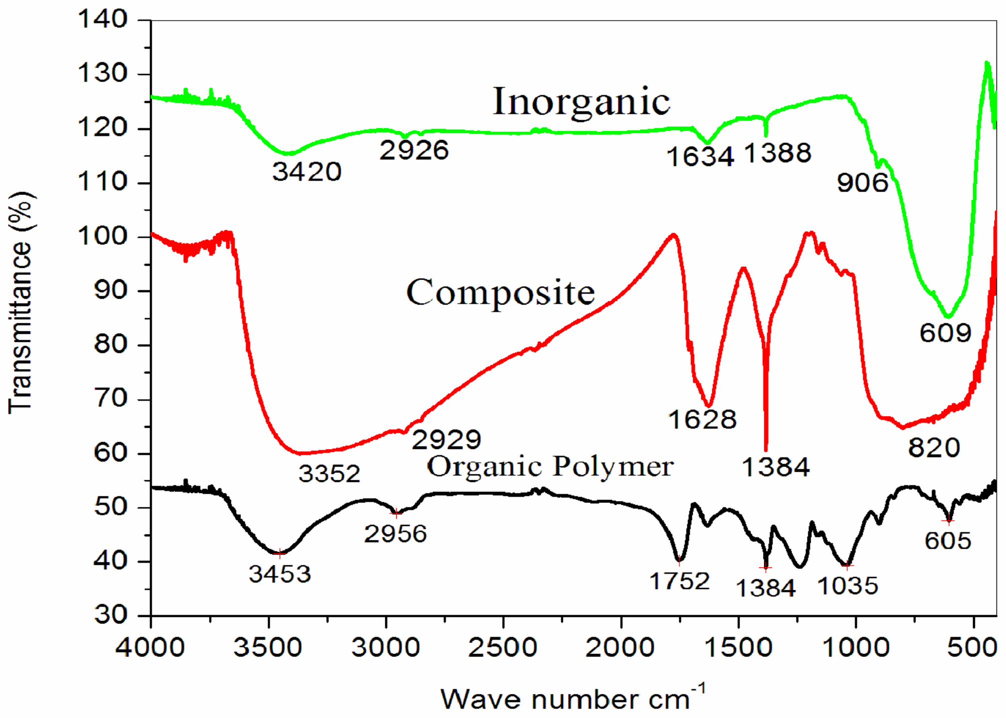


Figure 3. FTIR spectra of Titanium (IV) tungstomolybdate (Top), composite (Middle) and cellulose acetate (Bottom) exchangers.

4.7.2. XRD analysis

The XRD studies were conducted on the organic polymers (cellulose acetate), and accordingly, diffraction peaks observed at scattering angle 2θ of the data are illustrated in Figure.4. The XRD diffractogram showed peaks at 2θ equals to 17.05^{o}, 18.22°,18.87^{o} representing a typical cellulose acetate having semi crystalline nature (Nabi *et al*., 2007). The amorphous nature was observed in the powder XRD of Titanium (IV) tungstomolybdate and diffraction peaks belong to anatase phase of TiO_2. However, the presence of some sharp intensity peaks at 2θ values 23.24^{o} and 24.33^{o} indicates the formation of some crystal at very small scale up on formation of nanocomposite structure (Bamlaku *et al.,* 2016). The X-ray diffraction pattern of nano composite showed a few weak intensity peaks on a broad back ground suggesting the semi crystalline or amorphous nature of the composite. The strong peaks at 2θ values 25.71^{o} and 26.65° indicates the formation of some crystal at very small scale up on composite formation.

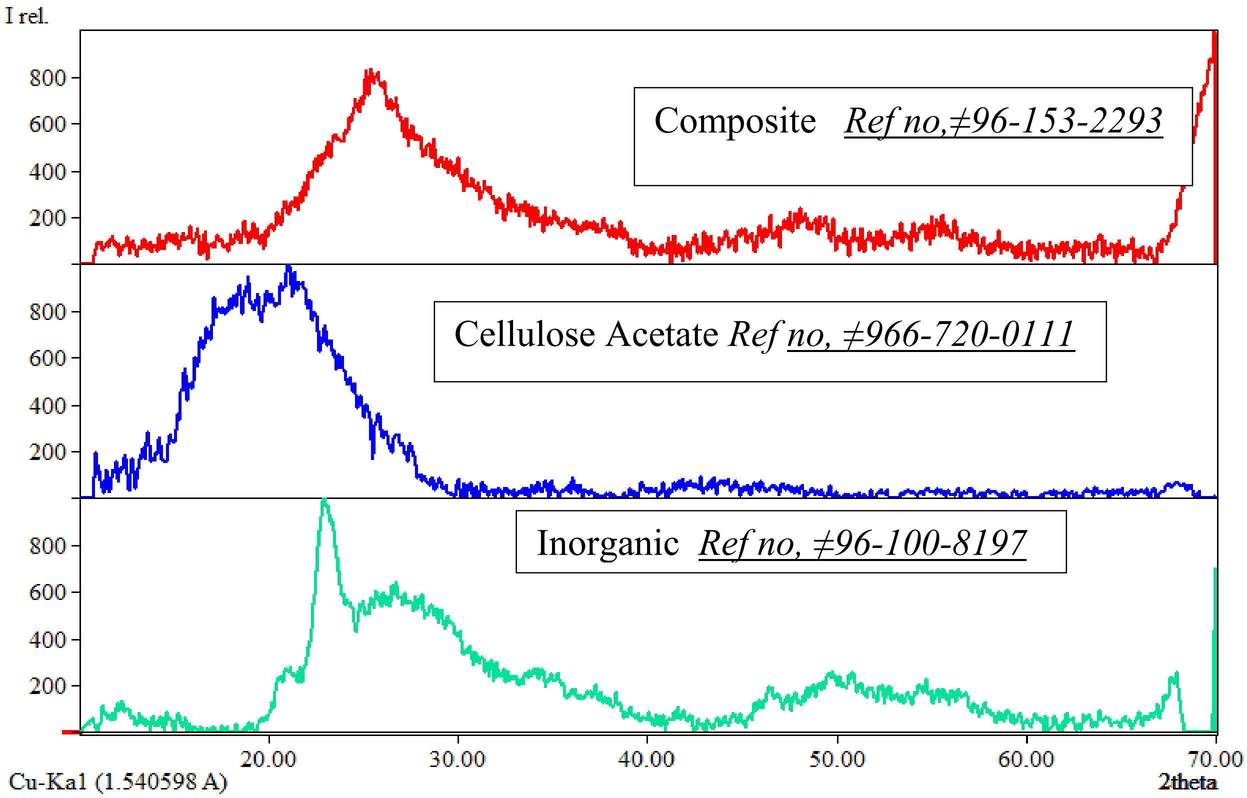


Figure 4. XRD Analysis of Organic Polymer, Inorganic and Nanocomposite.

The average crystallite size of each of the cellulose acetate (organic polymer), titanium (IV) tungstomolybdate, and cellulose acetate titanium(IV) tungstomolybdate nano composite was calculated using the Debye-Scherrer's formula;

$$D(nm)= \frac{K\lambda}{\beta \cos \theta}$$

Where, D= crystallite size in nm, K = the shape factor constant taken as 0.9; β is the full width at half maximum (FWHM) in radians and λ is the wave length of the X-ray (0.15406 nm) for Cu target Kα1, whereas $cos\theta$ is radiation and is the Bragg's angle.

Based on the above approach, we estimated the average crystalline size of as-synthesized cation exchangers. And all the as-synthesized materials were found to be in the nano range that means (organic polymer (24.9nm) titanium(IV) tungstomolybdate (38.8nm and composite was found to be ,to 55.41nm).

4.7.3. Thermogravimetric Analysis (TGA)

The TGA curve of cellulose acetate titanium (IV) tungstomolybdate nanocomposites is presented in Figure 10. As can be seen in the figure, the sample exhibited three stages of weight losses. The first step occurd between 25^{o}C- 100°C, shows a continuous weight loss of mass may be due to loss external water molecule present. The second step appeared in the temperature range of 100-150°C may be accounted for the evaporation of internal water molecules as the result of condensation of –OH groups from metal oxide (Nabi *et al* ., 2007). The third step appeared in the temperature range of 150^{0}C-400^{0}C may be due to complete decomposition of the organic polymer part of the material. After these range on wards, a smooth horizontal section shows the complete formation of oxide form of the material.

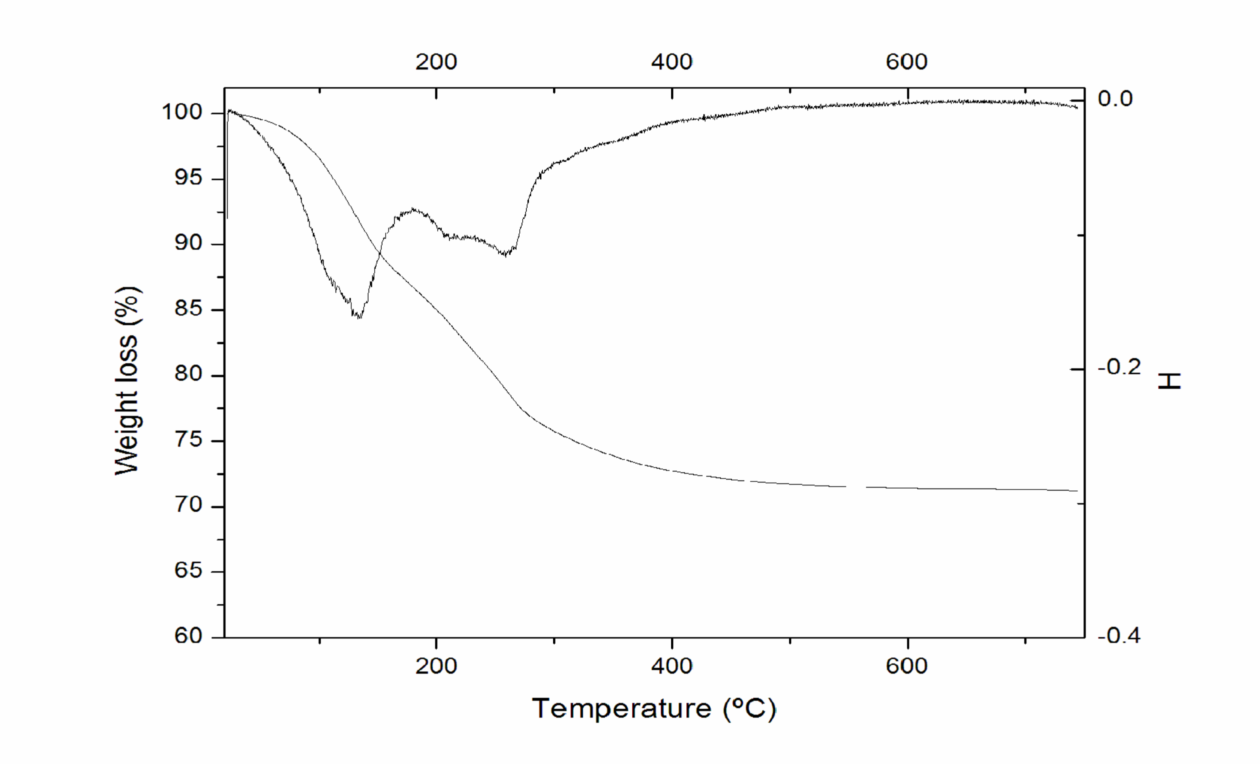


Figure 5. TGA curves of cellulose acetate Titanium (IV) tungstomolybdate nanocomposite

4.7.4. Surface area

Specific surface areas of the nanocomposites were determined using Brunauer–Emmett– Teller (BET) methods. The average specific surface area of cellulose acetate, Titanium (IV) tungstomolybdate and the nanocomposite cation exchanger cellulose acetate Titanium (IV) tungstomolybdate is indicated in (Table 9). Nanomaterials with high surface activity, high specific surface area and high surface energy, show promising potential in the preparation of high performance ion exchange and thus are widely used as ion exchanger. The nanocomposite shows highest surface area compared with organic polymer and Titanium (IV) tungstomolybdate. The difference in their surface area was due to the synergetic effect among the components such as titanium, molybdate and tungstate in the composite system (Li *et al.*, 2008). The increase in the surface area was significant; hence, the larger surface area of nanocomposite will benefit for the spatial separation of redox sites in the crystals which can enhance electron-transfer and ion exchange properties of the nanocomposite (Yang *et al.,* 2008).

Table 8. The calculated Surface area of the nano materials

Materials	Calculated Surface area
Cellulose acetate	3.2813 ±0.0157 m^2/g
Ti(IV) tungstomolybdate	4.66±0.032 m^2/g
Nanocomposite	51.8981±1.1625 m^2/g

4.7.5. SEM-EDX analysis

The SEM images of the organic polymer, the as-synthesized inorganic and nanocomposite exchangers with selected magnification are shown in (Figures.6-8). The SEM image of cellulose acetate presents (Figure .6) the inorganic exchanger (Figure.7) the image of inorganic and finally (Figure 8).

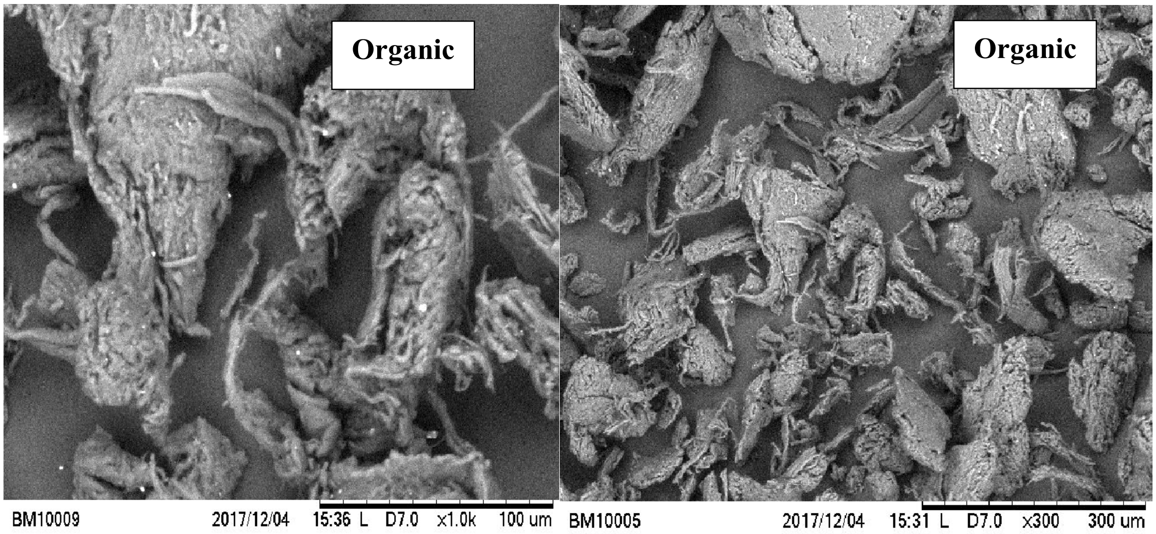


Figure 6. SEM images of cellulose acetate.

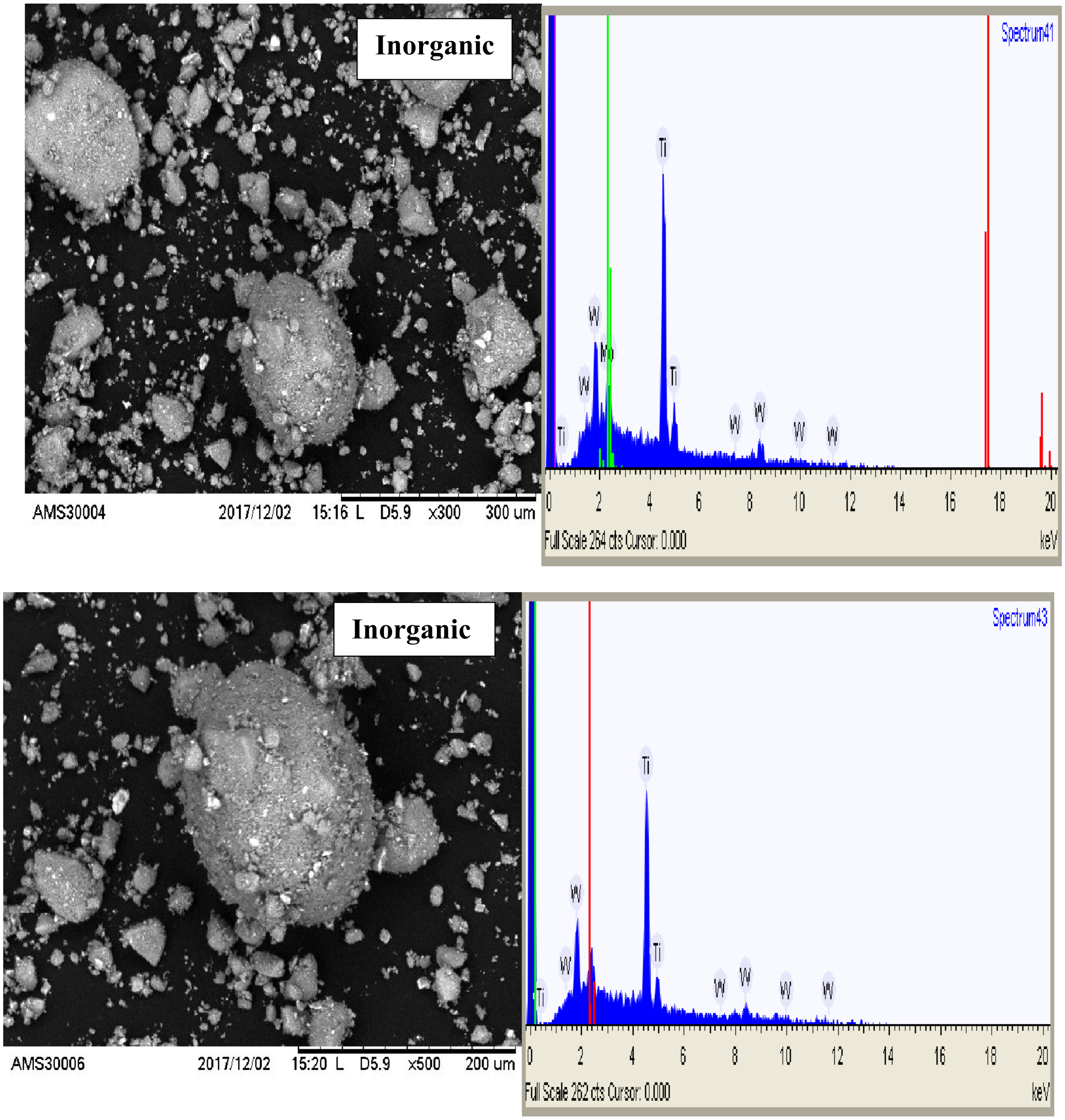


Figure 7. SEM images and EDX spectrum of titanium (IV) tungstomolybdate

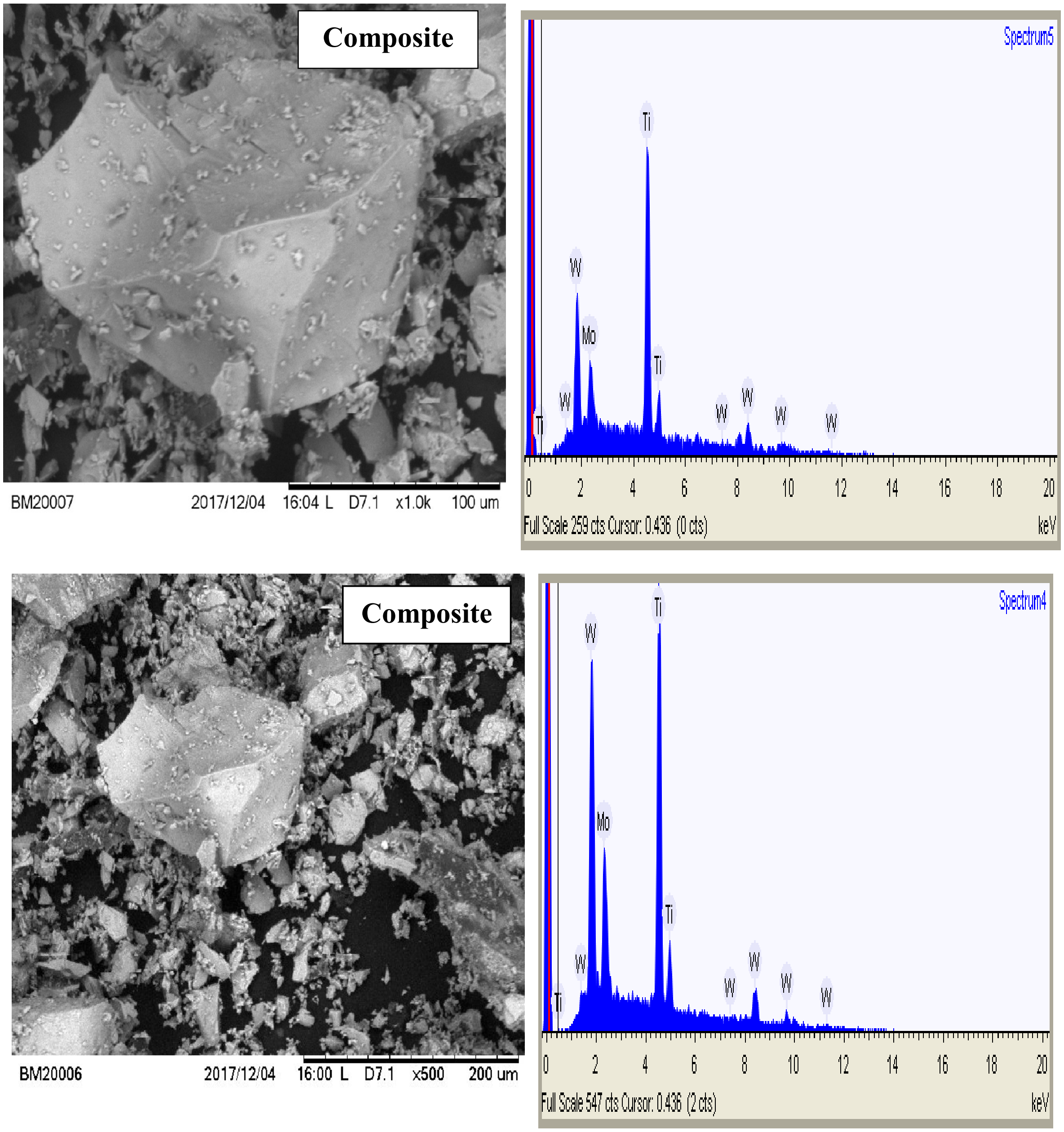


Figure 8. SEM images and EDX spectrum of cellulose acetate Titanium (IV) tungstomolybdate nanocomposite.

The energy dispersive x-ray analysis was done for elemental composition present in the as synthesized inorganic and composite nano powders. The presence of Ti, Mo and W is confirmed from the EDX spectra (figures7). The amount of Ti ranged from 45.0 to 62.1%, Mo from 13.8 to 18.6% and W from 24.1 to 36.3%; the average being 55%, 16% and 29% respectively(Appendix Table.3). The wider range of composition exhibited by Ti and W indicates the heterogeneity of the exchanger as a whole. The ratio Ti: Mo:W as inferred from the EDX is found to be (3:1:2). In the inorganic exchanger, the presence of Ti, Mo and W is confirmed from its EDX spectral analysis (figure 7); the amount of Ti ranged from 65.5 to74.2% , Mo from 7.2 to 11.9 % and W from 19.8 to 25.8 %, the average being 69.56 %, 9.6% and 22.7% respectively(Appendix Table.3) . Based on this information, the ratio of the three elements as inferred from the EDX is found to be (7:1:2) in Ti: Mo:W.

4.8. Antimicrobial Activities of as Synthesized of Nano Composite

In the present study, organic polymer and the composite were investigated for their respective antimicrobial potential. For this purpose, four bacterial species out of which two are Gram positive (*S. aureus and St. agalactiae*) and the remaining two are Gram negative (*E.coli and Shigella*) were selected for the antibacterial study. Similarly, for the antifungal test two fungal species (*Aspergillus niger and Fusarium oxysporum)* were used. The results of the biassay tests for the bacterial and fungal species are presented in Tables 10 and 11, respectively.

4.8.1. Antibacterial Activity

All the three tested groups of chemicals including the inorganic compound, organic polymer and the composite were found to be active against *St. aureus*, *St. agalactiae*, *E. coil* and *Shigella* at concentrations of 10 and 20 μL. The results of the zones of inhibition for the three chemical compounds against the tested bacterial species are presented in Table 10. The antibacterial assay figures are presented in the (Appendix figure.2).

Table 7. Zone of bacterial growth inhibition (mm) for inorganic, organic polymer and nano composite compound.

Sample	Dose (µl)	Types of bacteria with mean inhibition diameter (mm)			
		Gram (+) bacteria		Gram (-) bacteria	
		S. aureus	*St.agalactiae*	*E.coli*	*Shigella*
Inorganic	10	21±2.83	4.5±0.244	19.8±0.48	18.8±0.77
	20	29±1.63	24.2±1.79	26.7±1.13	23±1.63
Organic	10	12.6±0.58	-	4.3±0.36	7±0.16
	20	17.9±0.21	18.3±0.40	14.1±0.23	14.1±0.29
Composite	10	12.3±0.081	-	3.8±0.16	9.2±0.20
	20	16.8±0.16	17.5±0.32	14.8±0.09	14.6±0.43
Chloramphenicol	10	32±0.21	38±0.081	26.3±0.08	31.7±0.16
	20	35.7±0.081	37.7±0.12	34±0.04	38±0.09

Value represents, ZI = Zone of inhibition in (mm) mean of three replications ±SD; (-) stands for no inhibition.

4.8.2. Anti-Fungal Activities

The antifungal activities of the inorganic, organic polymer and the composite were also investigated against two fungal species (*Aspergillus niger and Fusarium oxysporum*). During this bioassay, a positive result was observed and the results are presented in table 11 and the figures corresponding for this bioassay are shown in (Appendix figure 3).

Table 8. Zone of fungal growth inhibition (mm) for inorganic, organic polymer and nano composite compound.

Sample	Dose (μL)	Types of fungus with mean inhibition diameter (mm)	
		Aspergillus niger	*Fusarium oxysporum*
Inorganic	10	-	-
	20	7.8±0.081	9.7±0.047
Organic	10	-	-
	20	3±0.047	1.75±0.04
Composite	10	-	-
	20	5.4±0.29	3.6±0.02
Tilt	10	-	-
	20	16.8±0.45	18.4±0.32

Value represents mean of three replication, ± SD, (-) Stands for no inhibition

5. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1. Summary and Conclusions

A new composite cation exchanger, cellulose acetate titanium (IV) tungstomolybdate, has been synthesized which has high thermal stability unlike the organic resins which have one of the severest limitation of their poor thermal stability. The material was successfully used for the separation of metal ions quantitatively from synthetic aqueous solution. The sodium ion exchange capacity of the material was found to be 1.64 meq/g. From the pH titration curves obtained under equilibrium conditions for NaOH- NaCl and KOH KCl systems; it was observed that cellulose acetate titanium (IV) tungstomolybdate has bi functional nature and strong acidic cation exchanger.

The thermal study results revealed that the material is appreciably thermally stable in terms of ion exchange capacity since it retains about 55% of its ion exchange capacity up to 600°C. The selectivity that cellulose acetate titanium (IV) tungstomolybdate of towards different heavy metal ion in demineralized water and other electrolytic solvents with varying concentrations was evaluated using distribution coefficients of the metal ions and it was found that the material is highly selective for Cr (III) and Pb (II) which are important heavy metal. Its analytical utility for the separation of these metal ions from synthetic binary mixtures was assessed based on the separation factor (α) and quantitative separation of metal ions with reasonably high efficiency (68.03%–98.98%) was achieved using the as synthesized composite exchanger.

Antimicrobial activity tests showed some antimicrobial potency of the synthesized nano composite even though it was very lower as compared to standard anti-biotic organic polymer compound was active against the four microbial pathogens tested. The synthesized inorganic compound showed the highest degree of antibacterial activity against *Staphylococcus aureus*, *Streptococcus agalactiae*, *Escherichia coli and Shigella flexneri* as compared to the organic and nano composite. Additionally the synthesized inorganic compound exhibited higher activity towards both fungal (*A. niger and F.oxysporium*) than organic polymer and nano composite. From this study, it can be concluded that this inorganic compound is very active than organic polymer and synthesized nano composite. But antimicrobials activities were comparatively lower than that of the standard drug used in the study.

5.2. Recommendations

In this study, the synthesis, characterization and evaluation of cellulose acetate titanium (IV) tungstomolybdate nano composite as an ion exchanger for selected metal ions under taken. The study showed that the exchanger has the promising features regarding its synthesis, characterization as well as cation exchange and other properties for which the exchanger is evaluated. Therefore, the following recommendations are made for further investigations.

- To investigate further by other characterization techniques Such as TEM and X-ray Fluorescence
- To improve thermal stability, chemical resistivity, distribution coefficient *etc*… through devising new preparation methods or coupling with organic substances.
- To try other synthetic approaches to fabricate with ternary system to get better ion exchange capacity.
- Preparation of ion selective electrode from this material would be important for analytical application of the electrode for real sample analysis.
- To involve nano composite parameters such as temperature and pH among many other important factors that should be given equal attention by further research works to lift the efficiency even better.
- To apply the synthesized nanocomposite for different applications including photocatalysis and environmental remediation.

6. REFERENCES

Abd El- Latif, M.M. and M.F. El kady, 2008. Developing & characterization of a new zirconium zirconium vanadate ion exchanger and its novel organic inorganic hybrid of Applied Sciences Research. 4(1): 1-13.

Abd El-Latif, M.M. and M.F. El kady, 2011.Synthesis, characterization and evaluation of Nano-zirconium vanadate ion exchanger by using three different techniques. Material Research bullet in. 46: 105-118.

Abdel-Galil, E.A.M. 2010. Chemical studies and sorption behavior of some hazardous metal ions on polyacrylamide stannic(IV)molybdophosphate as 'organic – inorganic 'composite cation exchanger: Thesis submitted to Ain Shams University, Faculty of Science

Abou Mesalam, M.M., 2003. Sorption kinetics of copper, zinc, cadmium and nickel ions on synthesized silico antimonate ion exchanger.Colloids and Surfaces A:*Physicochemical Enignering Aspects,* 225: 85 – 94.

Akram, M., Kanwal, Z., Rauf, A., Sabri, N., Riaz, S. and Naseem, S. 2016. Size and shapedependent antibacterial studies of silver nanoparticles synthesized by wet chemical routes.*Nanomaterials*6, 74; doi: 10.3390/nano6040074.

Alamir Mihertu.2014. Synthesis, Characterization and Ion-Exchange Applications of Poly-O-Toluidine Ti(IV)Tungstomolybdate Composite Cation-Exchanger.Thesis,Haramaya University, Haramaya, Ethiopia.

Awual M. R, M. M. Hasan, M. Naushad, H. Shiwaku,T. Yaita, 2015.Peparation of new class composite adsorbent for enhanced palladium(II) detection and recovery, Sensors and Actuators B: Chemicals, 209 : 790-797.

Bamlaku Semagne,Isabel Diaz, Tesfahun Kebede, Abi M. Taddesse 2016. Synthesis, characterizat ion and analytical application of polyaniline tin(IV) molybdophosphate composite with nanocrystalline domains. *Reactive and Functional Polymers* , 98 : 17–23.

Bushra. R,.Naushad .Mu, R. Adnan, Z. A. ALOthman,M. Rafatullah, 2015.Polyaniline supported nanocomposite cation exchanger: Synthesis, characterization and applications for the efficient removal of Pb^{2+} ion from aqueous medium, *Journal of Indian Engineering Chemistry*, 21 : 1112- 1118.

Bezabih, Kelta, Abi M. Taddesse, Yadav, O.P., Isabel, D., Mayoral, A. 2017. Synthesis, characterization and evaluation of nano titanium (IV) tungstomolybdate as inorganic cation exchanger. *Journal of Environmental Chemical Engineering*, 5: 1004–1014.

Bushra. Rani, M. Naushad, Anees Ahmad,2017. Removal of pollutants using organic/inorganic composite sorbents: a review 10: 6-16.

Byrappa, K. and M. Yoshimura,2011.Handbook of hydrothermal technology:Atechnology for crystal growth and materials processing.Noyes Publications/William Andrew Publishing LLC., USA. 891p.

Candido R.G , Godoy G.G and ,Adilson R. Gonc¸ alves . 2017. Characterization and application of cellulose acetate synthesized from sugarcane bagasse.

Chand, S., Seema, Arti and C.V. Chahal, 2011.Synthesis,characterization and ion exchnge properties of a new ion exchange material: Bismuth (III) iodophosphate.*Recent Research in Science and Technology,3(6): 01-08.*

Chithra, P.G., R. Raveendran and B. Beena, 2008. Parachlorophenol anchored tin antimonate an inorgano-ion-exchanger selective towards heavy metals like Bi(III) and Cu(II). *Desalination.* 232:20-25.

Coats, A.W. and Redfern, J. P. 1963.Thermogravimetric analysis: *A Review analyst.* 88 (1053): 906-924.

Corriu, R. and. Anh, N. T 2009. Molecular chemistry of sol-gel derived nanomaterials.John Willey and Sons PLC Ltd., 202p.

David, W.O., Colin, B.H. and Thomas, F.O. 2008. Heavy metals adsorbents prepared from the modification of cellulose. *Biosource Technology*, 99: 6709-6724.

Dhanitha, M.A. and Janardanan, C. 2015. Evaluation of the degradation power of polyaniline encapsulated titanium cerium molybdate nanocomposite ion exchanger for the removal of methyl red dye from aqueous solution.*International Journal of Innovative Science, Engineering & Technology*, 2(9): 2348–796.

Dorfner, K., 1991. Ion exchangers. Walter de Gruvter, Berlin, Germany.492p.El Naggar,I.M.,A. Mowafy, Y.F. El-Aryan, and M.G. Abd El-Wahed, 2007.Sorption mechanism for Cs+, Co^{2+} and Eu^{3}+ on amorphous zirconium silicate as cation exchanger.*Journal of Solid State Ionics,*178: 741–747

Ece, 2012.Modern methods for rapid X-ray diffraction data collection from crystals of macromolecules. *Methods in Molecular biology,* 56: 87-126

Fisseha Gebrewold, 2010.Synthesis, characterization and analytical application of a new inorganic cation exchanger titanium (IV) tungstomolybdate. An Academic Thesis Submitted to the School of Graduate Studies, Department of Chemistry, and Haramaya University, Ethiopia.

Gohil,G.S.,Nagarale,R.K.,Binsu,V.V;Vinod,K.Shahi.2006.Preparation and characterization of monovalent cation selective sulfonated poly (ether ketone) and poly(ether sulfone) composite membranes. *Journal of Colloid and Interface Science*, 298: 845–853.

Gupta,V.K.,P.Singh,N.Rahman,2005.Synthesis,characterization, and analyticalapplication of zirc onium (IV) selenoiodate, a new cation exchanger.*BioAnalytical Chemistry*. 381: 41–476.

Gupta,VK, AgarwalS, Pathania D, Kothiyal NC, Sharma G, 2013. Use of pectin thorium (IV) tungstombdate nano composite for photocatalytic degradation of methylene blue. *Carbohydrate Polymers*, 95: 434– 440.

Helfferrich, F1962. Ion exchange: McGraw-Hill Series in Advanced Chemistry. New York: McGraw-Hill Book Company, Inc.322p.

Hendricks, N. R., 2005. The application of high capacity ion exchange adsorbent material synthesized from fly ash and acid mine drainage, for the removal of heavy and trace metals from secondary co-disposed process waters. Academic Thesis Presented to University of Western Cape, South Africa.287p.

Hu, E. L., D. T. Shaw, R. W. Siegel, D. M. Cox, H. Goronkin, L. Jelinski, C. C. Koch, J. Mendel and M. C. Roco, 1999. R&D status and trends in nanoparticles, nanostructured materials, and nano devices (final report). WTEC Panel on Nanostructure Science and Technology. Loyal college, Maryland, USA.

InternationalAtomic Energy Agency (IAEA),2002.Application of ion exchange processes for the treatment of radioactive waste and management of spent ion exchangers.Technical report series No. 408. Vienna, Austria.115p.

Kamat, P.V. and D.Meisel,2002.Nanoparticles in advanced oxidation processes.*Current Opinion in Colloid & Interface Science.* 7:282-287.

Karkare, M.M. Int Nano Lett ,2014. Choice of precursor not affecting the size of anatase TiO_2 nanoparticles but affecting morphology under broader view Int Nano Lett 4: 111. doi:10.(1007/s40089-014-0111-x).

Khalil M,2012.chemical studies on polyaniline titanotungstate as a new composite cation exchanger and its analytical applications for removal of cesium from aqueous solutions, A PhD Thesis Chemistry Department Faculty of Science Ain Shams University

Khan, A., M. M. Alam and F. Mohammad, 2003. New and novel organic-inorganic'type crystalline polypyrrole/polyantimonic acid composite system; preparation, characterization and analytical applications as a cation exchange material and Hg(II) ion selective membrane electrode. *Analytical Chemicals.* 504 : 253-264.

Khan, A.A. and A. Khan, 2012. Synthesis and characterization of poly-o-anisidine Sn(IV) tungstate: A new and novel 'organic–inorganic' nano-composite material and its electroanalytical applications as Hg(II) ion-selective membrane electrode. *Journal of Advanced research.* 3(3) : 269-278.

Khan, A.A. and Alam, M.M. 2003. Synthesis, characterization and analytical applications of a new and novel 'organic–inorganic' composite material as a cation exchanger and Cd(II) ion-selective membrane electrode: polyaniline Sn(IV) tungstoarsenate. *Reactive & Functional Polymers,* 55: 277–290.

Khan, A.A., Inamuddin, Alam, M. M. 2005**.** Preparation, characterization and analytical applications of a new and novel electrically conducting fibrous type polymeric–inorganic composite material: polypyrrole Th(IV) phosphate used as a cation-exchanger and Pb(II) ion-selective membrane electrode. *Materials Research Bullett in,* 40: 289–305.

Kooti, M. and L.Matturi,2011.Microwave-assisted fabrication of γ-Fe_2O_3 nanoparticles from tris (acetylacetonato) iron (III). International Nano Letter. 1(1): 38-42.

Kung, H.H., and. Ko E.I, 1996. Preparation of Oxide Catalysts and Catalyst Supports - a Review of Recent Advances. *Journal of Chemical Engineering*. 64: 203-214.

Lalena, J.N.,D.A.Cleary,E.E.Carpenter, N. F.Dean,2008. Inorganic materials synthesis and fabriction. A john wiley & sons, inc., publication, Canada. 314p.

Lenntech. Water Treatment and Air Purification (2004).Water Treatment, Published by Lenntech,Rotterdamseweg, Netherlands(www.excelwater.com/thp/filters/Water-Purification.htm).

Li, F. S., Sun, S., Jiang, Y., Xia, M., Sun, M. and Xue, B. 2008. “Photo degradation of an azo dye using immobilized nanoparticles of TiO_2 supported by natural porous mineral.” *Journal of Hazardous Materials,* 152(3):1037–1044..

Lövestam,G., H. Rauscher,G. Roebben, B. S. Klüttgen, N.Gibson, J. Putaud and H.Stamm, 2010 Considerations on a definition of nanomaterial for regulatorypurposes.EUJRC Reference Report. 40p.

Marinella, S.L., Pallo, R.M., Olinde, C.D.S., Panra, D.A., Maria, T.V.R., Guilherm, M., Maria, A., Vasconcecos, P.B. and Marcia, G.D. 2012. Antimicrobial activity of marine sponges against coagulase negative *Staphylococci* isolated from bovine mastitis. *Journal of Veterinary Microbiology*, 155: 362-368.

Mohammad Mujahid Ali Khan, Rafiuddin, Inamuddin. 2012. Electrochemical characterization and transport properties of polyvinyl chloride based carboxymethyl cellulose Ce(IV) molybdophosphate composite cation exchange membrane. *Journal of Industrial Engineering Chemistry*,18:1391–1397.

Mousavi, H. Z., Hosseynifar, A., Jahed, V. and Dehghani, S. A. M. 2010. Removal of lead from aqueous solution using waste tire rubber ash as an adsorbent. *Brazilian Journal of Chemical Engineering*, 27(01): 79 – 87.

Nabi S. A,. Bushra, R, Z.Al-Othman .A,and Mu. Naushad,2011 Synthesis, Characterization, and Analytical Applications of a New Composite Cation Exchange Material Acetonitrile Stannic(IV) Selenite: Adsorption Behavior of Toxic Metal Ions in Nonionic Surfactant Medium 46:5, 847-857, DOI: 10.1080/01496395.2010.534759 .

Nabi, S.A.and A.M. Khan, 2006.Synthesis,ion exchange properties and analytical applications of stannic silicomolybdate:Effect of temperature on distribution coefficients of metal ions.*Reactive & Functional Polymers*. 66:495–508.

Nabi, S.A. and M. Naushad,2008. Synthesis,characterization and analytical applications of a new composite cation exchanger cellulose acetate Zr(IV) molybdophosphate.Colloids and Surf aces A: *Physicochemical Enginering Aspects*. 316: 217–225.

Nabi,S.A. and A.H.Shalla, 2009.Synthesis, characterization and analytical applicationof hybrid Acrylamide zirconium(IV)arsenatea cation exchanger,effect of dielectric constant ondist ribution coefficient of metal ions.*Journal of Hazardous Materials*.163: 657–664.

Nabi,S.A.,A.H.Shalla,A.M.Khan,S.A.Ganie,2007b.Synthesis,characterization and analytical applications of titanium(IV)molybdosilicate:Acation ion exchanger *Journal of colloids and surfaces* A, 302: 241- 250.

Nabi,S.A.,M. Naushad, and Inamuddin,2007a. Synthesis and characterization of a new inorganic cationexchanger Zirconium(IV)tungstomolybdate:Analyticalapplications for mement determination in real sample and synthetic mixture.*Journal of Hazardous Materials*,142:404 –411.

Nabi,S;A.Alimuddin and A.Islam, 2009. Synthesis and characterization of a new cation exchang zirconium(IV)iodotungstate: Separation and determination of metal ion contents of synthetic mixtures, pharmaceutical preparations and standard reference materil. *Journal. of Hazardous Materials.*172(1) 202-207.

Naggar,El-I.M., Mowafy, E.A., El-Aryan,Y.F. and Abd El-Wahed, M.G. 2007. Sorption mechanism for Cs^+, $Co^{2+}$and Eu^{3+} on amorphous zirconium silicate as cation exchanger, *Journal of Industrial Chemical Engineering* 19:1973–1980

Naushad,M.;2009.Inorganic and composite ion exchange materials and their applications (Reviw *Ion Exchange Letters*.2:1-14.

Naushad. M., Z.A. ALOthman, Inamuddin, H. Javadian,2015.Removal of Pb(II) from aqueous solution using ethylene diamine tetra acetic acid-Zr(IV) iodate composite cation exchanger: Kinetics, isotherms and thermodynamic studies, *Journal of Indian Engineering Chemstry,*25 :235-41

Nwinyi, O., Chinedu, N.O.O., Ajani, O., Ikpo, Chinwe. And Ogunniran, K.O. 2009. Anti-bacterial effects of extracts of *Ocimum gratissimum* and *Piper guineense* on *Escherichia coli and Staphylococcus aureus. African Journal of Food Science.* 3(3): 077-081.

Patrone, J.B. and Stein, D.C. 2007. Effect of gonococcal lipooligosaccharide variation on human monocytic cytokine profile. *Biology Medical Central Microbiology*, 7: 1-15.

Rao, C N.R., A. Mller and A. K.Cheetham, 2004. The Chemistry of nanomaterials:synthesis, properties and applications.Volume 1.WILEYVCH Verlag GmbH & Co.KgaA, Weinheim. 741p.

Rashad, M.M., E.M. Elsayed, M.M. Moharam, R.M. Abou-Shahba, A.E. Saba, 2009. Structure and magnetic properties of NixZn1−xFe2O4 nanoparticles prepared through co-precipitation method. *Journal of Alloys and Compounds*. 486:759–767.

Rathore, B.S., Sharmaa, G., Pathaniaa, D., Gupta, V.K. 2014. Synthesis, characterization and antibacterial activity of cellulose acetate tin (IV) phosphate nanocomposite.*Carbohydrate Polymers*, 103: 221–227

Sanchez, C., B. Julian, P. Belleville and M. Popall, 2005. Applications of hybrid organic inorganic nanocomposites. *Journal of Material Chemistry* 15:3559–3592.

Sears,W.G, 1956.Determination of Specific surface area ofcolloidal silica by titration with sodium hydroxide.*Journal of Anaytical chemistry*.28(12):1981-1983.

Siddiqui, W. A. and Khan, S.A. 2007. Synthesis, characterization and ion exchange properties of new and novel organic inorganic hybrid cation exchanger: Poly(methyl methacrylatene) Zr (IV) phosphate. *Colloids and surface A*.295:193–199.

Singh, N. J. and S. N. Tandon, 1979. Zirconium arsenophosphate as an ion exchanger. *Journal of Radio analytical Chemistry.49:195-203*

Tin(IV) molybdate nanocomposite ion exchanger: binary separation of heavy metal ions and antimicrobial activity *Ionics*, 21: 2069–2078.

Topp, N.E. and Pepper, K.W. 1949. Properties of ion exchange resins in relation to their structure, part I. titration curves. *Journal of Chemical Society*, 3299p.

Valaski, R., Muchenski, F., Mello R. M. Q., Micaroni, L., Roman, S.S. and Hummelgen, I. A. 2006.Sulfonatedpolyaniline/poly(3-methylthiophene)-based photovoltaic devices. *Journal of solid state Electrochemistry,* 10(1), 24–27.

Wang, S., Forzani Erica, S. and Tao, N. 2007. Detection of Heavy Metal Ions in Water by High-Resolution Surface Plasmon Resonance Spectroscopy Combined with Anodic Stripping Voltammetry. *Analytical Chemistry*, 79: 4427-4432

Yang, X., F., Ma, K., Li, Y., Guo, J., Hu, Li, W., Huo, M. and Guo, Y. 2008. Mixed phase titania Nanocomposite codoped with metallic silver and vanadium oxide: New efficient for dye degradation. *Journal of Hazard Materials* (175): 429–438.

Yohannes, A. 2014. Biosupported Fe-Al-Mn ternary oxide nano sorbent: synthesis, characterization and lead (ii) sorption property in aqueous solution. MSc Thesis, Haramaya University, Haramaya, Ethiopia

7. APPENDIX

7.1. Appendix Table

Appendix Table 1. The NaCl-NaOH and KCl-KOH mixing volume ratio for pH titration of synthesized nanocomposite.

Sample no	Volume of 0.1M NaCl (mL)	Volume of 0.1M NaCl (mL)	P^H	Volume of 0.1M KCl (mL)	Volume of 0.1M KOH (mL)	pH
BM-1	0	50	10.9	0	50	11.12
BM-2	5	45	10.2	5	45	9.97
BM-3	10	40	9.98	10	40	9.78
BM-4	15	35	9.94	15	35	9.93
BM-5	20	30	9.01	20	30	9.22
BM-6	25	25	8.98	25	25	9.20
BM-7	30	20	6.98	30	20	7.30
BM-8	35	15	5.50	35	15	6.18
BM-9	40	10	5.13	40	10	5.34
BM-10	45	5	2.25	45	5	2.35

Where BM = sample code

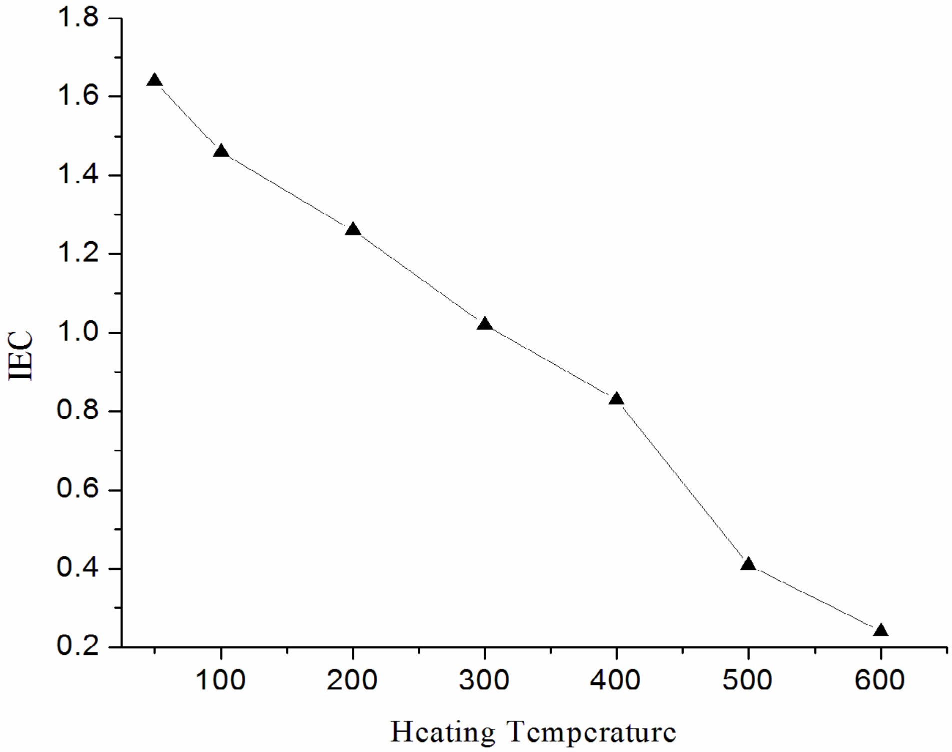
Appendix Table 2. The chemical dissolution of CATTM under different solvents

Chemical	Wt. before treatment (g)	Wt. after treatments (g)	% retentions	IEC (meq/g)of retained exchanger
0.1M HCl	0.2	0.136	68	0.66
0.1M H_2SO_4	0.2	0.165	82.5	1.67
0.1M HNO_3	0.2	0.138	69	0.46
0.1M NaOH	0.2	0.088	44	0.24
0.1M KOH	0.2	0.067	33.5	0.20
10% Acetone	0.2	0.154	77	0.62
10% Ethanol	0.2	0.134	89	1.41
0.1M DMSO	0.2	0.145	72.5	0.83
DMW	0.2	0.171	85.5	0.42

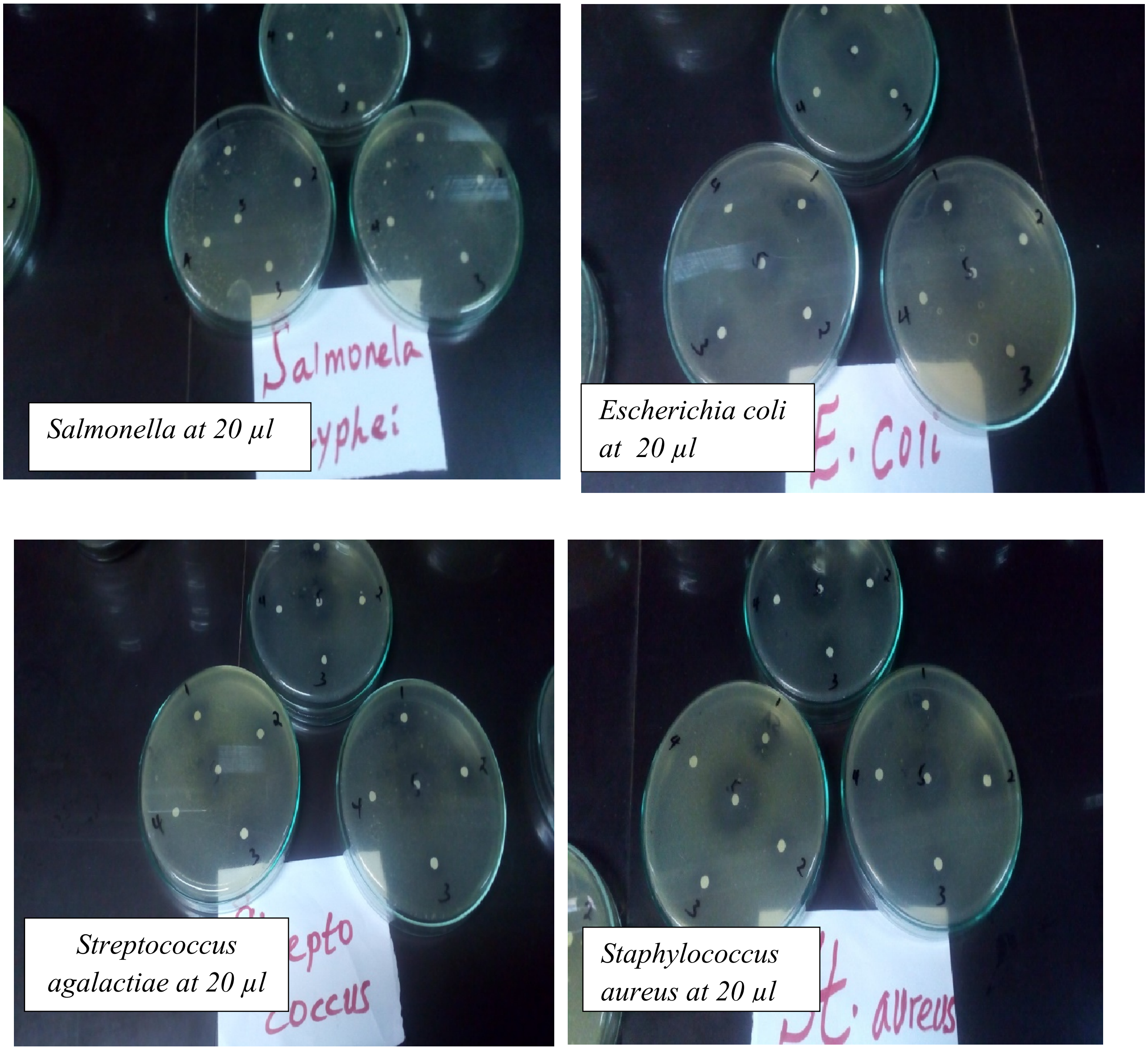
Appendix Table 3. Present composition EDX characterization of sample

Characterized material by SEM and EDX	Titanium	Molybdenum	Tungsten
Organic polymer	-	-	-
Inorganic	53.4-61.9%	12.4-14.1%	20.5-27.8%
Nano composite	45.0-62.1%	13.8-18.6%	24.1-36.3%

7.2. Appendix Figure



Appendix Figure 1. Effect of temperature on IEC of cellulose acetate titanium (IV) tungstomolybdate.



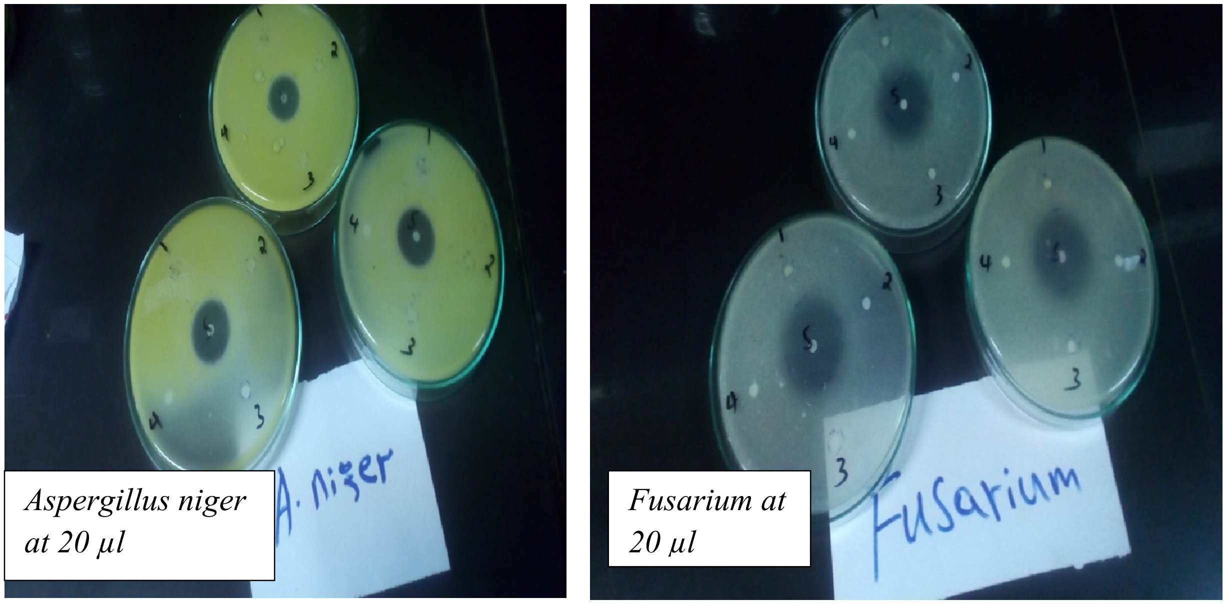
Salmonella at 20 µl

Escherichia coli at 20 µl

Streptococcus agalactiae at 20 µl

Staphylococcus aureus at 20 µl

Appendix Figure 2.Antibacterial activities of inorganic, organic polymer, nano composite, and Chloramphenicol.



Aspergillus niger at 20 µl

Fusarium at 20 µl

Appendix Figure 3. Anti-fungal activities of inorganic, organic polymer, nano composite, and tilt