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Recent advances of using polymer nanocomposites for the removal of heavy metal ions from waste water: a review

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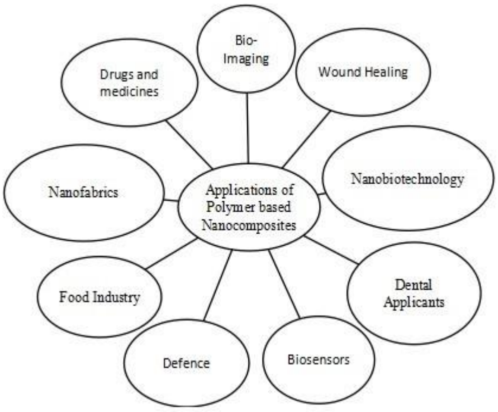
Graphical abstract



Applications of Polymer based Nanocomposites

Abstract

A major factor in the development of modern environmental engineering is the necessity of treating water pollutants. The effective removal of metallic ions of wastewater systems, using adsorption techniques, different adsorbents have been widely utilized; among these adsorbents, polymer-based composites have garnered a lot of interest due to their characteristics of environmental harmlessness and degradability. By combining the best features of both polymer and nanocomposites can offer improved chemical, physical, mechanical, and compatibility over single polymers. The review underscores the importance of polymer-based nanocomposites in offering inventive wastewater treatment methods. A thorough examination of current research and obstacles in the field of developing nanotechnology highlights these materials' ability to address the intricate problem of heavy metal ion contamination. The removal of heavy metal ions from various wastewater sources can be accomplished sustainably and effectively by integrating nanocomposites, with an emphasis on their design and manufacture. The investigation of new advances in polymer nanocomposites for the removal of heavy metal ions lays the groundwork for further study and creativity in this crucial area of environmental engineering. Using the adaptability of polymers and the special qualities of nanomaterials, this strategy develops cutting-edge solutions to deal with the intricate problems brought on by heavy metal ion pollution. Through a focus on accuracy in the design and manufacturing of these nanocomposites, scientists and industry professionals can create materials that are specialised, effective, and can make a substantial contribution to the development of wastewater treatment systems. The purpose of this research is recent analyses and challenges in the field of nanotechnology development. The data presented in this analysis will be helpful for future efforts to design and produce polymer-based Nanocomposites for the removal of a wide range of heavy metal ions

Keywords: Nanocomposites; chitosan; nanocomposites; polymer: gelatine

1. Introduction

Over the ages, humans have gradually increased their abilities to identify contamination of water. While the drinking taps water is portable and safe, all over the world. Tragically, this scenario is not generally relevant because more than 844 million individuals globally lack safe drinking water access according to the data of WHO/UNICEF in the year 2017. Meanwhile, under the auspices of the UN Sustainable Development Goals, these figures are decreasing day by day. In contrast, industrialization, changes in global climate and rural-to-urban movement of the population from rural areas to urbanization lead to a decrease in water availability, and it appears difficult to achieve additional gains. The growing pollution caused by industrialization and urbanization has harmed the future of humanity. Heavy metals, dyes, chemical compounds, and other pollutants are contaminating drinking water at an alarming rate.

Amongst some of the world's numerous environmental issues, one of the most pressing is the efficient use of water resources. The treatment of wastewater released from anthropogenic sources including such industries, shipping, nuclear, battery, metallurgical, mining, tannery, chemical, agriculture, and numerous others is the solution of all these. Wastewater treatment is necessary to reduce heavy metal discharge, which is among the most toxic or physiologically hazardous aspects of industrial wastes (Ariffin *et al*. 2017; Roccaro *et al*. 2013). As a result, contamination with heavy metals has become a major issue all across the world, particularly in developing nations. Metals with densities greater than 5 g/cm3, such as zinc (Zn), lead (Pb), chromium (Cr), arsenic (As), mercury (Hg), and others, are classified as heavy metals (Oves *et al*. 2012). These heavy metals' electronic shells and atomic structure indicate their reactivity, complexation and significant biological and physiological activity, which lead to a variety of health and environmental hazards. In 1797, chromium was recognized inside the mineral occurrences (PbCrO4) as a component with strong colouring potential and also was widely employed as a pigment, from where the word chromium was formed, where chroma' signifies colour. Cr is released into the environment via soil, water, soil, dust, volcanic, atmospheric gases, and rocks (Shanker *et al*. 2005). Typically, chromium is tightly linked to important rock-derived elements and Fe oxides (Quantin *et al*. 2008). Wastewater frequently contains lead, cadmium, mercury, arsenic, nickel, copper and zinc. The industrial operations, agricultural runoff, and technological waste disposal are some of the ways that these metals end up in water supplies (Tiwari *et al*. 2023; Sonone *et al*. 2020). Every heavy metal has unique health and environmental risks. Lead and cadmium, for instance, are recognised neurotoxins that, even in little amounts, have a negative impact on human health (Balali-Mood *et al*. 2021; Rehman *et al*. 2018). The mercury is hazardous to both people and wildlife since it is known to bioaccumulate in aquatic environments (Ali *et al*. 2019). Groundwater contamination is a common source of arsenic, which is linked to a number of health problems, notably cancer (kumar *et al*. 2021; Rahaman *et al*. 2021). Even while trace amounts of nickel, copper, and zinc are necessary, when their concentrations beyond allowable limits, they can cause ecological imbalances and adversely affect aquatic life (Uddin *et al*. 2021). To reduce the negative effects of these heavy metals on the environment and protect human health, appropriate treatment of wastewater methods has to address the various issues they raise (Srinivas *et al*. 2017). Most countries' monitoring agencies have set the permissible value for heavy metals in drinking water sources (Lilli *et al*. 2015). Thus, in order to avoid the negative implications of water pollution, such as contaminants in drinking water, wastewater must be treated before it is discharged into the environment (Burakov *et al*. 2018). The substantial heavy metal routes in wastewater and water can be caused by nature or by humans. Natural heavy metal discharges encompass particulates, aerosols, extraction operations, volcanic activity, urban runoff, soil erosion, and so on, whereas human impact includes metal finishing, mining, electroplating processes, textile industries, as well as the nuclear power (Akpor *et al*. 2014). Furthermore, anthropogenic activities including the release of heavy metal-containing harmful chemicals into river systems, massive population increase arising in focused household purposes, and the growth of industries and agriculture all had an impact on the environment (Su *et al*. 2013; Srebotnjak *et al*. 2012; Islam *et al*. 2014). Heavy metal contamination is a major concern because of its toxicity to animals, plants and humans. Heavy metal concentrations that are excessive have severe consequences for the environment. Heavy metals enter human tissues via a variety of absorption mechanisms, including the soil-food cycle, direct consumption, inhalation, skin contact, and oral intake (Singh and Prasad 2015). Heavy metals at an elevated level can operate as environmental poisons in both terrestrial and marine ecosystems (Nazemi *et al*. 2012; Veschasit *et al*. 2012). Developing and emergent pollutants are frequently discovered in natural water sources, wastewater effluents, as well as sources of drinking water with the danger of affecting the community and environmental quality. This fact underscores the importance of capital revitalization and technological modernisation of underutilized facilities for water treatment. Pollution management and better water treatment methods not only help to reduce lost productivity as well as health-care expenditures, but they also help to increase socioeconomic capability for economic growth (Hutton *et al*. 2004; Sunil *et al*. 2018). Technological innovation has proven crucial in reducing the cost burden of maintaining and operating aging wastewater as well as potable water treatment facilities. The world's population is increasing day by day, putting the globe at risk of acute water scarcity.

Although a trace amount of various heavy metals is vitally required for humans due to the presence of certain cofactors or vitamins or cofactors, overexposure or ingestion of them might have harmful consequences. Furthermore, these poisonous heavy metal ions can cause a variety of bodily and mental abnormalities, including vomiting, nausea, asthma, diarrhoea, pneumonia, skin degradation, liver and kidney malfunction, genetic malformations, losing weight, and various malignancies in accordance with the toxicities and effects of certain heavy metals are highlighted in **Table 1** by the World Health Organization (WHO) (Demirbas 2008).

2. Polymer-nanotechnology for water treatment

In the realm of heavy removal of metal ions in particular, polymer nanotechnology has shown itself to be a creative and promising method of treating water (Khoo *et al*. 2023; Khodakarami *et al*. 2021). The advantage of polymer nanocomposites, that combine the benefits of nanoscale substances with polymer benefits provide improved efficiency, selectivity, or adsorption in the removal of heavy metal ions in water sources (Al Harby *et al*. 2022; Zhao *et al*. 2011). These nanocomposites are frequently made of polymers that have been strengthened by graphene, metal oxides or carbon nanotubes, among other nanoparticles. The absorption capability of polymers is enhanced by the high surface area or reactivity of nanoparticles, offering an efficient way of eliminating heavy metal ions in wastewater (Arunachalam *et al*. 2018; Chaurasia *et al*. 2022; Moghaddam *et al*. 2023). Furthermore, because polymers are adjustable, it is possible to tailor their surface functioning and porosity in order to maximise the elimination of particular heavy metals. By providing enhanced selectivity or recyclability, polymer nanocomposites help solve issues related to conventional water treatment techniques, such as ion exchange and precipitation (Bao *et al*. 2020; Behera *et al*. 2022). Moreover, their adaptability enables the creation of economical and long-lasting heavy elimination of metal ions solutions, in line with the expanding market for green technology (Alsharabasy *et al*. 2021). Research endeavours in the past few years have concentrated on enhancing the performance while synthesis of polymer nanocomposites and investigating their practical applications (Fattahi *et al*. 2023; Gobi *et al*. 2021; Salimian *et al*. 2018). This multidisciplinary strategy, which combines nanotechnology along with polymer science, has enormous potential to improve water treatment techniques and guarantee the effective and environmentally responsible elimination of ions of heavy metals from water sources that have been contaminated (Surmenev *et al*. 2019; Kaur *et al*. 2021; Abbasi *et al*. 2019).Furthermore, the benefits of polymer-nanostructures are such as regulated shape, size, design flexibility, and surface chemistry using multivalent agents, are making them suitable for applications in diverse fields such as targeting and bio-imaging drug administration (Jiang *et al*. 2019; Karthik and Meenakshi 2015; Awual *et al*. 2014; Qiu *et al*. 2015). This will make it easier to optimize drug pharmacokinetics and significantly improve the effectiveness of therapeutic treatment at the single particle or molecular assembly level (Shahat *et al*. 2015; Kyzas and Kostoglou 2015; Kandah and Meunier 2007; Lakouraj *et al*. 2014).

Table 1. Toxicity and permissible limit of heavy metals and their ions in drinking water according to WHO

Heavy metals	Contamination Sources	Drinking water Permissible limit in ppm	Toxicity	References
Lead, Pb (II)	Industrial fuel leaded gasoline and mining sources, Mining resources	0.05	Anaemia, kidneys and liver damages abnormal mental growth in children, insomnia, muscle weakness, dizziness, headache, irritability, reproductive system damage	(Demirbas 2008)
Arsenic, As (V), As (III)	Industrial and chemical wastes	0.05	Bladder, lungs and skin cancers	(Singh *et al*. 2015)
Mercury, Hg (II)	Chemicals, trash incineration, electronic components, barometers, thermometers, batteries, dental amalgams, textile, photography, or pharmaceutical industries, as well as the burning of fossil fuels are all examples of environmental issues.	0.001	Dyspnea, Neurotoxic, chest pain kidney, pulmonary dysfunction, etc.	(Sanfeliu *et al*. 2003)
Chromium, Cr (VI), Cr (III)	Industries involved in leather tanning, electroplating, metal polishing, nuclear power, dyeing, photography, and textiles	0.05	Skin irritation, Lung cancer	(Aroua *et al*. 2007; Bhaumik *et al*. 2012)
Cadmium, Cd (II)	Ni and Cd batteries, nuclear fission, welding, electroplating, plastics and paints, fertilizers, etc.	0.005	Kidney damage, High blood pressure, testicular tissue loss, osteoporosis, as well as red blood cell apoptosis are all symptoms of Itai-Itai illness.	(Nawrot *et al*. 2010; Saleh *et al*. 20)
Zinc, Zn (II)	Industrial procedure	5.0	Stomach pains, rashes on the skin, vomiting, nausea, or anemia	Saleh *et al*. 2022
Copper, Cu (II)	Industrial procedure	1.5	Diarrhea, stomach pain, nausea, vomiting, or even death	(Li *et al*. 2023; Dutta and Sharma 2019)
Cobalt, Co (II)	Electroplating, batteries, dye, mines, nuclear power plants, petroleum, etallurgical, and electronics industries	0.01	Nausea, diarrhoea, asthma, kidney congestion, wrinkling of the skin, and loss of weight, pneumonia,	(Iqbal *et al*. 2024; Noah 2023)
Nickel, Ni(I)	Manufacturing batteries, forging, mining, and electroplating are other related industries.	0.1	Lung and renal issues, dermatitis, immunological hypersensitivity, and carcinogenic	(Dhass *et al*. 2023; Dey *et al*. 2024)

3. Nanocomposites based on polymers

Nanoparticles of various sizes and shapes are distributed throughout the polymer matrices, creating nanocomposites. The nanocomposites made from polymers can vary in size and form. Particulate sizes between 10 and 500 nm have indeed been reported for the majority of the fibrous, platelet-shaped polymer as well as spheroidal nanocomposites. These nanocomposites are subject to a multiphase system that calls for mixing, stabilizations, and compressions (Tseng *et al*. 2009; Sanip *et al*. 2011; Sun *et al*. 2017; Baker *et al*. 2008). Extremely active and responsive these also displayed strong adhesion and adsorption properties (Fu *et al*. 2017). Dimensional and film-forming versatility variations characterize polymer-associated nanocomposites as well. They have superior chemical, mechanical and physical properties, and they contain a variety of binding groups to make them effective for removing pollutants from the sewage disposal (Tseng *et al*. 2009; Sanip *et al*. 2011). Utilizing polymeric materials is an effective method for improving polymers' functional and structural features. In many cases, the characteristics of composites enhanced with nanoparticles exceed those of the polymer itself. The polymers as well as inorganic nanofillers work together to create polymer nanocomposites. Nanofillers, as defined by their large interfacial area to volume ratio, have dimensions of less over 100 nm (Jiao *et al*. 2017). Metals, carbon nanotubes, metal oxides, ceramics and silicates are the most common forms of nanofillers. Some of the characteristics of these filler particles are chemical, mechanical, thermal, electrical, etc. In this regard, manufacturing of components for different applications necessitates a basic knowledge and comprehension of nanostructures. Tuning different parameters as well as attempting to control the interconnection between nanostructured materials and polymers allows for the achievement of novel property combinations, which are the foundation of the physical and psychological characteristics of polymer nano–composites (Giorno *et al*. 2015; Kononova *et al*. 2018).

3.1. Polymer based nanocomposites in environmental remediation

The globe is concerned about the inorganic and organic toxins that are contaminating water supplies worldwide. Pollutants are typically readily mobilised in the environment due to their synthetic nature, high solubility in water, and lack of biodegradability (Nouri *et al*. 2021). Both ecosystems and human health are negatively impacted by their interactions with the environment and accumulation there. The ecosystem is becoming more and more degraded as a result of human activity, which releases harmful pollutants like pesticides, heavy metals, and toxic dyes into the atmosphere, endangering human health and polluting the environment (Tajik *et al*. 2021). Nanocomposites are widely used in many different disciplines, including soil improvement, flame retardancy, removing heavy metals from wastewater, purifying the air, and fertiliser delivery systems (Zhao *et al*. 2011). The composition of nanocomposite provides a vast surface area with unique characteristics. These days, nanocomposite structures are used for food packaging, water purification, soil fertiliser retention, and plant growth enhancement that leads to agricultural development. The characteristics of these nanocomposites depend on the combination of the polymer and nano-filler as well as the characteristics of their constituents.

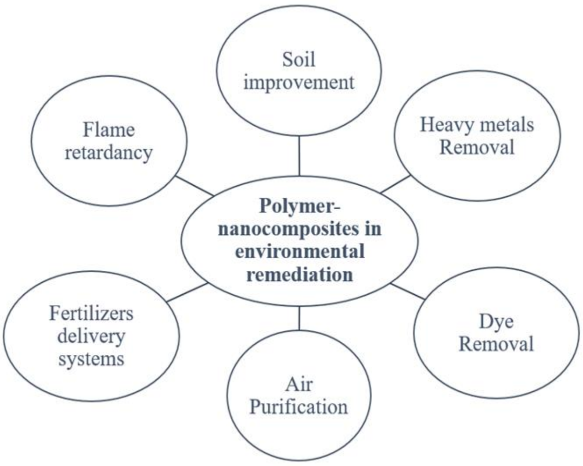


Figure 1. Applications of Polymer based Nanocomposites

Designed through the incorporation of nanoscale elements into polymer matrices, these sophisticated composites present a diverse strategy for tackling environmental issues. Polymeric nanocomposites have outstanding adsorption capabilities in the field of water cleanup, which enables them to effectively remove a variety of pollutants such organic contaminants and heavy metal ions. Their specialised qualities, such as their large surface area and selective affinity, make it possible to target particular pollutants precisely. In addition to treating water, these nanocomposites are essential for soil remediation because they capture and immobilise pollutants, stopping their spread and reducing environmental damage (Khan *et al*. 2021). Furthermore, by absorbing and neutralising airborne contaminants, polymeric nanocomposites in air purification systems improve the quality of the air. Their uses include environmentally friendly packaging materials, where the addition of nanoparticles improves barrier qualities and offers antibacterial capabilities. Polymeric nanocomposites are positioned to continue influencing environmental remediation tactics as continuous research opens up new avenues, providing effective and sustainable solutions to a range of environmental problems.

3.2. techniques for manufacturing of polymer nanocomposites

Most polymeric nanocomposites are produced by the solution approach, which necessitates requiring substantial amounts of organic solvents and has the potential to create environmental pollution. There has been a lot of focus on finding green synthetic alternatives that are also effective. One possible replacement for the standard technique is the use of supercritical carbon dioxide ($scCO_2$). Throughout general, there are three approaches to produce inorganic filler/polymer nanocomposites (**Figure 2**). They include melt mixing and solution mixing, whereby the polymer with inorganic fillers is mixed together directly; (ii) the sol-gel technique, whereby a molecular preparation is reacted with water at room temperature to generate a metal oxide structure; and (iii) in-situ polymer of monomers with in context of fillers.

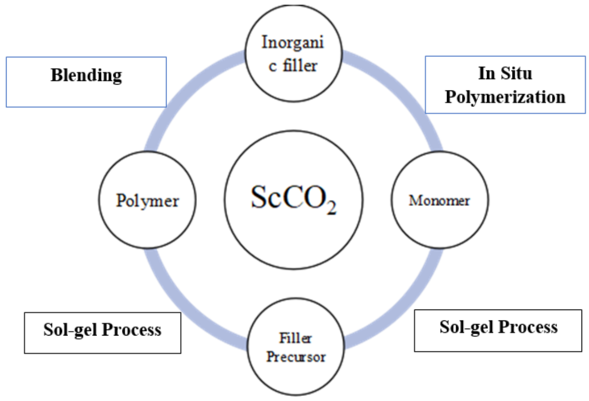


Figure 2. Methods for making nanocomposites out of polymers and inorganic fillers in supercritical carbon dioxide

3.2.1. *Solution processing*

In this technique, several layered silicates are dissolved in a solvent that may dissolve the polymer. These silicate layers form a multi-layered, organised structure around the polymer as the solvent evaporates (**Figure 3**). Exfoliation is another name for this procedure.

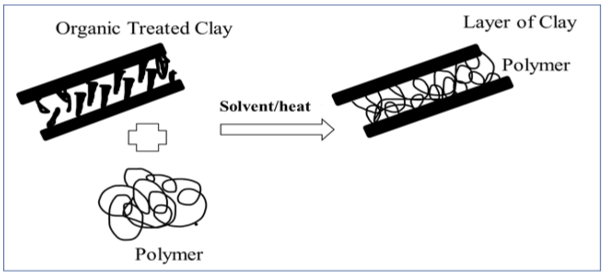


Figure 3. Nanocomposites by employing by solution and melt processing

3.2.2. *Melt processing*

Melt processing is the most sought-after method because of its low cost and adaptability to different formulas (Nazemi 2012). While the polymer is still liquid, it is combined with a layered silicate. Whereas if specified polymer is compatible with layer interfaces, the nanocomposite can be formed by inserting the polymer into the diffusion layer. In this instance, a solvent is unnecessary.

3.2.3. *In-situ polymerization*

In-situ polymerization involves bringing monomers as well as initiators to a site where clays will facilitate the polymerization process. Polymer-clay nanocomposites are formed when growing polymer chains disperse clays and invade interlayer space.

3.2.4. *Polymerization processes*

Polymerization of colloidal sols comprising metal ions as well as monomers is used to generate nanomaterials in this technique. Particle size is affected by factors such as Ostwald ripening, heat coagulation and colloidal sol characteristics.

3.2.5. *Sol-gel technique*

Dissolution of the alkoxides of metals and subsequent polymerisation of the hydrolysis precursors are both part of this process. This process can be used to convert halides, organic metal alkoxides, esters, etc. into inorganic oxides of metallic nanoparticles. Alkyltrimethoxysilane-tetramethoxysilane combinations have indeed been co-hydrolysed and polycondensed to produce transparency films of inorganic/organic hybrid materials. Making organic/inorganic hybrids via the sol-gel technique with metal alkoxides is a viable option.

3.2.6. *Mechanical stirring of nanoparticles and polymers*

Physical forces combining of a precursor solution with such a pre-synthesised, extremely dispersive nanomaterials mixture is technique Gamma-irradiation has been used to create polyacrylamide/cdS nanocomposites.

3.2.7. *Carbon nanotubes nanocomposites*

Changes in characteristics have sparked strong interest in nanocomposites made from polymer with carbon nanotubes (CNTs). The dispersal of CNT through into matrix material is an issue during the fabrication of CNT-polymer nanocomposites. Alternatively, the nanocomposite can be made via in-situ synthesis in the vicinity of CNT or by producing thin films from CNT-suspended polymer solutions. Melting blending nanomaterials with polymers is another method for creating nanocomposite.

3.3. *Adsorption potential of polymer nanocomposites*

Due to the high productivity and relatively low operating expenses, adsorption is a method that is both desirable and realizable. Because of their remarkable performance in a variety of industrial operations (Agboola *et al*. 2019), numerous types of biomasses have been used as adsorbents in a variety of different adsorption processes. On the converse hand, there is a widespread requirement around the world for the development of highly specific adsorbents that can remove hazardous metals and organic pollutants (Msaadi *et al*. 2019). Polymer nanocomposite activated adsorbents have recently come to be regarded as possible components for the removal of various pollutants from effluents. This is due to the fact that these adsorbents possess robust mechanical properties, excellent hydraulics performance, good stability, as well as a surface chemistry that can be manipulated. In particular, the adsorption of the targeted contaminant is highly dependent upon the surface functionality, pore structure, encapsulating moieties, and physical and chemical structure of the adsorbents (Pan *et* *al*. 2018). Nano adsorbents have a very high sorption efficiency and a very fast processing kinetics. This seems to be due to the vast surface area that they contain as well as the ease with which sorption sites can be accessed (Bhaumik *et al*. 2013). Both the design of materials and the dynamics of adsorption are the subject of extensive research (Zhu *et al*. 2013). In addition, the remarkable advantageous, in addition to its low cost and wide availability, are accountable for the outstanding attention that it has garnered to such an extended degree (Kotal *et al*. 2015).

3.3.1. Nanocomposites of copolymer used as an adsorbent for the metal ions removal

The industrial effluents from manufacturing processes, which contain metal ions, are either directly or discharged directly into water sources such as lakes, rivers, streams and lakes (Fu *et al*. 2011). In most cases, heavy metals are incapable of being digested or biodegraded; as a result, they are persistent pollutants in the ecosystem. Nowadays, metal ion contamination in wastewater has become the primary ecological concern that poses a threat to human beings on a global scale (Zare *et al*. 2018). This is due to the movement of pollutants in water bodies that are natural as well as the toxicity of the contaminants themselves. The removal of different metal ions from effluent can be accomplished by the utilization of a wide variety of techniques, comprising electrochemical, ion-exchange, membrane filtration, and adsorption techniques (Bernardo *et al*. 2009). As a consequence of the low capital cost of a system, the simplicity of the approach, the simplicity of the functioning principles, as well as the lack of sensitivity to harmful contaminants, adsorption is the one that is utilized the most frequently amongst them (Javadian *et al*. 2014). In addition, the production of harmful chemicals is not a consequence of the adsorption process (Hua *et al*. 2012). The metal ions adsorption is influenced by an array of factors, including ph of the solution, the amount of adsorbent used, the length of time the two substances are in contact with one another, the content of initially metal ions, or temperature (Zare *et al*. 2015).

In the past ten years, polymeric biosorbents have emerged as potential replacements for traditional adsorbents because of their huge surface area, surface characteristics that is amenable to modification, superior mechanical rigidity, pore size distribution, and feasible reinforcement under numerous reasons (Mahmoodi *et al*. 2013). Conducting polymers are made up of molecules that are organic by their very make-up as well as their capacity to carry electricity and imitate the properties of metals thanks to the presence of electrons that act as charge transfer. Certain kinds of polymers might have a semi-conducting property. Polymer electrolytes constitute non-thermoplastic by their very character and belong to the category of organic materials (Shahabuddin 2016). Throughout conductive polymers do not conduct electricity. For the most part, trying to conduct organic polymers including such polythiophene, polyaniline and polypyrrole have been the subject of a great deal of research over the course of the past two decades (Ansari 2006). This can be attributed to the outstanding conductivity of electricity that these materials exhibit in addition to their better environmental stabilisation. The potential application of these conducting polymer associated adsorbents and their composites for adsorbents for metallic ions found in wastewater, such like manganese, iron, magnesium, cobalt, arsenic, nickel, etc., has sparked considerable interest (Zare *et al*. 2018; Bernardo *et al*. 2009).

As a result of the high number of amine or imine chemical bonding present in their respective polyaniline, polymer chains and its derivatives have demonstrated strong adsorption capabilities. As a consequence of this, they are utilized in the process of adsorption in order to remove wastewater that contains metal ions. Polyaniline as well as its derivatives have lately come to the attention of researchers who are looking into their potential use as effective nanoadsorbents for such removal of metal ions (Zhu *et al*. 2013). It has been determined that polyaniline particles are effective at removing mercury ions from water-based solutions (Wang *et al*. 2009). Based on the results of the study, it was determined that the potential of polyaniline nanoparticles for the adsorbed of metallic ions was found to be 600 mg g-1 (Wang *et al*. 2009). Furthermore addition, a pH of around 5.5 was found to be optimal for the adsorption process of mercury ions upon that polymer matrix. This was possible due to the presence of nitrogen-containing functional groups here on polymer matrix, that are thought to be important for mercury sorption. Chromium ion is yet some other metal ion that is of importance. Because of the toxic and carcinogenic effects that chromium Cr(VI) has on people's health as well as the diverse range of applications that it has in sectors such as mining as well as electroplating (Wang *et al*. 2012), there has been a growing amount of focus on this research field.

Riahi Samani and colleagues conducted research on the removal of Cr(VI) ions in water solution using polyaniline nanoparticles (Riahi Samani *et al*. 2011). These scientists found that the type of solvent that was used in the creation of polyaniline had a significant impact on the shape of the polyaniline, as well as its ability to remove Cr(VI) from a solution. In addition, the peak removal efficiency of Cr(VI) was achieved with the use of the generated polyaniline, which was greater than 90%. In light of the findings of these experiments, it was concluded that the elimination process of polyaniline that has been accountable for the aggregation of surface complexation. Samani and his team also released an investigation on the absorptive properties of polyaniline that was synthesized using an average amount of water and acetonitrile (Samani *et al*. 2012). The powdered polyaniline that had been manufactured was put to use as an adsorption in order to get rid of the harmful chromium (VI) that was present in water solution. The pH of around 7 (a balanced environment) provided the most chances of getting rid of hexavalent chromium, whereas a pH of near about 3 (an acidic situation) provided the greatest possibility of getting rid of total chromium. The highest possible chromium adsorption rate for polyaniline reported determined to be 36.1 mg/g (Samani *et al*. 2012).

Despite the fact that polyaniline is useful for the process of adsorption, the material suffers from a number of significant drawbacks. These include its inability to be separated, its weak conductivity particularly compared to metals, its inefficient usage technology, its propensity to absorb water, and its fragile nature (Nezakati *et al*. 2018). Polyaniline nanocomposites of varying types have indeed been produced with a variety of metal oxides, metals and various nanotubes, among other things, with intention of enhancing the characteristics of polyaniline. Polyaniline nanocomposites were shown to offer valuation qualities, both physically and physiochemically, in a research (Shahabuddin 2016), which supported this finding. Organic and inorganic contaminants have both been absorbed by polyaniline composites, which have been used as an adsorption by researchers (Ayad *et al*. 2013). In addition, polypyrrole biosorbents play a significant part in the removal of metal ions because of the ease and high degree of flexibility with which they can be synthesized, as well as their biocompatibility, high conductivity, stability, good mechanical properties, as well as electrochemical stability (Mahmud *et al*. 2016). In spite of the fact that the effectiveness of sorption process is largely determined by the conditions under which polypyrrole is prepared, there have been a few attempts made to get rid of metal ions by using polypyrrole conducting polymers. These polymers are created through the chemical polymerization of compounds pyrrole with in presence of a number of different oxidants under a variety of conditions (Ansari *et al*. 2006; Kudoh *et al*. 1996, Deng 2004). At a pH of around 5, a significant amount of bovine albumin serum (BSA) was adsorbed on conducting polymers that included chloride adsorption. On the other hand, at a comparable pH, almost little lysozymes were adsorbed. In instance, a significant amount of lysozyme were adsorbed upon polypyrrole containing dodecyl sulfate/polypyrrole containing octadecyl sulfate adsorption at nearly a pH of 10; on the contrary hand, almost no bovine serum albumin were adsorbed through either of these two adsorbent types at that pH.

Polypyrrole's usage has expanded beyond the preliminary application of traditional polymeric materials as a consequence of its ease of use and convenience in replicating the adsorbent once at low cost. Additionally, polypyrrole's good electrical and thermal conductivity, environmentally friendly characteristics, and simplicity in amending into nano - composites have contributed to this development. Taking these characteristics into account, the fusing of nanoparticles in polypyrrole for such manufacturing of polypyrrole-associated nanocomposites has been currently receiving an enormous reaction as a helpful site for advantageously replicating strongly adsorbents to counteract ecological problems (Deng 2004). This is due to the fact that the fusing of nanoparticles in polypyrrole again for manufacturing of polypyrrole-associated nanocomposites is currently receiving an enormous response. Lately, bifunctional nanocomposites made of magnetite as well as maghemite have been utilized for the removal of metal ions. This is primarily due to the stimulatory properties that these nanoparticles possess, such as a vast surface area, a high magnetization, and a massive number of active sites for the adsorbent of metals. In addition, because of their magnetic qualities, they have the capacity to be easily removed from aqueous solutions with the application of an appropriate magnetic field (Olatunji *et al*. 2018). This ability is made possible by the fact that they are magnetic.

3.3.2. Adsorbent properties of polymer nanocomposites for the removal of dye

Because dyes can have hazardous effects on humans, animals, plants and aquatic organisms, their mobility and distribution in waterways has been the subject of a great deal of study over the last three decades. This research has been carried out in great detail. The water's overall quality will suffer if dyes are allowed to be discharged into the source of water. Textiles, dyes, cosmetics, paper, rubber, leather, plastics, foodstuff, as well as plastic enterprises can use massive amounts of dyes for the reason of providing colour to their products. Additionally, these industries imbibe substantial amounts of water, that also results in the generation of a huge considerable quantity of coloured wastewater (Chávez-Guajardo *et al*. 2015). It's indeed possible to categorize the colours found in wastewater according to their excessive oxygen consumption, variable pH, indestructibility, and dependence on a variety of oxidants. Many wastewaters discharged have proven out to be a problem for decolouration as well as demineralization (Vijayakumar *et al*. 2012). This is due to the complicated structures of these industrial wastewaters as well as their strong battle to dilapidation. With in textile industry, almost twenty-five percent of the dyes is wasted during the dyeing techniques, and between 2 and 21% of the dye is lost to various ecological factors as a result of an useful method. Since dyes are so colourful, it can be challenging for aquatic life to receive the necessary amount of sunshine (Saad *et al*. 2017). Because dyes have such a long half-life, its harmful effects have reached a point where they are becoming increasingly difficult to control. Dye residues remain in the environment for an extended time frame because there is no remediation method that can be considered acceptable. Due to the extraordinarily complex nature of their architecture and the chemical basis upon which they are built, dyes are notoriously difficult to eliminate (Kahlon *et al*. 2018). In addition, because of the chemical composition of dyes, they are resistant to an extensive variety of oxidizing agents, chemicals, and heat, all of which are examples of substances that are not physiologically degradable. As a consequence of this, decolorizing the wastewaters once soon as they're released through into aquatic system is not exactly a simple task. Reverse osmosis, Ion exchange, precipitation, reverse osmosis and adsorption are four of the most important technologies that can be used to remove harmful waste out wastewater. There are various different methods that can be used for this purpose. The adsorption method has become the most adaptable and widely used way for the dyes to be removed (Achmad *et al*. 2012; Chagas *et al*. 2013). Among such procedures, it is the adsorption approach which is most widely utilized. In addition to the fact that they are non-toxic as well as biodegradable, naturally synthetic polymers as adsorbents have been gaining more interest as an option for the wastewater management process (Chang *et al*. 2004). The accessibility and affordability of polymer nanocomposites like an adsorbent has stimulated their application for a wide range of purposes. One of these uses is the extraction of waste-water. In addition, the use of polymer nanocomposites since adsorbents has taken on a significant role in recent years. These nanocomposites have outstanding granulometric characteristics, a large surface area, increased active surface area, and are bioactive as well as thermally stable. This makes them an ideal candidate for this role. The chemical and physical properties of functionalized polymer nanocomposites, as well as the ease with which they can be separated and the variety of reactive groups that can be found on the backbone chain, have attracted a significant amount of research (Tanasa *et al*. 2019). In addition, as a result of advancements in adsorbent synthesis as well as functionalization, a reliable forecasting has been made to guarantee that materials are organized in an improved state with a continued to improve presentation of the favoured characteristics of a highly competitive sorbent (Mudhoo *et al*. 2019). This has led to the successful completion of a number of research projects. Because these adsorbents have been functionalized in this way, they are now more receptive to interaction with big dye molecules. In addition to this, it allows for the nature of adsorption to be studied, as well as the subjecting of this behavior to a test performed in binary mixtures (Maleki *et al*. 2017) and ternary dyes complexes (Debnath *et al*. 2017). It is necessary to improve the properties raw adsorbents before they can be used because these materials often have relatively poor adsorption capabilities (Maleki *et al*. 2017; Sojoudi *et al*. 2016). The functionalization of adsorbent can be accomplished through a variety of approaches can be broken down into three primary categories: biological, chemical and physical alterations. The creation of a covalent link between the carbon -bond which is not saturate as well as other groups is an essential component of the process for the covalently derivatization of molecules. The non–covalent interactions functionalization approach is not as long-lasting or sturdy as the coordinate covalent crosslinking technique. Van der Waals interactions, π-π interactions, while ionic interactions are the primary ones that are responsible for noncovalent derivatization (Lau *et al*. 2019). Nevertheless, adsorbent substances can be used for a variety of uses, including the removal of biological pollutants, dyes and metal ions.

4. Nanocomposite matrices based on chitosan

With the advancement of nanotechnology, the chitosan may now be combined with various nanostructures, either incorporated into in the solid matrix or coated on its surface, expanding its applications beyond its traditional role as a pure matrix biocompatible material. Purified biopolymers, like chitosan, can have issues in several key areas: thermal strength, mechanical strength, thermal stability, and barrier characteristics (Bakshi *et al*. 2020). Like a filler spread throughout the entire matrices, and as a coating there at inorganic/organic material surface, in the nanometer level have indeed been introduced to chitosan to eliminate the majority of these structure disadvantages (Kankala *et al*. 2020). Nanotechnology, nanosheets, nanocapsules, nanorods, nanofibres and nanowires are just few of the many nanostructures that can be added to it and disseminated in chitosan for additives (**Figure 4**).

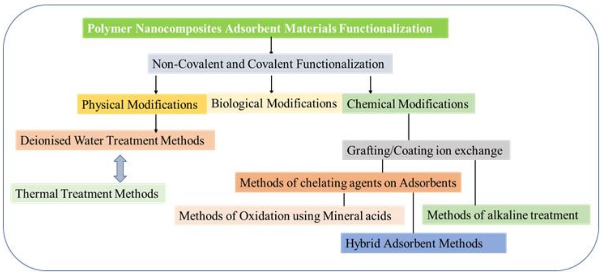


Figure 4. Adsorbent Materials Polymer Nanocomposites Functionalization

4.1. Treatment of wastewater by chitosan

The safe and effective disposal of trash and wastewater is a major issue in every region. Many recent material advancements have highlighted the need of having ready access to clean water as well as effluents disposal. The multi–layered coatings to increase resistance to corrosion (Nasrollahzadeh *et al*. 2021) have seen a rise in attention in chitosan as an entire standalone material and also as composites (Mohammadzadeh *et al*. 2018; Thirugnanasambandham *et al*. 2013). Using chitosan allows for the selective adsorption and removal of many different metal ions, as detailed by Crini *et al*. (2017) looked into the use of chitosan nano - composites in the heavy metal cleanup and shown promising results (Al-Sherbini *et al*. 2019; Cheraghipour and Pakshir 2020; Kenawy *et al*. 2019). Chitosan nanocomposite have been employed to remove contaminants like heavy metal ions Cu(II) as well as Cr(VI) (Anush *et al*. 2020), Cr (VI) (Reis *et al*. 2021), Co (III) (Abdelbasir *et al*. 2021), and dyes (Krishna *et al*. 2021; Mostafa *et al*. 2020) and iron (Shehap *et al*. 2021). Notwithstanding their carcinogenicity, toxicity and hazard to public health, organic dyes are frequently utilized in business. Nanocomposites made from chitosan have great potential as a material for the efficient and environmentally friendly disposal of waste (Rashid *et al*. 2018). There have been an increasing number of recent attempts to eliminate organic dyes by combining chitosan with various ceramic nanotechnology or nanoclays (Rashid *et al*. 2018; da Silva *et al*. 2021). Asgari *et al*. (2020) investigated the feasibility of using chitosan nanomaterials for the elimination of antibiotics in sewage (Krishna *et al*. 2021). The combination of chitosan as well as magnetic Fe3O4 nanocomposites has been studied for its ability to remove metronidazole off wastewater in medical and industrial settings. The ability of chitin to attach semiconductors and metals enables the development of photocatalyst nanocomposites (Ashassi-Sorkhabi and Kazempour 2020). The breakdown of organic contaminants (Huang and Peng 2021) and dye removal efficiency via the Fenton methods can both benefit from the use of these novel nanomaterials (Midya *et al*. 2020). The multipurpose chemical surface groups, high solubility in water, strong chemical reactivity, as well as a polymer with a flexibility all contribute to chitosan and its derivatives' impressive heavy metal ability of adsorption (Alimard 2019). Properties of chitosan's polymeric polymeric chains, which includes several hydroxyl and amino units at the interface, were detailed by Gupta *et al*. (2012) (Vunain *et al*. 2016). Strong chelates bonding with metallic ions including Pb^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} and Cd^{2+} and Zn^{2+} can be made using these chemical groups. According to a recent survey by Zhu *et al*. (2021) (Gupta *et al*. 2012), the adsorption capability of chitosan is limited because of its small particular area of surface. Nanofibres made from chitosan have the potential to vastly improve upon the already impressive effectiveness of the material's individual attributes. Nonetheless, there is still room for development in areas like mechanical strength, stability, as well as reusability. New insights into nanocomposites utilizing chitosan as the substrate may help fill this knowledge gap. Even while chitosan has shown promise in the lab for removing metals from water, there are still challenges to overcome before it can be used on a larger scale to remove the toxic metals found in industrial effluent.

5. Metal oxide nanocomposites

Metal oxide nanotechnology configurations range from nano range particles to tubes, wires and nano frameworks. During this study, we focused mostly on nanocomposites composed of meta/metal oxides loaded filler nanomaterials such as carbon nanofibers or nanotubes and polymers, among many other aspects. Metal oxide or metals nanomaterials such as iron oxide (Fe_2O_3, Fe_3O_4), manganese oxide (MnO_2), zinc oxide (ZnO), titanium dioxide (TiO_2), silica (SiO_2), magnesium oxide (MgO), silver (Ag), aluminum oxide (Al_2O_3), tin (Sn), and among others, have proven to be outstanding due to their related economic feasibility, chemical and biological stability, photocatalytic and non-photocorrosivity (Zhu *et al*. 2021; GLofrano *et al*. 2016). Size changes are expected to influence three major properties of every substance. The structural features, such as crystalline symmetry as well as cell size, come first. Oxide macroscopic particles exhibit stable and long-lasting systems with well-explainable crystallographic pictures. However, as cell size decreases, thermal sustainability can cause changes in cell characteristics or morphological inversions (Shannon *et al*. 2008; Qu *et al*. 2013; Joshi and Rajput 2019). Second, the restriction and quantification of electrons inside a limited container improves nanocomposites electronic and optical conductivity properties (Ray 2012; Liff *et al*. 2007). Once the diameter of the oxide is decreased, the amplitude of the energy band changes (energy gap raises) by modifications in conductance and biochemical activity enabling material processes (Gaharwar *et al*. 2011). Nanoporous oxides have a larger surface area, allowing for effective adsorbents uptake of particulates and small nano-sized pollutants. Permeable structures enable a large number of accessible active sites, significantly shortening the dispersed ion transmission distance, and thus allowing for restricted ion flow. As a result, the productivity of nanoporous metallic nanoparticles in applications like energy storage can be significantly increased as compared to firm structured metal oxide.

5.1. Synthesis of metal oxides nanomaterials

The controlled production of metal oxide nanomaterials is the first stage in nanostructures and is crucial for successful implementations. The two most common methods for creating nanomaterials from gaseous, liquid and solid phases are "top-down" and "bottom-up" (Paul *et al*. 2008). The first strategy involves decreasing the size of the subject matter to the nanoscale, as in erosion processes for example grinding. As shown in **Figure (5)** the bottom-up strategy promotes particle material synthesis from the bottom: atom via atom, molecule through molecule, or cluster through cluster in a gas state or solution form. The latter path is strongly favoured and is widely used in the creation of metal oxide nanoparticles. The controlled production of metal oxide nanomaterials is the first stage in nanotechnology and therefore is essential for successful implementations. There are several known synthetic approaches for metal oxide Nanoparticles includes sol-gel (Goenka *et al*. 2014), chemical precipitation (Mitragotri and Lahann 2009), solvothermal procedure (Satarkar *et al*. 2010), microemulsion (Vaia *et al*. 2008), surface functionalized methods (Dundigalla *et al*. 2005), multiple-pulsed laser deposition (Alayoglu *et al*. 2016) and chemical vapor deposition (Pecquenard *et al*. 1998; Li *et al*. 2008). Among these approaches the methods such as hydrothermal, sol-gel, microemulsion synthesis, and chemical precipitation were shown to be the most versatile and straightforward.

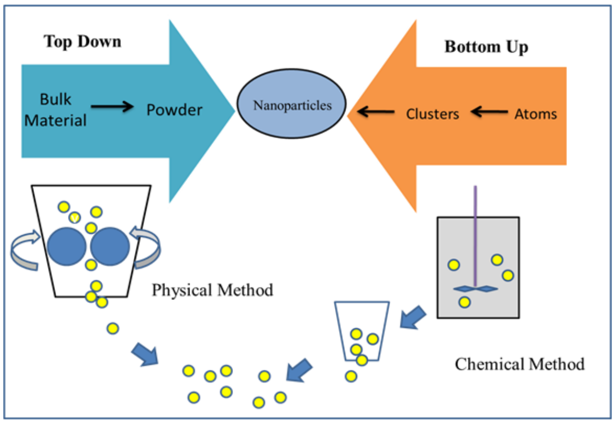


Figure 5. Schematic synthesis pathway of top-down and bottom-up strategies

5.1.1. Chemical precipitation method

Due to the ease of application and effectiveness, it represents the simplest as well as a promising technique. This approach requires the presence of precipitation, coarsening of growth, and/or particle bundling. It is accomplished by adding a base to a metal salt solution within proper circumstances (Mitragotri and Lahann 2009).

5.1.2. Hydrothermal method

It is one of the successful methods for developing the crystalline of several various materials, as well as the particles generated in this system has higher crystalline nature. The reactions are carried out in an autoclave utilizing an aqueous medium, at pressures greater than 2000 psi with temperatures considerably beyond the boiling temperature of the in-usage solvent. Among the main disadvantages of the hydrothermal approach is the slow reaction rate at any specific temperature. Heating in microwave can be employed in conjunction with hydrothermal process, and it has been discovered that the kinematics of crystallization improves with this approach (Mitragotri and Lahann 2009). This combination is known as microwave based hydrothermal biosynthesis.

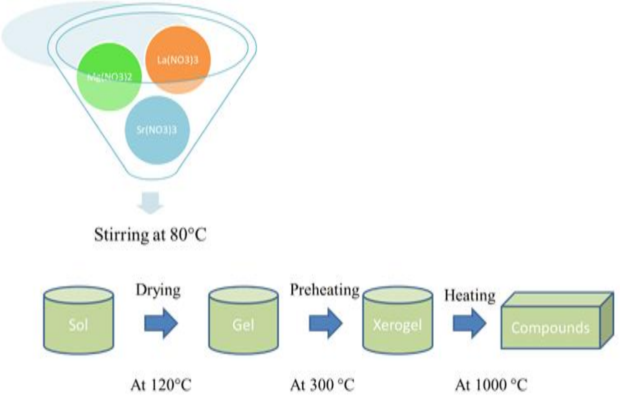


Figure 6. The Sol-gel process is depicted schematically

5.1.3. Sol-gel method

The gentle reaction conditions and the ability to create nanomaterials from precursors, the sol-gel method has attracted attention as a viable technique for the production of nanomaterials (Guglielmi *et al*. 2014). The sol-gel process produces either film (Joshi and Rajput 2019; Ray 2012) or colloid granules (Jeon *et al*. 2003). Micro and nanostructures can be created using the sol-gel process. The reaction conditions have a significant impact on the size, shape, and texture of the finished product (Lee and Park 2003). The procedure incorporates a basic wet chemical change based on condensation and hydrolysis that results in the development of sol, which then ages to form an integrated matrix as gel (Figure 6). The sol-gel approach is also particularly appealing for the creation of multi-component nanostructures, because the slow response kinetics enable efficient engineering structures of the final result. Additional advantage is the fact that reactions are carried out at moderate or ambient temp. Within sol-gel method, artificial substrates experience a series of chemical reactions, resulting in the development of a 3-dimensional molecule network. Among the most popular ways is the breakdown and condensing of metal alkoxides, which results in bigger metal oxide particles that polymerize to create the coating. The sol-gel method allows the coating of surfaces with complicated forms on the nanoscale to micrometer range, which is not possible with other regularly used covering procedures. Inorganic/organic crystals, colloidal particles, even fibers nanotubes have been used as substrates (Goenka *et al*. 2014).

5.1.4. Microemulsion technique

The W/O microemulsion method seems to be another way for creating metal oxide nanoparticles. It's a thermodynamically and isotopically solid Uniphase system composed of a combination of immiscible fluids with nanosized subdomains of distinct polarity-maintained surface-active chemicals interfacial film known as surfactant. Irrespective of metal composition, microcapsules allow for control of metallic particle size with a fine size distribution (Chen and He 2001).

5.1.5. Ceramic methods

The ceramic approach is the oldest method of producing rutile organized metal oxide (Ennas *et al*. 1998). Mechanical treatment is used to crush metal cations carbonates or oxides in the desired rutile phase. However, this technology has a problem because it is unable to generate fine particles, as well as the prolonged milling pulls out undesired environmental contamination, resulting in a broad range of particulate dimensions. The main difficulty encountered with this process is a lack of homogeneity in the synthesized material. Furthermore, the increased temperatures of 1200 K are required to complete the reaction and produce the resulting product of narrow size distribution via sintering.

5.1.6. Combustion synthesis

Combustion biosynthesis is a series of heat energy-releasing (exothermic) events between a reagent as well as an oxidative connection and species conversion. The predominance of the organic compounds, such as hydrocarbons, exists in liquid, gas and solid forms. Combustion technique is a novel way for producing rutile organized particles by exploiting an exergonic oxidation and reduction reaction between metallic nitrate ions and oxalic hydrazine. Metallic nitrate ions are dissolved in a suitable quantity of water in a Pyrex dish in this technique, followed by boiling at 350 °C in an electric furnace. The thermal evaluation frequency of 75 °C min-1 was chosen to create optimum conduction. This method can be utilized to create Ni-Zn as well as Co rutile structures (Nazir *et al*. 2008).

5.2. Characteristics of metal/metal oxide

To properly utilize and select metals and metal oxides, we must first understand their various physical and chemical properties. The chemical and physical properties of unique importance in science are mostly related to the commercial use of metal oxides in ceramics, sensing, and water treatment (Chen *et al*. 2010).

5.2.1. Optical properties

Reflectance, as well as absorbance optics, as well as absorbance optics, are required. The reflectance's dependent on dimensions that are in the frequency of the electromagnetic spectrum, and absorption characteristics establish the principal absorbance actions of solids. Excitation of electrons from conducting to valence band via discrete levels of energy causes semiconductor characteristics (Benvenutti *et al*. 2009; Akhtar *et al*. 2008).

5.2.2. Transportation properties

The electronic/ionic conductivity of oxide compounds has been tentatively determined and is influenced by the nanoscale dimensions of the particles. According to Boltzmann's studies, the number of electrical ion carriers in a molecule contributes to the difference in energy between vibrational modes. Transmission is referred to as p-type doped whenever the bulk of the electric charge is n-type doping and holes when the electric charges carriers are electrons. For ion transport, four mechanisms are available: directly interstitial, vacancy, or growth. Ion deformity occurs in solids in an even distribution and alters the bulk material. Because of the constrained electrical potential reduction at the outermost layer of nano-sized chemicals, the existence of ions aids in the progression of the entire materials (Byrappa and Yoshimura 2012).

5.2.3. Mechanical properties

The main mechanic features are lower releasing stress or toughness and superplasticity at high temperatures. The mechanical property of the metal oxides is primarily concerned with examining sintering, superplastic, and conductility properties. Specifically, a significant number of workings have shown significantly increased sinterability up to 600 K lesser temperatures than that of bulk (Köseoğlu *et al*. 2011; Wang *et al*. 2007; Wang *et al*. 2007).

5.2.4. Chemical properties

Transition metal oxides are used for oxidation-reduction reactions and acidic and basic properties. They are also utilized for absorbance and catalysis. Metal oxides have crucial properties such as synchronizing of outer atoms, oxidation, redution properties, and oxide formation at the outermost surface. Metal oxides with only s or p-type systems in the outer orbital are generally feasible for acidic and basic catalysis (Wang *et al*. 2007; Zhang and Chen 2009; Azari *et al*. 2015).

Conclusions

Nanocomposites have several applications and have advanced rapidly. Improved thermal, physical and other one-of-a-kind qualities can be engineered into nanocomposites. These can be manufactured utilizing straightforward and low-cost methods, and they exhibit better characteristics to common microscale composites. The composite substances have acquired new capabilities thanks to the incorporation of nanoparticles in minute quantities. Due to their significance in both academia and industry, polymer nanocomposites have garnered a lot of interest in recent years.

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