

Nanomaterials as Sorbents for Environmental Remediation

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Introduction

The rapid pace of industrialization and its resulting by-products have affected the environment by producing hazardous wastes and poisonous gas fumes and smokes, which have been released to the environment. Conventional technologies have been used to treat all types of organic and toxic waste by sorption, biological oxidation, chemical oxidation and incineration. Super-critical water oxidation (SCWO) is an emerging technique for treatment of organic waste. Nanomaterials find extensive applications [1] and their use in environmental remediation is becoming quite attractive. The removal of pollutants from the environment is based on the reactivity of the nanomaterial used and the pollutants may either be sorbed or degraded. The advantages of using nanosorbents are the ability to fine tune the sorption properties by changing the shape, size, morphology etc. Most of the nanomaterials have multifunctional properties including sorption, antimicrobial, photocatalytic or redox. Magnetic sorbents can be easily phase separated from the aqueous stream after use.

There are two general approaches viz bottom-up and top-down, for the synthesis of nanomaterials [2,3]. The bottom-up approach includes the self assembly of smaller components to form nanostructures during which the physical forces operating at nanoscale are used to combine the basic units into nanostructures. A typical example of this kind of approach is the formation of quantum dots during epitaxial growth and nanoparticles formation from colloidal dispersion. In top-down approach, macroscopic structures are broken down into the smaller size particles. Top-down methods begin with a pattern generated on a larger scale, then reduced to nanoscale and are very quick for small scale production but quite expensive and not suited for large scale production. Bottom-up methods start with atoms or molecules and build up to nanostructures and fabrication is much less expensive. Some of the

commonly used techniques include milling and mechanical alloying, physical or chemical vapour deposition or vacuum evaporation, sol-gel chemical synthesis, gas-phase synthesis flame pyrolysis, laser ablation and plasma synthesis, microwave, sonochemical etc. Surface modification of the nanomaterials is usually carried out to improve surface activity, decrease aggregate formation and reduce interaction with other species.

It is normally assumed that smaller the nanoparticles, better will it be for separation due to increased surface area. But this may not always prove to be useful especially in case of column separations. Hence for such applications, surface modified nanomaterials or nanocomposite become very attractive. The polymer-based nanocomposite (PNC) [4-6] retains the inherent properties of the nanoparticles with additional advantages like increased stability, ease of use etc. In addition, the incorporation of nanoparticles (NPs) into polymeric supports leads to an enhancement of the mechanical, electrical and optical properties. The fabrication of membranes with metal oxide NPs was showed an increase in the permeability and resistance to membrane fouling with a significant enhancement of selectivity. Different studies showed that the incorporation of nanoparticles within membrane results in increase in the porosity, the hydrophilicity of the surface and its surface properties. It is seen that nanofibres show better performance with respect to small sized contaminants and higher flow rate due to the presence of interconnected porous structures.

In this overview the use of nanomaterials for applications of water remediation has been discussed. Remediation is a process by which remedy is given to problems that arise due to environmental pollution. Environment is surroundings along with the human beings and due to continuous growth, results in pollution, a term derived from the Latin word "pollutionem" meaning, "to make dirty".

Environmental pollution is defined as the unfavorable alteration of the surroundings, wholly or largely as a by-product of man's actions and the substances that cause pollution is known as pollutant. A pollutant is generally defined as the substance that is present in the wrong place, at the wrong time and in the wrong quantity. There is always an ongoing effort for developing newer procedures for the removal of these contaminants and this is known as remediation.

There are different types of approaches for carrying out environmental remediation. The first approach is the chemical degradation method including oxidation using ozone/UV radiation/H₂O₂, photocatalytic degradation, supercritical water oxidation, the Fenton method, sonochemical degradation etc. Ozone or UV radiation-based technologies (O₃/UV/H₂O₂) are chemical oxidation are used for the removal of specific pollutants or for reducing the organic load (COD) and to enhance the biodegradability of waste water and also for disinfection uses. These techniques involve oxidation/photolysis routes. The use of ozone or peroxide in combination with UV radiation results in the insitu formation of hydroxyl free radicals and pollutants like phenols, organic pesticides etc are attacked very easily. Photocatalytic degradation involves photons and a catalyst and is dependent on the temperature and external conditions and involves different steps. The first step is the sorption of the species onto the surface of the catalyst and then reacts with the UV radiations and then finally the degraded products should be removed from the surface. The chemistry occurring at the surface of a photo excited semiconductor is based on the radicals formed from O₂, H₂O and electron-rich organic compounds [7,8]. Supercritical water oxidation (SCWO) is a very attractive approach that uses conditions above the critical point of water (374 oC, 218atm) which leads to a change in the solubility properties in water (i.e. an increase in the organic solubility and a decreased inorganic solubility) with a great reduction in the viscosity of the media thus leading to a sharp increase in the mass transfer. Under these conditions, nearly complete oxidation of the organics is achieved. The inorganic salts present in the water are converted to nanoparticles in situ and act as a catalyst for the oxidation process. Due to this the reaction temperature or the residence time can be reduced [9-11]. Fenton oxidation using the Fenton reagent (aqueous mixtures of Fe(II) and hydrogen peroxide) is used extensively for degradation of the pollutants by the formation of hydroxyl radical which is a strong and non-selective oxidant [12,13]. Sonochemical reactions are related to new chemical species produced during acoustical cavitation effects which result in an increase in the surface area between the reactants, regeneration of catalyst surfaces and accelerated dissolution. Sonochemistry provides a unique, high-temperature gaseous environment inside the cavitation bubbles, where the thermolysis of CCl₄ molecules takes place at fast rates, Nanoparticles synthesized by sonochemical procedure in combination with light and ultrasound are used for the degradation of pollutants [14-16]. Biological treatment procedures have also been explored for their utility [17-19]. Permeable reactive barriers (PRBs) are also

used for decontamination. Zerovalent metals (ZVMs) and PRBs involve the physical removal of pollutant from the aqueous phase and the chemical reaction occurs to reduce the toxicity of the pollutants. The first step is the sorption onto the nanomaterial and the subsequent irreversible changes occur. For cations, the remediation occurs by only sorption. Biological processes based on the biochemical reactions use natural processes to bring about degradation under very mild conditions. But the main disadvantage of these reactions is that the rate cannot be changed as it is dependent on the microorganism used. Also the microorganisms may themselves be damaged under severe conditions of pH, temperature, concentration of pollutants etc and so these reactions cannot be controlled over a long term. As these reactions involve large amounts of bioorganisms, large scale generation of biomass occurs and care needs to be taken for disposal of the secondary waste. In order to overcome the issues with biological processes, an new attempt of using the enzymes directly is being made to treat the contaminants including those that are not biodegradable. The use of enzymes minimises the sensitivity of severe conditions of pH, salinity, concentration etc [20,21]. Remediation by metals/metal oxides involves the use of various metals like silver, iron etc. The size, shape and surface charge are the crucial factors that decide the applicability of the nanomaterials for remediation. Silver nanoparticles are extensively used for disinfection of water due to their antimicrobial (against bacteria, virus, fungi) properties [22-23]. It is believed that the silver after adhesion to microbes membrane surface reacts with the thiol groups in the proteins and causes pits which lead to increased penetration of silver [24-26]. With an increase in the silver nanoparticles penetration, the damage increases and finally generation of cationic silver occurs [27]. The size of the silver nanoparticles decides the type of microbes being attacked (size < 10 nm used for bacteria like E. coli; 1 to 10nm inhibit certain viruses) [28-30]. Elemental iron has been used extensively both in its bulk and nanoform for water purification [31,32] and also used for degradation of halocarbons [33,34]. Amalgamation after reduction was a technique used for the removal of toxic mercury from water using gold nanoparticles [35,36]. Metal oxides (MgO, TiO₂, MnOx, Fe₂O₃, Al₂O₃), in combination with gold was used for desulphurization [37,38]. Zero-valence state metals (Fe⁰, Zn⁰ etc in pure / bimetallic forms cluster in cluster or core shell structures) are used for remediation of water [39-49]. Nanoxides have been used for removal [50] and degradation of both organic and inorganic pollutants [51-58].

In our studies, we have used metal nanoxides, tungstates and molybdates for removal of toxic and radioactive species [59-72]. In all these studies it was seen that the surface charge of the nanomaterials was of great importance as this decided the applications. Since the sorption was a surface phenomena, it was thought probably selectivity would not be possible. However, the use of zinc oxide nanomaterials for removal of transition metal ions showed a very high selectivity with respect to copper uptake [60]. The use of nanocomposites helped in the enhancement of

the properties as it gives a combination of the two nanomaterials used. We had used such nanocomposites and also functionalized nanomaterials for removal of toxic speices like Hg and Pb [62]. The tailoring of surface charge on zinc oxide nanorods using suitable synthesis protocol has been achieved in the present study. The synthesized zinc oxide nanorods were characterized using different techniques and tested for their efficiency as sorbents for uptake of transition metal ions. These studies revealed that the uptake capacity was high and showed selectivity with respect to Cu²⁺ ions. Tungstate and molybdate nanoparticles with high specific surface area show excellent sorbent properties with respect to organic (Rhodamine B and Methylene blue) and inorganic (Cu²⁺) pollutants resulting in near complete removal within a very short time. Antimony phosphate nano ribbons showed a clean separation of uranyl ion from its various mixtures. Nano crystalline manganese oxide showed a very selective sorption as a function of pH and kinetics and this was used for separation of uranium from different metal ions.

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