Advances in Inorganic Ion Exchangers and Their Applications
A Review Article

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Abstract
This material is a brief review of ion exchange materials with emphasis of inorganic ion exchangers aimed at giving a short and precise discussion of the role of separation, the preference of inorganic ion exchangers than that of organic once and advances of inorganic ion exchangers. Thus, it begins with brief introduction of ion-exchange materials and their types as well as their many derivatives and describes inorganic ion exchangers to nanocomposite cation exchange materials and their technological improvement from old era to latest age of nano. In addition, this review tries to address so many applications of ion-exchange materials such as, antimicrobial activity, catalysis, hydrometallurgy, bimolecular separations, chromatography and environmental science engineering etc., which are directly related with green chemistry and making processes easier for humans well being.

Keywords: Inorganic ion exchangers, cation exchange materials, nanocomposite cation exchangers.

Introduction

Separation has very important applications in various fields namely medicine, agriculture and environmental analysis. It is basically a pre-treatment method which, usually proceeds any quantitative or qualitative analysis. Separation involves both classical and modern techniques. The examples of the classical methods are precipitation and distillation. The general methods of separation include distillation, extraction, precipitation, crystallization, dialysis, diffusion etc. The most modern and versatile techniques used for the purpose of separations are chromatography, electrophoresis and ion exchange chromatography. Ion exchange chromatography has emerged as a most versatile and standard analytical tool (Naushad, 2009).

Ion exchange

Ion exchange as a separation process is relatively facile and energy-efficient compared to other common solution phase separation procedures used in industry (e.g. solvent extraction and precipitation) (Teresia Moller, 2002). Furthermore, it has high treatment capacity, high removal efficiency and fast kinetics and can also be utilized in metal recovery and water reuse, which are of economical importance (Akieh *et al.*, 2008).

Ion exchange was originally discovered to take place in soils, such as clays and zeolites. These materials found application as water softeners, but the first commercially available ion exchangers were amorphous aluminosilicate gels. They were of low chemical stability and a need for alternatives led to the development and synthesis of organic ion exchange resins in the 1930's. However, the beginning of nuclear technology in the 1940's demanded materials with better thermal (>150°C) stability (Clearfield, 1982).

Organic ion exchangers

Generally, the organic exchanger is built from a cross-linked hydrocarbon polymer backbone, such as the polystyrenedivinylbenzene (SDVB), to which charged functional groups are attached. Depending on the nature of the functional group, the resins range from strong acidic cation exchangers ($-SO_3^-$) to strong basic anion exchangers ($-N(CH_3)_3^+$) (Lehto, 2000). Another group of organic resins is the chelating resins, which have donor atoms such as the nitrogen in $R-N-(CH_2COOH)_2$ (iminodiacetic acid) which can form covalent or ionic bonds with metals that are being sorbed (Helfferich, 1995). However, chelating resins are kinetically rather slow and more expensive than conventional resins. The organic resins are widely used in hydrometallurgic industry.

Although inorganic ion exchange materials were first to be recognized, they lost their utility after the discovery of organic resins due to their relatively low ion exchange capacity and chemical instability (Teresia Moller, 2002). The main advantages of synthetic organic ion exchange resins are their high capacity, wide applicability and wide versatility relative to some synthetic inorganic materials (Nabi *et al.*, 2007b; Nabi and Naushad, 2008). But they also have some severe limitations.

The main limitations are their limited radiation and thermal stabilities (Nabi and Naushad, 2008). At a total absorbed radiation dose of 109 to 1010 rads most organic resins will exhibit a severe reduction in their ion exchange capacity (10 to 100% capacity loss); due to physical degradation both at the molecular and macroscopic level (IAEA, 2002; Naushad, 2009). In addition, organic resins are not selective (Malinen *et al.*, 2009; Zonoz *et al.*, 2009). Hence, revival of the interest in inorganic ion exchange materials took place in the 20th century because of their use in the field of nuclear research. At that time there was need of some new materials that were stable at high temperatures and in presence of intense radioactive radiations (Naushad, 2009). Nowadays inorganic ion exchangers are used in different applications at various fields as it has been reported in several literatures.

Inorganic ion exchangers

Interest in the industrial use of inorganic ion exchangers has increased rapidly since the mid 1980's. Increased environmental awareness has resulted in stricter regulations for waste releases and more effective treatment methods are required to meet these conditions. Toxic metal ions are serious health hazard and every possible care should be taken to keep them isolated from getting mixed into air, water and soil. Hence, scientists have developed methods to determine and isolate them before entering to our ecosystem (Shashkova *et al.*, 1999). Ion exchange is considered as a time-honored analytical tool for analysis of the complex mixtures in diverse fields (Nabi *et al.*, 2007b).

It was found that inorganic ion exchangers can operate in extreme conditions (high temperature or strong radiation fields, in the presence of organic solvents and/or oxidants (Clearfield *et al.*, 1998). These materials also had other important and advantageous properties needed in efficient separation of ions, such as high selectivity and capacity (Zhang *et al.*, 2009; Nabi *et al.*, 2009; Akieh *et al.*, 2008). Most synthetic inorganic ion exchangers proved to be superior to many organic resins in these respect. Common organic ion exchange resins were found to be inadequate under these conditions, as they were greatly degraded and lost their ion exchange properties (Nilchi *et al.*, 2006, 2009). Moreover, inorganic ion exchangers have advantage in that they have a smaller tendency to swell in contact with water (Yoshitaka and Silva, 1990). Therefore, the focus of researchers turned to inorganic ion exchangers.

An active search for new selective ion exchangers and adsorbents undertaken in the past several decades resulted in discovery of a wide variety of synthetic inorganic compounds exhibiting ion-exchange properties (Parida *et al.*, 2004). Because of their being disadvantageous in unsuitable granulometric and mechanical properties, many methods have been proposed for improving the properties of inorganic ion-exchangers (Yavari *et al.*, 2008).

Traditionally the development of new materials for specific, desired conditions by the 'trial and error' approach has required a great deal of experimental effort and time. With the understanding of the origin of selectivity in inorganic ion exchangers, one could achieve greater control over the properties of the materials through synthetic design, and thus fine-tune the ion exchange properties for highly selective separation applications for almost any desired conditions. By slightly altering the composition through systematic changes in synthetic variables and framework cation substitution, ion exchangers with desirable properties may be developed (Behrens *et al.,* 1998)

Hybrid organic - inorganic ion exchangers

Incidentally, materials that contain both organic and inorganic moieties offer an attractive field of research due to their composite properties and appear as creative alternative for obtaining new materials. The limitations with the existing organic ion exchangers is that the mechanical strength and removal capacity tend to decrease at high temperatures and degradation of ion exchange properties under high radiation conditions whereas problem with inorganic ion exchangers is their low mechanical and chemical strength and difficulty in obtaining granulated materials with suitable mechanical properties for use in column application than organic ion exchangers. To overcome these limitations hybrid ion exchangers have been introduced which conjugate mechanical properties of poly-mer with intrinsic properties of inorganic compound. Synthesis of hybrid ion exchangers with controlled functionality and hydrophobicity open new avenues for organo-metallic chemistry and there use as sorbents (Nilch *et al.*, 2006), ion exchangers (Siddiqui *et al.*, 2007), catalysts (Arrad and Sasson, 1989) and in ion-selective electrodes (Rai and Chattopadhyaya, 2002). In the continuing quest for these materials large number of hybrid ion exchangers based on acrylonitrile (Varshney *et al.*, 1998), nylon-6,6 (Inamuddin *et al.*, 2007), acrylamide (Varshney *et al.*, 2003), triethyammonium (Singh *et al.*, 2002), polypyrrole/polyantimonic acid (khan and Alam, 2004) and poly-*o*-toluidine (Khan *et al.*, 2007) have been synthesized.

Many investigators have introduced organic–inorganic ion-exchangers consisting of inorganic ion-exchangers and organic binding matrices (Sundaram, and Meenakshi, 2009). These materials have conjugated the mechanical properties of the inorganic compound creating a new class of hybrid inorganic – organic materials. These hybrid materials have better mechanical, chemical, thermal and radiation stabilities, reproducibility and high selectivity for toxic metal ions (Chubar *et al.*, 2005).

In order to obtain associated organic and inorganic materials as ion-exchangers, attempts have been made to develop a new class of composite ion-exchangers by the incorporation of electrically conducting organic polymers (polyaniline, polypyrrole, polythiophene, poly-o-toluidine, poly-o-anisidine etc.) into the matrices of inorganic precipitates of multivalent metal acid salts. These composite materials are attractive for the purpose of creating high performance or high functional polymeric materials that are expected to provide many possibilities, termed as ‘organic-inorganic’ hybrid ion-exchangers with better chemical, mechanical, and thermal stabilities, reproducibility and possessing good selectivity for heavy metals indicating its useful environmental applications. Many ‘organic-inorganic’ composite ion-exchangers have been developed earlier by incorporation of organic monomers into inorganic matrix, by way of pillaring or non-pillaring methods (Khan *et al.*, 2012).

Nano composite ion exchangers

Conventional, macroscopic composite materials such as adobe is a mixture of clay and straw that serves as an effective structural composite material which has been used to make bricks and wall in arid regions and these along with reinforced concrete has shaped our world during the past. Yet when it comes to the microscopic world, reduced particle size boosts the importance of the interphase in composite mixtures and this is especially important for a new class of recently developed materials named, the nano - composites. The definition of “nanocomposite material” has broadened significantly to encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional materials, amorphous or crystalline, made of distinctly dissimilar components which are mixed at the nanometer scale (Gomez-Romero, 2001).

Nanocomposite is a distinct form of composite materials, which involves embedding nano or molecular domain sized particles into an organic polymer, metal or ceramic matrix material. In all cases, it is perceived that the intimate inclusion of these nanoparticles in these matrices can completely change the properties of these materials. The nanoparticles can serve as matrix reinforcement in order to change the physical properties of these base materials. With such small inclusions, a large amount of interfacial phase material is now included in the bulk of these nanocomposites, enabling a complete transformation of the material’s chemical, mechanical and morphological domain structure. Much of today’s research activity in the field of polymer based organic-inorganic hybrid nanocomposites exhibits mechanical, electrical properties superior to those of their separate components (Khan *et al.*, 2012).

The nanocomposite ion exchangers are multifunctional materials which show diverse applications due to their surface tailored properties in nano dimensions range. Biopolymer based nanocomposite materials are interesting field of investigation. As incorporation of biopolymers provides mechanical strength and greater surface arewith largenumber of surface active sites forenhancedion exchange activity. Thus, polymer based nanocomposite ion exchanger is a new and novel field of research focusing on fabrication and implementation of these materials for environmental remediation. The attachment of organic counterpart makes them suitable for column operations, leading to enhanced ion exchange capacity and better physicochemical properties. The nano composite ion exchangers are finding various applications in diverse fields including ion selective electrodes, antimicrobial activity, catalysis, hydrometallurgy, bimolecular separations, chromatography and environmental science engineering, etc. (Sharma *et al.*, 2014).

Applications of Inorganic and nano composite ion exchangers

Ion exchangers, organic and inorganic, have been used in different fields. However, synthetic and natural inorganic ion exchangers and adsorbents offer definite advantages over well-known and traditionally used organic resins to the extent that their chemical properties, radiation and thermal stability, resistance to oxidation and selectivity to certain ions are concerned (Maria *et al.*, 2005). Because of their high thermal/chemical stability, resistance to oxidation and radiation, and greater affinity to certain ions, these compounds (hydrated oxides, insoluble acid salts of polyvalent metals, heteropolyacids, metal ferrocyanides, etc.) are regarded as promising materials for different applications (Parida *et al.*, 2004). Many selective inorganic ion exchange materials have been synthesized during the last four decades and found many applications in the areas of separation technology, ion exchange catalysis, and nuclear industry (Claudia *et al.*, 2005).

A number of natural and synthetic inorganic ion exchangers that exist today have been used in different applications. Inorganic exchangers are used in heavy toxic metal removal (Pan *et al.*, 2007; Akieh *et al.*, 2008; Sepehrian *et al.*, 2009; Dabrowski *et al.*, 2004), in radionuclide removal (Zonoz *et al.*, 2009; Dhara *et al.*, 2009; El-Naggar *et al.*, 2007; Harjula *et al.*, 2002), in separations (Sarzanini and Bruzzoniti, 2005; Colenutt and Trenchard, 1985), in water treatment systems (Naushad, 2009) and the like.

The Nano composite ion exchangers are finding various applications in diverse fields including ion selective electrodes, antimicrobial activity, catalysis, hydrometallurgy, bimolecular separations, chromatography and environmental science engineering, etc.

Conclusions

This review is all about advances with respect to ion exchangers with more emphasis on inorganic and composite organic –inorganic ion exchangers. It tried to review briefly the inorganic ion exchangers and composite ion exchangers from the micro to the nano level with their advantages and limitations. Hence, From this review it can be concluded that nano composite ion exchangers has shown a great advances with respect to their mechanical, physical and chemical properties which make them an attractive materials in making the environment more greener and make processes very easy as they have various applications.

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