Review on the Superiority of Composite Materials as Ion Exchangers in Environmental and Material Sciences

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ABSTRACT

There are various techniques available to check and separate the toxic metal ions under variable conditions. But among the available processes, ion exchange has received much attention. The applicability of ion-exchange has been extended by the preparation of composite ion exchangers. The hybrid ion-exchangers have received much superiority than organic and inorganic exchangers because the practical applicability of organic and inorganic exchangers is limited. The present article describes the applications of various types of materials which are being used as ion exchangers and the superiority of composites among them.

Key words: Ion exchangers,inorganic,organic,Composite, nanocomposite, ion exchange chromatography

INTRODUCTION

Separation is useful in a variety of sectors, including medicine, agriculture, and environmental study. Separation is a pre-treatment procedure that occurs before any quantitative or qualitative analysis. Separation uses both traditional and modern methods. Precipitation and distillation are two examples of traditional processes. Distillation, extraction, precipitation, crystallization, dialysis, and diffusion are examples of general separation procedures. Chromatography, electrophoresis, and ion exchange chromatography are the most contemporary and diverse separation techniques available. Ion exchange chromatography has become a highly versatile and widely used analytical technique. Ion exchange chromatography is a reversible procedure that involves the exchange of ions of the same sign between a solid and a liquid, as well as a very insoluble material in contact with it. Ion exchangers are known to exist in soil, yet no significant organic polymer has been employed as an ion exchanger [1,2]. Cation anion exchange chromatography is another name for it. Ion exchange chromatography, commonly known as adsorption chromatography, is a popular and valuable technique because of its:

 * High capacity.

 * Excellent resolving power.

* Separation conditions are mild.

* Versatility and broad scope of use.

* A proclivity to concentrate the sample at a cheap cost.

Ion exchange chromatography can be used to separate and purify a variety of charged or ionizable compounds from natural or synthetic sources, such as proteins, peptides, enzymes, nucleotides, DNA, antibiotics, vitamins, and so on [3]. The following are some of its applications:

(I) Separation of ions that are similar:

Ion exchange chromatography is used to separate comparable ions because different ions undergo variable a mounts of exchange reactions [4,5].

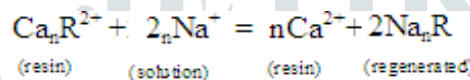For example, cation exchange resin can be used to separate a combination of H^+, Na^+, and K^+.

Similarly, travelling via a basic anion exchanger can separate Cl^-, Br^-, and I^-.

(2) Hard water softening:

The presence of Ca^{2+}, Mg^{2+}, and other divalent ions in water can be eliminated by running the hard water vi a a cation exchanger charged with Na+ ions. After that, the following exchange response occurs:

$$2Na_nR^+ + nCa^{2+} = Ca_nR^{2+} + 2Na^+$$
$$\text{(resin)} \quad \text{(hard water)} \qquad \text{(resin)} \qquad \text{(solutions)}$$
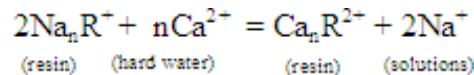
Water ions Ca^+ and Mg^+ are kept on the column, whereas Na^+ ions flow into the solution. These Na^+ ions are safe to use for washing. After a period of use, the ion exchange becomes active. When the following reverse reaction occurs, percolating a concentrated solution of NaCl through it can reactivate its activity [4,5].

$$Ca_nR^{2+} + 2_nNa^+ = nCa^{2+} + 2Na_nR$$
$$\text{(resin)} \qquad \text{(solution)} \qquad \text{(resin)} \qquad \text{(regenerated)}$$

(3) Complete water demineralization:

This necessitates the removal of all ions, including both cations and anions. This is accomplished by passing water through an acidic cation exchanger, which subsequently exchanges metallic cations for H^+ ions. The resulting water is then sent via a basic anion exchanger, where the anions in the water are swapped by the exchanger's OH. Unionized water is formed when H^+ and OH^- ions pass into solution [6].

(4) Organic compound purification:

Many natural products extracted in water have been shown to include ions that were present in the water at the time of extraction. Ion exchange can be used to get rid of such ions [7].

(5) Sugar separation

Khym and Zill invented this approach in 1951 [7]. The separation of borate complexes has been done quantitatively on columns employing ion exchange chromatography after sugars have been transformed into borate complexes. Disaccharide may be separated from monosaccharide, and individual hexose and pentose molecules can be resolved from the combination.

(6) Separation of amino acids

The complex mixture of 18 amino acids generated by acid hydrolysis of proteins can be separated using ion exchange techniques. The amino acid combination is initially injected on a short column at pH 2 and then eluted at pH 5.25 with 0.35 N sodium citrate buffers. Acidic and neutral amino acids first exit the column unseparated, followed by the separation of other amino acids [7].

(7) Pharmaceutical purification and recovery:

During the production process, the method is used to purify and recover antibiotics, vitamins, alkaloids, hormones, and other pharmaceutically important compounds.

(8) Medical significance:

Anionic resins are used to cure ulcers, while cation exchangers are utilized to remove Na^+ from the body in the treatment of hypertension and edema. In gastric acidity tests, the resins are also utilized as a diagnostic assistance. Other pharmaceutical substances have been effectively combined with the resins to achieve delayed action doses.

(9) Biochemical separations:

Used to separate biochemical compounds such as medicines or metabolites from blood, urine, or other bodily fluids [8].

(10) HPLC ion exchange column:

In HPLC, ion exchange is utilized to separate compounds of mixed nature, such as acidic and basic chemicals.

(11) Ionic solution concentration:

A cation or anion from a large volume of solution can be adsorbed onto ion exchange resins and then eluted with a small volume of eluent [8].

(12) Lanthanide separation:

A solution containing a lanthanide combination is run through a column filled with particles of an appropriate ion exchange resin. In the presence of hydrogen ions, cations in solution undergo hydrogen exchange.

(13) Actinide separation:

The IEC method was essential in the finding of the Trans plutonium elements in the actinide series. The sequence of elution of lanthanides (4f) and actinides (5f) ions in the +3-oxidation state from a cation exchange resin column using an aqueous solution of ammonium hydroxyl isobutyrate demonstrates the method's power. Because of actinide contraction, elution occurs in the reverse order of the atomic number in the actinide series, proving that IEC is the only means to identify these elements [9].

(14) Removal of interfering radicals:

The oxalate or sulphate approach, in which the phosphate ion interferes, is used to estimate Ca^+ or Ba^+ ions. As a result, it must be removed, which is accomplished by passing a solution of Ca^+ or Ba^+ ions via an appropriate ion exchanger in the column. To entirely eliminate the phosphate ions, the process must be repeated. Using an appropriate eluent, the calcium and Ba^+ ions retained by the resin will now be extracted. Finally, these ions are calculated using standard procedures. [10]

(15) Other uses include:

*For determining the concentrations of various active components in pharmaceutical formulations.

*For drug and metabolite measurement in blood and urine, as well as residue analysis in food raw materials.

*For the measuring of food and beverage additives such as vitamins and preservatives.

Chemists were well aware of ion exchange at the turn of the nineteenth century, and they were hard at work on new studies. Clay, according to Gazzari (1819), retains dissolved fertilizer particles. Sprengel claimed in 1826 that humus liberates some acids from soils. Lime, according to Fuchs (1833), liberates potassium and sodium from some clay. By the middle of the nineteenth century, enough experimental observations and data had been gathered, but the principle of ion exchange had yet to be identified. Thompson [11] in 1845 and Way [12] in 1850 set the groundwork for ion exchange in soil via base exchange. They discovered that when soils are treated with ammonium salts, the soil absorbs the ammonium ions and releases an equal quantity of calcium and magnesium ions. The phenomena of ion exchange was first documented in 1850 by two British Agricultural Chemists. Natural and synthetic inorganic cation ex-changers (soils, clays, and Zeolites) were employed to soften hard water after Gan's work in 1913. Adams and Holms were the first to employ modern ion exchange resins in 1935, and since then, a significant number of synthetic resins have been produced [13]. This technology has been evolving since the nineteenth century, when it was initially employed to purify drinking water.

THE PROCESS OF ION EXCHANGE AND ITS MECHANISM

The ion exchange technique is very useful analytical tool in laboratories and industries. The stoichiometry is the most important criterion in the ion exchange process. It is a well-known fact in organic resins [14]. The ion exchange occurs stoichiometrically, that is, by the effective exchange of ions between stationary and movable immiscible phases. In order to describe equilibrium and understand the mechanism of an ion exchange process it is important to have a study of its kinetics and thermodynamics. Inorganic ion exchangers have a solid matrix, they do not swell as much as organic resins, making such experiments easier to carry out. Two theoretical approaches to ion exchange equilibrium exist: (i) based on the law of mass action, and (ii) based on Donnan theory.   The Donnan theory has the advantage of allowing a more elegant interpretation of thermodynamic behavior in an ion exchanger from a theoretical standpoint. It was perhaps the first time Gane used the mass action rule in its simplest form to quantitatively create ion exchange equilibrium without invoking the concept of activity coefficients. Kielland [15] elaborated on this approach, while Gaines and Thomas [16] suggested a suitable general treatment. The thermodynamics of cation ions on zirconium phosphate samples was investigated in a series of articles. Ion-exchange isotherms and exchange on zirconium (IV) phosphate has been researched by a number of researchers [17, 18, 19]. The influence of crystallinity on the thermodynamics of ion exchange of alkali metal ions/H^+ calorimetric heats of exchange were determined on samples varying from amorphous to highly crystalline [20-23]. However, from the practical point of view, the mass action approach is simpler. Nancollas and coworkers [24,25] have interpreted the thermodynamical functions in term of the binding nature between alkali metals

and the ion-exchange matrix. The ion-exchange equilibria of Li(I), Na(I) and K(I) on zirconium (IV) phosphate have also been studied by Larsen and Vissers [26] who calculated the equilibrium constants and other thermodynamical parameters viz. ΔG^o, ΔH^o and ΔS^o. Similar studies have been made on anion-exchanger also [27]**.** Ion-exchange equilibria of alkaline earth metal ions on different inorganic ion-exchangers such as tantalum arsenate [28], iron (III) antimonate [29]**,** antimony (V) silicate [30], zirconium (IV) phosphosilicate [31] and alkali metal ions on iron (III) antimonate [32] and α-cerium phosphate [33] Other relevant thermodynamic investigations in these facilities have looked at the adsorption of pesticides on inorganic and composite ion exchangers [34,35]. The study found that adsorption is stronger at lower temperatures, and that the presence of an ion exchange substance in the soil considerably increases its pesticide adsorption capacity. Nachod and Wood [36] completed the earliest and most thorough study of ion exchange kinetics. They looked at the pace at which solid ion exchangers remove ions from solutions, as well as the rate at which the exchangeable ions are released from the exchanger. Later, Boyd et al. [37] investigated the kinetics of metal ions on resin beads, resulting in a better understanding of the particle and film diffusion phenomena that govern ion exchange processes. The first is correct at larger quantities, whereas the second is correct at lower concentrations. Reichenberg had researched metal ion kinetics on sulphonated polystyrene, who, once again, confirmed that the rate is independent of the ingoing ion (particle diffusion) at large concentrations, while the opposite is true at low concentrations (film diffusion).

Classification

Although inorganic ion exchanger materials were the first to be recognized, they became obsolete once organic resins were discovered.

RESINS:

Resins are amorphous organic particles made up of polystyrene and divinely benzene. Polystyrene has locations for functional groups that can be swapped out. Divinelybenzene, on the other hand, functions as a crosslinking agent and provides appropriate strength, i.e. mechanical stability. Small molecules are separated using ion exchange resins.

Resins are categorized based on their chemical nature:

1. Strong cation exchange resin: These resins are useful for chromatographic separation of amino acids, rare earths, and other compounds with sulphonic acid groups as ionizable groups.

2. Weak cation exchange resin: These resins contain carboxyl groups and are based on polymers of methacrylic acid.

3. Strong anion exchange resin: This category includes resins with positively charged quaternary ammonium groups coupled to a crosslinked polystyrene framework. This resin contains trimethyl ammonium groups.

4.Weak anion exchange resins: This includes tertiary amine resins and polyamine resins with a mixture of primary, secondary, and tertiary amine groups on the polystyrene network.

Resin needs in general:

*Chemically, it should be stable.

*In most common solvents, it should be insoluble.

*It should have a high ion exchange rate.

*It should be denser than a water molecule if it swells.

*A sufficient number of ion exchange groups must be present.

Because exchange functional groups are lost during separation, the ion exchange resin may not be suitable for subsequent separation. They cannot, however, be disposed of due to the high expense of ion exchange resins. As a result, reactivation and resin regeneration are critical. Regeneration restores the efficiency of used ion exchange resins to that of virgin resins. The term "regeneration" refers to the process of replacing the resin's exchangeable cations or anions. As a result, the cation exchange resin is regenerated by charging the column with a strong acid such as hydrochloric acid, and the anion exchange resin is regenerated by employing a strong alkali such as sodium hydroxide or potassium hydroxide. However, because of their employment in nuclear research, there was a resurgence of interest in these minerals in the twentieth century. At the time, novel materials that were stable at high temperatures and in the face of powerful radioactive radiations were required. Metal ion separation, catalysis, environmental studies, medical science (kidney dialysis), ion-selective electrodes preparation, heterogeneous solid state membranes formation, and ion-exchange fibers preparation, among other disciplines, have all benefited from inorganic ion-exchange materials based on polyvalent metals. These materials are essential because they are more stable to high temperature radiation fields than biological materials [38]. The following are the several types of synthetic ion exchangers:

1. Synthetic zeolites

2. Polybasic acid salts

3. Hydrous oxides

4. Metal ferrocynides

5. Insoluble ion exchange materials

6. Hetropolyacids

1 SYNTHETIC ZEOLITES:

Zeolites were the first inorganic materials to be employed on a significant basis for removing waste effluents. Zeolites are aluminosilicate based crystalline materials that can be made into micro crystalline powders, pellets, or beads. Synthetic zeolites offer some advantages over naturally occurring zeolites in that they can be created with a wide range of chemical characteristics and pore sizes, and they are stable at high temperatures, but they also have certain drawbacks.

Synthetic zeolites have the following drawbacks:

    • Relatively expensive cost as compared to natural zeolites

    • Limited chemical stability at extreme pH ranges (high or low)

    • Ion selectivity is subject to influence from similarly sized ions

Because the bed is changed during the early stages of breakthrough and because the waste streams usually contain other ions that will occupy some of the exchange sites and thus reduce the processing capacity, the actual processing capacities obtained with zeolites are lower than their maximum capacities.

For technical purposes, synthetic silica-based ion exchangers were made by fusing soda, potassium carbonate, feldspar, and kaolinite (Schmaltz permutite) and later by precipitating aluminium sulphate solution containing sodium silicate with sodium hydroxide solution (Gel permutite). Artificial crystalline zeolites have been successfully made since then.

The following are the advantages of a crystalline silicate-based ion exchanger over modern synthetic resin-based ion exchangers:

- More resistant to high temperatures

- Structure that is rigid and consistent

- More selective and appropriate for separating ions based on their various sizes

Some are now employed as molecular or ionic sieves as well. A systematic investigation into the performance of locally accessible synthetic zeolites for the removal of cesium, strontium, and thorium from solution has been carried out in India [39,41]. After exchange with cesium, strontium, or thorium, the zeolites were thermally treated to success fully fix the ions in the same matrix [42].

2 SALTS OF POLYBASIC ACIDS

Acidic salts of multivalent metals are created by combining acidic oxides of metals from the IV, V, and VI periodic table groups. The quadrivalent metals' acid salts are the best investigated of this class. They are incredibly difficult to dissolve. They have a non-stochiometric composition that is dependent on the conditions in which they are precipitated. Phosphates, arsenates, molybdates, tungstates, antimonates, silicates, vanadates, and tellurates of zirconium, titanium, thorium, tin, cerium, chromium, iron, niobium, and tantalum are among the minerals that have been synthesized thus far.

3 OXIDES OF HYDROUS

Some metal ion's hydrous oxides have also been well-established materials for ion exchange purposes. Freshly precipitated trivalent metal oxides, such as hydrous ferric oxides and ferric hydroxides, are highly successful in this regard, as they quickly absorb alkaline earth cations according to the law of mass action, while other bivalent cations are absorbed above pH 7. Alkali metals and alkaline earths are adsorbed on the surface and easily eluted, but more highly charged cations such as $Ce(III)$, $Y(III)$, $Pm(III)$, and $Ru(IV)$ are adsorbed in bulk and only eluted with difficulty [43]. The amphoteric behavior of this type of ion exchangers is dependent on the pH of the solution. The following equilibria can be used to explain the process [44].

$$Al\,(OH)_2^+ + OH^- \longleftrightarrow Al\,(OH)_3$$

Amphoteric exchange characteristics of zinc oxide have also been discovered [45]. Second cations with a higher charge than the parent cation can be inserted into the structure to make mixed oxides. The presence of anions other than oxides and hydroxides balances the net positive charge that results. Zn $(OH)_2$, in Zn^{2+} is partially replaced by Al^{3+}, and Al $(OH)_3$, which contains Si^{4+}, Ti^{4+}, or Zr^{4+}, are examples of such materials. $Zn_{n-1}Al_n(OH)_2X_n$ and $Al_{n-1}M_n(OH)_3Xn-1$ are typical formulas, where M^{4+} is a tetravalent oxide and X is a monovalent anion. Quadrivalent metal oxides, such as SnO_2, SiO_2, ThO_2, and ZrO_2, are often utilized as inorganic ion exchangers. Unless they are burnt at a high temperature, these materials do not have the simple oxide formula listed above. They are discovered to contain changing amounts of water, which is not present as hydration water because it is lost continually throughout a temperature range when heated. As a result, these oxides are commonly referred to as hydrous oxides. Hydrous oxides have been studied extensively by Inoue et al. [46-48] and A.K. De et al. [49-52].

4. METAL FERROCYANIDES

Metal ferrocyanides that are insoluble can be employed as inorganic ion exchangers. They're also known as alkali metal scavengers. They're simple to make and can be used to separate radioactive wastes and fissionable materials [53] with less radiation damage than their biological counterparts. Xray investigations were used by Baetsley et al. [54] to identify the structure of ferrocyanide molybdate. In an acidic media, they employed molybdenum and tungsten ferrocyanides to Separate Cs-137 and Sr-90 from fissionable products. Ferrocyanides of amine- based metals have also been studied. Hahn and Clein [55], who prepared a cobalt amine ferrocyanide, were the first to present them. Ferric hydroxides have also been employed as an adsorbent for the removal of arsenic from natural water [56], and they have a rapidly rising number of uses in the separation of metal ions.

ION EXCHANGE MATERIALS THAT ARE INSOLUBLE

Various ion exchanging materials that are insoluble are also of interest. There have been a huge number of these compounds created. Precipitation of metal salt solutions with Na_2S or H_2S was used to make these materials. Insoluble sulphides' ion exchange characteristics (e.g. Ag_2S, SnS, CuS, PbS, FeS, NiS, As_2S_3) Sb_2S_3) has been looked into. Sulphides are selective for cations and create insoluble sulphides as a result. The exchange reaction happens through metathetical reactions in which the sulphide metal is displaced from the solution by a suitable ion. Tl+, Ni2+, Co2+, Mn2+, Cu2+, and Pb2+ quantitative sorption on ZnS, CdS, and PbS [57], Uranium on PbS [58], Cu^{2+} separation from Zn^{2+} and Cd^{2+} on SnS [59], as well as noble metal separation on CuS [60, 61].

6 HETEROPOLYACIDS

- Inorganic ion exchangers can be made from heteropolyacid salts. This class of exchangers is made up of 12-heteropolyacids with the general formula $H_nXY_{12}O_{40}.nH_2O$, where X can be any of the elements P, As, Si, B, or Ce, and Y can be any of the elements Mo, Si, B, or Ce. Heteropoly compounds, particularly those containing 12molybdo, are powerful oxidizers. This sort of exchanger is stable in moderately concentrated

acid. They do, however, dissolve in an alkali solution. Heavy alkali metals, thorium, and silver have a strong affinity for the heteropoly acids. The size of these elements' univalent ions allows them to be retained in the crystal lattice of heteropoly acids. Aside from heteropoly acid salts, numerous additional compounds, such as mixed salts, have been produced and their ion exchange characteristics examined in depth. Double salts or mixed salts of metal ions have been discovered to have distinct ion exchange characteristics than single salts. In most cases, they outperform simple salts in three key areas. They are more thermally and chemically stable, and they are also more selective in nature, with better ion exchange capacities than simple salts. With this in mind, researchers have worked to synthesize and explore the ion exchange capabilities of this type of ion exchanger. Table 1 lists some mixed salts or double salts that were created previously.

The following features may be explored in the order of preference in order to characterize a novel material as an inorganic ion exchanger, its utility in various domains, and its limitations. Ion exchange capacity

- Chemical and thermal stability
- Composition
- pH titration
- Structural studies
- Selectivity
- Analytical applications

Inorganic ion exchangers have various restrictions in addition to their applications:

- Relatively low exchange capacities
- Relatively low mechanical durability
- Non-controllable pore size
- Clay minerals tend to peptize (i.e. convert to a colloidal form)
- Zeolites are difficult to size mechanically
- Partial decomposition in acids or alkalis
- Limited chemical stability in many solutions
- Need for a chemical or thermal pretreatment (especially those with a very low salt content)

Table 1 Three-component ion exchange materials with their properties

S. No.	Ion exchange Materials	Type	Composition	Empirical Formula	IEC (meq g^{-1})	Selectivity	References
1	Amine tin hexacyanoferrate	-		-	-	-	62
2	Ammonium dodeca molybdoantimonate	Crystalline		$(NH4)3(Mo12 SbO40).11H2O$	-	-	63
3	Ammonium molybdophosphate	Crystalline		$(NH4)3PMo12O40$	1.57	-	64
4	Ammonium tungstophosphate	Crystalline		$(NH4)3PW12O40$	0.66	-	65
5	Anilinium zirconium phosphate	-		$(ZrO2)2(C6H5NH2)2.HPO4.3.7H2O$	1.87	Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}	66
6	Anilinium tin phosphate	-		-	-	-	67
7	Chromium arsenophosphate	Amorphous	Cr:As:P=2:1:1	$[Cr2O3.H3AsO4.H3PO4].nH2O$		K^+	68
8	Cesium zirconium phosphate	-		-	-	-	69
9	Chromium arsenosilicate	Amorphous		$2 Cr2O3.2.5 As2O5. 3 SiO2.nH2O$	-	K^+	70
10	Cerium phosphosilicate	Amorphous	Ce:Si:P=2:5:4	$(CeO2)2 (SiO2)3 (H3PO4)4.nH2O$	-	-	71

11	Dipotassium tri-zinc hexa cyano ferrate	-		-	-	-	72
12	Nickel aluminosilicate	Amorphous		-	-	-	73
13	Stannic arsenoborate	Amorphous		-	0.99	-	74
14	Stannic arsenosilicate	-		-	-	-	75
15	Stannic boratomolybdate	Amorphous	Sn:B:Mo=1:1:1	-	1.12	Zr^{4+}, Th^{4+}	74
16	Stannic boratophosphate	Amorphous		-	1.10	-	76
17	Stannic boratosulphate	Amorphous		-	0.55	-	74
18	Stannic boratotungstate	Amorphous		-	1.15	-	74
19	Stannic iodophosphate	-		-	-	-	77
20	Stannic molybdophosphate	-	Sn:Mo:P=1:0.33:2	-	-	-	78
21	Tin(IV) arsenosilicate	-		-	-	Amino acid	79
22	Tin(IV) vanadopyro-phsosphate	Micro-crystalline		-	3.17	-	80
23	Tin(IV) tungstovanado-phosphate	-		-	-	-	81
24	Tin(IV) tungstoselenate	Crystalline	Sn/Se/W=7:1:18	-	1.43	Ba^{2+}	82
25	Titanium tungstophosphate	-		-	-	-	83
26	Titanium phosphate ammonium Tungstophosphate	-		-	-	-	84
27	Titanium tungstoarsenate	-		-	-	-	85
28	Titanium arsenosilicate	-		-	-	Pb^{2+}	86

29	Titanium vanadophosphate	-		-		-	-	87
30	Titanium tungstovanado-phosphate	-		-		-	Amines	88
31	Titanium phosphosilicate	Amorphous		-		-	Zr^{4+}, Nb^{5+}, Cs^+	89
32	Titanium aluminium silicate	-		-		-	Pb^{2+}	90
33	Titanium molydophosphate	-		-		-	-	91
34	Titanium phosphate ammonium Phosphomolybdate	-		-		-	-	92
35	Titanium (IV) tungstosilicate	Crystalline		-		0.44	-	93
36	Zirconium hydrogen arsenate hydrogen phosphate	Amorphous		$Zr(HAsO4)(HPO4).H2O$		-	-	94
37	Zirconium iodooxalate	Amorphous	Zr:IO3:C2O4H =2:1:3	$(ZrO)2(IO3)(HC2O4)3.nH2O$		-	-	95
38	Zirconium alumino pyrophosphate	-		-		-	-	96
39	Zirconium arsenophosphate	Amorphous	Zr:As:P=2:1:1	$(ZrO2)(H3AsO4)(H3PO4).nH2O$	-		Rb^+, Ag^+, Tl^+	97, 98
40	Zirconium arsenosilicate	Crystalline		-		-	Hg^{2+}	99
41	Zirconium	-		-		-	-	100

	phosphoantimonate						
42	Zirconium phosphoborate	-	Zr:P:B=1:1:1	-	-	-	101
43	Zirconium pthalo phosphate	-		-	-	-	102
44	Zirconium vanadophosphate	-		-	-	Li^+, Na^+, $NH4^+$	103
45	Zirconium sulphosalicylate	Semi-crystalline		-	-	-	104, 105
46	Zirconium phosphosilicate	Amorphous		-	2.2	Cs^+	106, 107
47	Zirconium molybdophosphate	-		$ZrH_2MoO_2.xH_2O$	1.6	-	108
48	Zirconium(IV) selenophosphate	-		$(ZrO)_5(OH)_4(HSeO_3)_2(H_2PO_4).2H_2O$	-	-	109
49	Zirconium(IV) iodomolybdate	-		-	-	Hg^{2+}	110
50	Zirconium(IV) iodophosphate	-		-	1.78	-	111
51	Zirconium titanium phosphate	Crystalline	Zr/Ti=3.25	$Zr_xTi_{1-x} (HPO_4)_2.H_2O$	6.87	-	112-117
52	Zirconium molybdovanadate	-	Zr:V:Mo=1.68:1:0.088		-	Li^+, Na^+	118
53	Zirconium tungstoarsenate	Amorphous		-	-	UO_2^{2+}, Cs^+, Tl^+	119

54	Zirconium(IV) tungstophosphate	-	Zr:W:P= 18.8%:25.4%:4.3%		1.00	Pb^{2+}	120, 121
55	Zirconium cerium phosphate	-		-	-	-	122
56	Zirconium(IV) 4-amino-3-hydroxy naphthalene sulphonate	-		-	-	Hg^{2+}	123
57	Zirconium bis (monooctyl) Phosphate	Crystalline		-	-	-	124
58	Zirconium(IV) iodovanadate	Amorphous	Zr/IO3/VO3=2:1:3	$(ZrO_2)(IO_3)(V_3O_9)$	4.20	Electron exchanger	125
59	Zirconium(IV) tunsto-molybdate	Amorphous		$(ZrO)(OH)_2(H_2WO_4)_4(H_2MoO_4)_3 \cdot 8H_2O$	2.40		126
60	Acryl amide zirconium phosphate	Crystalline		-	2.26	-	127

COMPOSITES

Synthetic organic ion exchange resins, like some synthetic inorganic materials, offer a high capacity, broad applicability, adaptability, and low cost. They do, however, have some limits. Their primary drawbacks are their low radiation and heat stability. Due to physical deterioration at both the molecular and macroscopic levels, most organic resins will demonstrate a severe drop in their ion exchange capacity (a 10 to 100 percent capacity loss) at a total absorbed radiation dose of 10^9 to 10^{10} rads. The most recent advancement in this field is the conversion of inorganic ion exchange materials into composite ion exchange materials. For the purpose of developing high performance or high functional polymeric materials, composite materials generated by the mixture of organic polymers and inorganic materials, referred to as "organic inorganic hybrid materials," are appealing. The most recent advancement in this field is the conversion of organic ion exchange materials into hybrid ion exchangers. The binding of organic polymers, such as polyaniline, polyacrylonitrile, and polystyrene, is used to make hybrid ion-exchangers. These polymer-based hybrid ion exchangers demonstrated improved chemical, mechanical, and radiation stability, as well as improved ion exchange capabilities and a selective nature for heavy hazardous metal ions. One of their most essential characteristics is their granulometric nature, which makes them more ideal for use in column operations. Hybrid ion exchangers can be made as three-dimensional porous materials with crosslinked layers or layered compounds with sulphonic acid, carboxylic acid, or amino groups. Numerous uses of sol-gel generated composite materials have been discovered in the fields of chemistry, biology, engineering, and material science [135]. In the literature, 'organic-inorganic' hybrid materials created using the sol-gel process have gotten a lot of attention [136]. Hybrid materials are created by combining organic and inorganic precursors to produce mechanical properties not found in pure materials. In the end product, composite ion exchange materials, the binding of organic polymer also introduces higher mechanical qualities. Many organic inorganic composite ion exchange materials have been produced in this area. Khan et al. reported polypyrroleTh(IV) phosphate [137], polyaniline Sn(IV) arsenophosphate [138], and polystyrene Zr(IV) tungstophosphate [139] as materials for the selective separation of Pb^{2+}, Cd^{2+}, and Hg^{2+}, respectively, as well as ion exchange kinetics of M^{2+}- H^+ exchange and pesticide adsorption [140]. Such ion exchange materials, such as o-chlorophenol Zr (IV) tungstate and p-chlorophenol Zr (IV) tungstate, have been produced by Beena Pandit et al. [141]. Varshney et al. reported that styrene-supported Zr (IV) phosphate hybrid material [142] and fibrous ion exchange materials based on polymethyl methacrylate, polyacrylonitrile, styrene and pectin-based Ce (IV) phosphate, Th (IV) phosphate, and Zr (IV) phosphate [143] have numerous analytical applications. These materials can be utilized as electrodes and ion exchange membranes.

Nanocomposite materials

Traditional, macroscopic composite materials such as adobe, a mixture of clay and straw that has been used to produce bricks and walls in arid locations, have shaped our world in the past, and they, along with reinforced concrete, have shaped our environment. Reduced particle size, on the other hand, increases the importance of the interphase in composite mixes at the microscopic level, which is especially true for a new class of recently developed materials known as nanocomposites. The term "nanocomposite material" has broadened greatly to

include a wide range of systems, including one dimensional, two dimensional, and three-dimensional materials, amorphous or crystalline, consisting of distinctly diverse components blended on a nanoscale. Nanocomposite is a type of composite material in which nano or molecular domain sized particles are embedded in an organic polymer, metal, or ceramic matrix. The close presence of these nanoparticles in these matrices is thought to completely affect the characteristics of these materials in all circumstances. To modify the physical properties of these base materials, nanoparticles can be used as matrix reinforcement. A considerable quantity of interfacial phase material is now incorporated in the bulk of these nanocomposites, allowing for a full alteration of the material's chemical, mechanical, and morphological domain structure. Much of today's research in the field of polymer based organic inorganic hybrid nanocomposites demonstrates mechanical and electrical qualities that outperform their individual components. The employment of sol-gel technology to generate homogeneous dispersions of minute sized inorganic particles throughout a polymer matrix gave birth to nanocomposite plastics in the 1970s. The inorganic phase may or may not be chemically linked to the organic phase in such systems. Coating applications have been discovered to benefit from these first-generation nanocomposites. Second generation nanocomposites appeared in the 1980s as a result of a resurgence in the usage of tiny particles, minerals, and clay fillers in plastics. To make these nanocomposites, it was necessary to have limited compatibility between the filler and the polymers, as well as sophisticated polymer processing requirements. Third generation nanocomposites, which are polymeric materials reinforced with nanofibers such as carbon nanotubes, SiC whiskers, colloidal silica, nano-clay particles, and so on, appeared in the 1990s and beyond. As a result of this unique ability to influence nanoscale structures using creative "bottom-up" synthetc techniques, various difficulties and opportunities have arisen. Taking on this task allows you to create new materials that have synergistic behavior and boost performance [144]. When compared to their macro composite counterparts, practically all types and classes of nanocomposite materials produce new and better properties, according to research. Nanocomposites thus hold potential in a variety of sectors, including mechanically reinforced lightweight components, non-linear optics, battery cathodes, sensors, and optoelectronics. The broad class of organic inorganic nanocomposites may be relevant to bio-ceramics and biomineralization concerns, as in-situ growth and polymerization of biopolymer and inorganic matrix occurs [146-148].

Ion exchangers are used in numerous industrial, household, governmental, and laboratory applications. The composite ion exchangers have improved granulometric properties, making them more stable in column operations, particularly for ionic species separation, filtration, and preconcentration. The column's appropriateness for operation makes it more convenient for regenerating fatigued beds as well. These hybrid ion exchangers exhibit a high ion exchange capacity, excellent stability, repeatability, and selectivity for heavy metal ions, indicating that they could be useful in the environment. Water softening, metal ion separation and preconcentration, nuclear separations, catalysis, redox system, electrodialysis, hydrometallurgy, effluent treatment, ion exchange fibers, and ion-selective electrodes are some of the applications for these materials.

References:

1. B.K. Sharma; Instrumental Methods of Chemical Analysis; page. No: 123-160.

2. W. M. Dean Settle; Instrumental Methods of Analysis; 7th edition; page. No: 633-639.

3. Siddiqui; Pharmaceutical Analysis; volume-I; page. No: 216 – 236.

4. G. R. Chatwal, S. K. Anand; Instrumental Methods of Chemical Analysis; page. No: 2.662-2.672.

5. A. V. Kasture, K. R. Mahadik, S. G. Wadodkar, H. N. More; Pharmaceutical Analysis; volume-II; page. No: 39 – 47.

6. P. Parimoo; Pharmaceutical Analysis; page. No: 284 - 286.

7. G. D. Rao; A Text Book of Pharmaceutical Analysis; volume-II; page. No: 54 – 57.

8. S. R. Sankar; Text book of pharmaceutical analysis; 4th edition; page. No: 16-2 – 16- 10.

9. R. A. Day, A. L. Underwood; Quantitative Analysis; 6th edition; page. No: 535-543.

10. M. u, X. ang, Z. Zhang, R. ang; Isolation and Purification of Bioactive Proteins from Bovine Colostrum.

11. H.S. Thompson, J. Roy, Agr. Soc. Eng. 11(1850) 68

12. T. Way, Agr. Soc. Eng. 11 (1850) 313

13. B.K. Sharma; Instrumental Methods of Chemical Analysis; page. No: 123-160.

14. F.Hellferich, Ion-Exchange,McGraw-Hill,NewYork,1962.

15. J.Kielland,J.Soc. Chem.Ind.(London), 54(1935)232.

16. G.L. Gaines(Jr).,H.C.Thomas, J.Chem.Phys.,21(1953)714.

17. G.Alberti,U.Costantino, S.Alluliand M.A.Massucci,J. Inorg.Nucl.Chem.,35 (1973)1339.

18. A.L.Ruvarac andV.D.Marizonac,J.Chromatogr.76(1973)22.

19. G.Alberti,U.Costantinoand M.Pelliccioni,J.Inorg.Nucl. Chem.,33(1973)1327.

20. A.ClearfieldandD.A.Tuhtar, J.Phys.Chem.,80(1976)1296.

21. L.Kullbergand A.Clearfield,Ibid., 85(1981)1578.

22. A.ClearfieldandJ.M.Kallnius,J.Inorg. Nucl.Chem.,38(1976)849.

23. A.Clearfield,G.A.Day, A.Ruvaracr andS.Milonjic, JInorgNuclChem., 43 (1981)165.

24. G.H.Nancollas andB.V.K.S.R.A.Tilak,J.Inorg.Chem.,31(1969)3643.

25. G.P.Harkin, G.H.Nancollas andR.Paterson,J.Inorg. Chem.,26 (1964)305.

26. E.M. Larsen andD.R.Vissers, J.Phys.Chem.,64(1960)1732.

27. G.H.Nancollas and D.S. Reid,J.Inorg.Nucl. Chem.,31(1969)213.

28. J.P.Rawat andP.S. Thind, J. Indian. Chem.Soc.,57(1980)819.

29. J.P.RawatandK.P.S.Muktawat,J. Inorg.Nucl.Chem.,43(1981)2121.

30. K.G.Varshney,R.P.Singhand S.Rani,Acta.Chem.Hung, 115(1984)403.

31. K.G.Varshney,R.P.SinghandU.Sharma,Coll.Surf;(A),16(1985)207.

32. J.P.RawatandB.Singh,Bull. Chem.Soc. Jpn.,57(1984)862.

33. R.G.HermanandA.Clearfield, J.Inorg.Nucl.Chem.,38(1976)853.

34.K.G .Varshney,S. Raniand R.P.Singh,Ecotox.Environ. Safety,1(1986) 179.

35. A.A.Khan,R. NiwasandO.P. Bansal, J.IndianChem.Soc.,76 (1999)44.

36. F.C. NachodandW.Wood, J.Inorg.Am.Chem.Soc.,66(1944)1380.

37. G.E.Boyd,A.W.AdamsonandL.S.Myers,J.Am.Chem. Soc.,69(1947)2386.

38. A.Clearfield;editor.Inorganicionexchangematerials,CRCPressInc.,BocaRaton,Florida,1982.

39.Sinha, Panicker, P.K. Amalraj, R.V. Krishnasamy, Waste Management 15 (1995) 149

40.Sinha, P.K. Panicker, P.K. Amalraj, R.V. Krishnasamy, Radiochem. Acta 73 (1996) 157

41.Sinha, P.K. Panicker, P.K. Amalraj, R.V. Krishnasamy, Radiochim. Acta 65 (1994) 125

42.Sinha, P.K. Krishnasamy, J. Nucl. Sci. Technol. 33 (1996) 333

43. S.A. Voznesenku, G.A. Sereda, P.F. Polgikh, L.I. Basakov, Report of soviet scientists to Second International Conf. Peaceful Uses of Atomic Energy, 189 (1958).

44. B.P. Nikol'skii, Zh. Fiz. Khim. 5 (1934) 266

45. S.N. Tewari, Kolloid-Zeitschrift 149 (1956) 65

46. Y. Inoue, H. Yamazaki, Bull. Chem. Soc. Jpn. 53(4) (1980) 811

47. Y. Inoue, M. Tsuji, Bull. Chem. Soc. Jpn. 51(2) (1978) 479

48. Y. Inoue, M. Tsuji, Bull. Chem. Soc. Jpn. 51(3) (1978) 749

49. A.K. De, S.K. Das, J. Ind. Chem. Soc. 53(10) (1976) 1063

50. A.K. De, N.D. Chawdhury, Chromatographia 11(10) (1978) 586

51. A.K. De, S.K. Das, Sep. Sci. Technol. 13(5) (1978) 465

52.A.K. De, S.K. Das, P. Charaborty, J. Inorg. Nucl. Chem. 43(8) (1981) 1909

53.S. Kuamura, H. Kuraku, K. Kurotaki, Anal. Chim. Acta (1970) 317

54.L.H. Baetsle, D. Huys, D. van Deyck, J. Inorg. Nucl. Chem. 27 (1965) 2385

55.R.B. Hahn, H.C. Clein, Anal. Chem. 40 (1968) 1135

56.W. Drehaus, M. Jekel, U. Hildebrandt, J. Water Services Res. & Tech.-Aqua 47(1) (1998) 30

57.Z. Goerlich, Zes. Nauk. Univ. Jagiel. Nauk.Chem. 7(1962) 5

58. Yu. P. Novikov et al., Radiokhimiya 19 (1977) 660

59.Yu. P. Novikov et al., Radiokhimiya 19 (1977) 653

60.M. Qureshi, J.P. Rawat, A.P. Gupta, Ind. J. Technol. 15 (1977) 80

61. S. Aleksandrov, God. Sofii. Univ. Khim. Fak. 68 (1977) 291

62. K.G. Varshney, S. Naheed, J. Inorg. Nucl. Chem. 39 (1977) 2075

63. R.P. Singh, R.P. Khatri, J. Dubois, S.S. Gaur, M. Abe, J. Chem. Soc., Dalton Trans. (1990) 947

64. R. Van, J. Smith, W. Robb, J.J. Jacobs, Nucleonics 17(g) (1969) 116

65. Y. Xintian, S. Zhaoxiang, Chim. J. React. Polym. 7(1) (1998) 25

66. D.K. Singh, P. Mehrota, Bull. Chem. Soc. Jpn. 63 (1990) 3647

67. D.K. Singh, A. Darbari, Bull. Chem. Soc. Jpn. 61(1988) 1369

68 K.G. Varshney, A.A. Khan, J. Inorg. Nucl. Chem. 41 (1979) 241

69.A. Dyer, A.M. Yosuf, J. Inorg. Nucl.Chem.41 (1979) 1479

70.K.G. Varshney, A.A. Khan, M.S. Siddiqui, Colloids Surf. 36 (1989) 405

71.K.G. Varshney, A. Premdas, J. Liq. Chromatogr. 4 (1981) 245

72.T.N. Dave, V.K. Induse Khar, J. Chem. Technol. Biotechnol. 36 (1986) 31

73.N.Z. Rajie, D.R. Stojakovic, Croat. Chem. Acta. 60 (1987) 735

74.S.A. Nabi, Z.M. Siddiqui, W.U. Farooqui, Bull. Chem. Soc. Jpn. 55 (1982) 503

75. K.G. Varshney, U. Sharma, S. Rani, Ind. J. Technol. 22 (1984) 99

76. S.A. Nabi, Z.M. Siddiqui, W.U. Farooqui, Bull. Chem. Soc. Jpn. 55 (1982) 2642

77. S.A. Nabi, W.A. Siddiqui, J. Liq. Chromaogr. 8(6) (1985) 1159

78. M. Qureshi, N.A. Shakeel, S.N.A. Rizvi, A.P. Gupta, J. Ind. Chem. Soc. 64 (1987) 15

79. Y. Su, M.L. Balmer, B.C. Bunker, Mater. Res. Soc. Symp. Proc. 465 (1997) 457

80. M.G. Marageh, S.W. Hussain, A.R. Khanchi, J. Radioanal. Nucl. Chem. 241 (1999) 139

81.K.G. Varshney, A.A. Khan, J. Inorg. Nucl. Chem. 41

(1979) 241

82. S.A. Nabi, Z.M. Siddiqi, Bull. Chem. Soc. Jpn. 58 (1985) 724

83. X. Yu, Z. Sun, Chin, J. React. Funct. Polym. 7 (1998) 25

84. J.P. Rawat, M.A. Khan, Ann. Chem. 69 (1979) 525

85. K.G. Varshney, K. Agrawal, S. Agrawal, V. Saxena, A.R. Khan, Coll. Surf. 29 (1988) 175

86. J.N. Singh, S.N. Tandon, G.S.Gill, Ind. J. Chem. A 20A (1981) 1110

87. W.A. Siddiqi, S.T. Ahmad, Chem. Anal. (Warsaw) 42 (1997) 377

88. S.J. Naqvi, D. Huys, L.H. Baetsle, J. Inorg. Nucl. Chem. 33 (1971) 23

89. S. Kuznicki, R.J. Madon, S. Gerald, K.A. Thrush, Eur. Pat. Appl. E.P. 405, 978, 28 (1989).

90. Z. Sun, S. Tao, Li Zi Jiao Huan Yu Xifu 6 (1990) 431

91. X. Yu. Z. Sun, Beijing Shifan Daxue Xuebao Zirankexueban 32 (1996) 243

92. X. Xintian, Z. Sun, X. Sun, Li Zi Jiao Huan Yu Xifu 13 (1997) 239

93. Z.M. Siddiqi, D. Pathania, J. Chromatogr. A 987 (2003)147

94. L.M. Berardelli, A. Laginestra, M.A. Massucci, K.G. Varshney, J. Chem. Soc. Dalton Trans. 9 (1985) 1737

95. P.V. Singh, J.P. Rawat, N. Rahman, Ind. J. of Chemistry 41A (2002) 1616

96. T. Nishi, I. Fugiwara, Kyoto Daigaku Kogaku Kenkyusho Iho 39 (1971) 23

97. N.J. Singh, S.N. Tandon, J. Radioanal. Chem. 49(1979) 195

98. K.G. Varshney, A.Premdas, Sep. Sci. Technol. 18(1) (1983) 59

99. K.G. Varshney,, S. Agrawal, K. Varshney, Sep. Sci.Technol. 18(11) (1983) 59

100. A.K. Mishra, R.P.S. Rajput, J. Planar Chromatogr. 3(1990) 83

101. P.S. Thind, S.K. Mittal, S. Gujral, Synth. React. Inorg. Met. Org. Chem. 18 (1988) 593

102. E.S. Boichinova, G.N. Strelnikova, Zh. Prikl. Khim.(Leningrad) 40 (1967) 1443

103. J.S. Gill, S.N. Tandon, J. Radioanal. Chem. 13 (1973) 391

104. E.S. Boichinova, R.B. Chetverina, Zh. Prikl. Khim.(Leningrad) 41 (1968) 2656

105. S.A. Nabi, A. Islam, N. Rahman, Ann. Chim. Sci. Mat.2(7) (1997) 463

106. D. Naumann, Kerenergie 6 (1963) 173

107. K. V. Barsukova, G.N. Radionova, Radio Kimiya 14(1972) 225

108. B. Buna, U. Chudasama, Bull. Mater. Sci. 19 (1996) 405

109. S.Z. Qureshi, N. Rahman, Bull. Chem. Soc. Jpn. 60(1989) 2627

110. S.Z. Qureshi, N. Rahman, Ind. J. Chem. Sec. A 28A(1989) 349

111. S.A. Nabi, R.A.K. Rao, W.A. Siddiqui, J. Liq. Chromatogr. 6(4) (1983) 777

112. Y. Yazawa, T. Eguchi, K. Takaguchi, I. Tomita, Bull. Chem. Soc. Jpn. 53 (1979) 2923

113. S.K. Shakshooki, N. Naqvi, J. Kowalczyk, S. Khalil, M. Rais, F. Tarish, Reac. Funct. Polym. Ion exch. Sorbent 7 (1988) 221

114. S.K. Shakshooki, L. Szites, O. Azzabi, N. Naqvi, J. Kowalczyk, J. Radioanal. Nucl. Chem. 121 (1988) 175

115. S.K. Shakshooki, L. Szites, A. Dehair, Y. Elmismary, S. Haranga, N. Benfaid, A. Benhameed, A.Maiof, J.Radioanal. Nucl.Chem. 121 (1988) 185

116. S.K. Shakshooki, L. Szites Prikl. Khim. 46 (1973) 2432

117. A.K. Jain, S. Agrawal, R.P. Singh, J. Radioachem. 54 (1979) 171

118. A.P. Gupta, P.K. Varshney, K. Pradeep, Synth. React. Inorg. Met-Org. Chem. 28 (1998) 105

119. S.K. Mittal, P. Singh, J. New Mat. Electrochem. System 4 (2001) 221

120. T. Nishi, I. Fujihara, Kyoto Daigabu Kagabu Kenkyusho Iho 39 (1971) 23

121. S.Z. Qureshi,G. Asif, M.R. Khayar, Ann. Chim. 24 (1999) 545

122. Z. Sun, X-Lui, Beijing Shifan Daxue Xuebao Zirankexueban 32 (1996) 102

123. J.P. Rawat, R.A. Khan, Ind. J. Chem. A 19 (1980) 925

124. P.V. Singh, J.P. Rawat, N. Rahman, Talanta 59 (2003) 443

125. S.A. Nabi, Mu. Naushad, Inamuddin, J. Hazard. Mater.142 (2007) 404

126. K.G. Varshney, V. Jain, N. Tayal, Ind. J. Chem. Technol. 10 (2003) 186

127. M.M. Collinson, Crit. Rev. Anal. Chem. 29 (1999) 289

128. G. Philipp H. Schmidt, J. Non- Cryst.Solids 63 (1984) 283

129. A.A. Khan, Inamuddin, M.M. Alam, Mater. Res. Bull. 40 (2005) 289

130. A.A. Khan, Ram Niwas, K.G. Vershney, Coll. Sur. (A) 150 (1999) 7

131. A.A. Khan, Ram Niwas, K.G. Vershney, Ind. J. Chem. 37A (1998) 469

132. A.A. Khan, R. Niwas, M.M. Alam, Indian J. Chem. Technol. 9 (2002) 256

133. B. Pandit and U. Chudasma; Bull. Mater. Sci. 24(3) (2001) 265

134. K.G. Varshney, A.H. Pandith; Chem. Environ. Res. 5 (1996) 1

135. K.G. Varshney, P. Gupta, A. 22ndNational Conference in Chemistry Agrawal;'03, Indian Council of Chemists, I.I.T., Roorkee, (2003).

136. P.Gomez-Romero,Adv.Mater.,13(2001)163.

138 H. Shirawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang and A. Heeger, J. Chem   . Soc.Chem.Communication,(1977)578.

139.K. Gurunathan, A.Vadivel Murugan, R. Marimuthu, U.P. Mulik and D.P. Amalnerkar,Mater.Chem.Phys., 61 (1999)173.

140.G. Gustaffson, Y.Gao, G.M. Treacy, F. Klavetter, N. Colaneri and A.J. Heeger, Nature, 357(1992) 477

141.J.C. Carlbergand O. Inganas, J. Electrochem.Soc.,144(1997) L61