APPLICATION OF MESOPOROUS METAL OXIDE NANOPARTICLES IN WASTEWATER TREATMENT

Abstract

In the last few decades, material science and technology have rapidly emerged as a very potential area of research due to their versatile applications in various fields. In the field of material science, enormous development has been made in the fabrication of mesoporous metal oxide nanomaterials based on smart and advanced devices. From the study of various research groups, it was found that nanodimension and mesoporosity have a great influence on the improvement of physicochemical properties of materials in comparison to their bulk counterparts. Modification of the shape and size of pores in mesoporous nanomaterials leads to a successful generation of multifunctional and desirable materials. At present, both developed and developing countries suffer from the scarcity of clean water ascribed to various types of water pollution. Currently, various types of mesoporous metal oxide nanoparticles exhibit efficient application in removal of the organic and inorganic pollutants from wastewater. Mesoporous metal oxide nanoparticles have great potential for treating contaminated water due to their large surface area and were established as a promising material for wastewater treatment.

Keywords: Material Science; Nanomaterials; Mesoporous; Metal Oxide; Wastewater Treatment.

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I. INTRODUCTION

1. **Mesoporous Materials:** In the present time, the study of nanomaterials with mesoporous structure has attracted significant attention from the many materials research groups due to their efficient use in diverse areas of applications. These materials are widely used in the fields of applications like sensors, energy storage devices, bio separation, gas separation, agriculture, cosmetics, biomedicine and drug delivery, catalysts, adsorption, photocatalytic and environmental applications and many more [1-11]. These materials display outstanding physicochemical properties ascribed to their unique structural features, such as high surface area, tunable pore size, large numbers of surface defect sites and surface functionality [12-14]. In accordance with the “International Union of Pure and Applied Chemistry (IUPAC)” nomenclature, porous materials containing 2 to 50 nm sized pore materials are described as mesoporous materials [15]. Furthermore, materials with a pore diameter less than 2 nm are known as microporous and larger than 50 nm are called macroporous materials. These mesoporous metal oxides are extensively applied in several types of environmental applications, such as wastewater treatment, photocatalytic degradation of organic pollutants, photocatalytic water splitting and removal of heavy metal and many more.

2. **Water Pollution and Waste Water:** Clean and fresh drinking water is a necessity for the life of all living organisms. Water pollution is the result of contamination of water resources by pollutants, and has immensely increased as a result of rapid industrialization and the massive population explosion [16]. Water pollution is either surface water pollution or groundwater pollution. Also, the consumption of fresh and clean water has been rapidly increased in the sector of agriculture, industry, household sectors, and other forms of consumption, which is the main reason for water pollution [17]. The wastewater is described as a municipal waste liquid product which contains contaminants or pollutants. The main categories of pollutants are organic and inorganic contaminants [18-19], such as microorganisms, toxic heavy metal ions and dyes, which have vast toxicity and hazards to the environment. These types of contaminated water are not used for drinking purposes as the chemical, biological and physical properties of clean water are affected by these harmful contaminants [20]. Currently, clean and fresh drinking water is not available to about 780 million people worldwide [21]. Consequently, wastewater treatment has become very important because of the hazards and toxic effects of the contaminants of wastewater on the environment and ecosystem. Recently, various research groups have focused their research activities on the removal of these pollutants from different water sources [22]. The wastewater treatment can utilize physical, chemical, and biological methods for water purification from various hazardous contaminants. Numerous strategies such as solvent extraction, evaporation, reverse osmosis chemical treatment, ion-exchange, adsorption, separation and ultra filtration [23-26] are applied to remove hazardous elements from wastewater. Amongst these, photocatalysis and adsorption are the most interesting and efficient methods due to their unique features [27-30]. Basically, adsorption is a chemical process of adhering or depositing particles of matter from gases or liquids onto the porous interface of solids. Adsorbent is a solid substance whose surface is utilized to accumulate harmful particles from a liquid or gaseous phase. In the last few decades, researchers have reported the application of various materials in water treatment processes, such as charcoal, activated carbon, clay, silica, zeolites and sand as adsorbents. Although their applications have

been limited due to many drawbacks, such factors, such as low processing efficiency, low regeneration capability, high energy requirements along with less economic benefit. Currently, mesoporous metal oxide nanomaterials have been considered as promising adsorbents for purification and recycling of wastewater due to their unique characteristics such as large surface area to volume ratio, variable valences, vast number of structural geometries and polycrystalline nanostructures along with a large number of active sites for adsorption. Nanodimensional mesoporous metal oxide has many excellent features, like high removal capacity and heavy metal selectivity as an adsorbent. On the other hand, photocatalysis is a photo-activated chemical reaction based on nano-catalysts which happens when free radical mechanisms are started as soon as the chemical compound is exposed to the photons (solar radiation) with sufficiently high energy. In wastewater treatment, photocatalysis mechanisms are divided into two categories: solar photocatalysis and artificial ultraviolet (UV)-light assisted photocatalytic activity. Due to their high surface area and small particle size, mesoporous metal oxide nanoparticles show excellent photocatalytic properties and are considered potential candidates for nano-catalysts in polluted water purification. This chapter focused on the study of the application of various mesoporous metal oxides as nano-adsorbent and nano-catalysts in wastewater treatment.

II. APPLICATION OF MESOPOROUS METAL OXIDES IN WASTEWATER TREATMENT

1. **Copper Oxide Nanoparticles:** Copper is the oldest metal used in human civilization for sanitization as copper has many positive characteristics like abundance in nature, good corrosion resistance and antimicrobial activity [31]. Copper (II) oxide is a monoclinically structured nontoxic p-type semiconductor material with a band gap of 1.2 eV [32]. It shows many unique chemical and physical properties, like high electrochemical capabilities which are utilized in photocatalysis, removal of toxic pollutants and antimicrobial applications. Various synthesis methods have been used to prepare mesoporous CuO nanostructures like sol–gel, chemical precipitation route, thermal decomposition, solvothermal, hydrothermal, microwave-assisted etc. Mesoporous CuO was obtained via a simple sol-gel method in ethanol-water mixed with solvent by M. I. said and coworkers [33]. They used Copper (II) acetate monohydrate, Sodium hydroxide and ethyl alcohol as precursors. The photocatalytic study showed the prepared materials exhibited higher efficiency for the degradation of Congo red (dye) and exhibited complete dye removal after 35 min. Also, the water/ethanol ratio has a potential impact on the tuning photocatalytic properties of the prepared CuO nanoparticles, which help in wastewater treatment. N. Jing and group reported the preparation of mesoporous CuO with novel architecture via a conventional hydrothermal method followed by a facile heat treatment [34]. They used hydrated $Cu(NO_3)_2$ salt and $CO(NH_2)_2$ as starting materials. Prepared mesoporous CuO exhibits excellent photocatalytic activity and high durability under visible light for methyl orange (dye) in an acidic environment. The adsorption/desorption of the dye on the CuO surface occurred due to the action of H^+ ions and H2O2 using a state-changing mechanism and the reaction rate of degradation of the contaminants was increased up to 3.5 times only by controlling the methyl orange ratio. In another work, hollow mesoporous CuO microspheres were prepared via a rapid one-pot hydrothermal process by S. Ghosh et al. [35]. Copper acetate, urea and water are utilized as starting materials. The hollow CuO microspheres were formed by the self

assembly of 5–20 nm-sized particles with a stone-wall-like structure. The hollow CuO microspheres exhibit high efficiency as recyclable catalysts in the decomposition of H2O2 during the water rectification process. One of the potential applications of CuO during water purification is bacterial disinfectants. Gustavo Faúndez et al. [36] observed the activity of copper oxide against suspension Campylobacter jejuni and Salmonella enteric at various temperature conditions. These results confirmed that the copper and copper oxide surface has excellent antibacterial activity at these temperatures.

2. **Zinc Oxide Nanoparticles:** ZnO is considered as a highly efficient photocatalyst in wastewater treatment, ascribed to its excellent photocatalytic activity and high chemical stability. ZnO is a direct and wide bandgap (3.37 eV) semiconducting material. Also ZnO possesses strong oxidation capability and high exciton binding energy (60 meV) at room temperature. Porous ZnO nanomaterials with various morphology such as nanosheets, nanowires, nanobelts, nanorods, and complex structures were developed by several research groups. Mesoporous ZnO is a potential candidate for photocatalytic activity due to high electrochemical stability, nontoxicity, super oxidative capability as well as, because it provides a large surface area to volume ratio. Also, ZnO is cheap and abundant in nature. Preparation of mesoporous zinc oxide nanoparticles within a silica matrix was reported by W. M. Saod and groups [37]. The nanocomposite system shows excellent efficiency in removal of pollutants Pb, Cd and Cr from solution at pH 6 and above within less time. The photocatalytic activity of ZnO in different proportion in polluted water has been observed by M. A. Gondal et al. [38]. Using $Zn(NO_3)_2$ and $(NH_4)_2CO_3$ as precursors, ZnO nanoparticles of 20–40 nm size are prepared. An increase in the constant decay of bacteria has been reported with increased photocatalytic efficiency ascribed to the effect of the reduced particle size and the effect of quantum containment activating ZnO to generate reactive oxygen species.

3. **Titanium Oxide Nanoparticles:** At present times, the most extensively studied metal oxides in the field of water rectification are titanium oxide (TiO_2) nanoparticles. Titanium oxide is a very efficient photocatalyst due to its unique features such as photostability, affordable price and high biological and chemical stability [39]. TiO_2 is a semiconducting material with a large bandgap energy (3.2eV) and ultraviolet (UV) excitation. Several works have been reported where titanium oxide is also used in disinfection, removal of pigment, dye and in the decomposition of complex organic compounds into simple, less toxic materials [40-41].

4. **Iron Oxide Nanoparticles:** At present times, iron oxide nanoparticles have been extensively used in various fields due to their low cost and availability. Currently, mesoporous iron-based nanomaterials have exhibited excellent adsorption capacity for removal of heavy metals, dyes and organic compounds from contaminated water. In iron oxide, magnetism is a unique physical characteristic which extensively helps in water rectification by controlling the physical properties of pollutants in the water. As a result, the combination of adsorption procedure along with magnetic separation makes iron oxide nanomaterials an outstanding nanosorbent in the field of wastewater treatment. Nowadays, many research groups have concentrated on developing water treatment technology using magnetic nanomaterials, especially iron oxide [42-45].

III. SUMMARY

In recent times, material science and nanotechnology have led to huge developments in smart and advanced devices using multifunction materials. Currently, nanoparticles have drawn great attention from research for their interesting physical and chemical characteristics compared to their bulk counterparts. Furthermore, mesoporous nanomaterials have outstanding applications as they provide a large surface area to volume ratio and a tunable porous structure. Nowadays, the requirement for the management of water pollution is increasing. Metal oxides with a mesoporous structure are becoming very efficient as adsorbent materials for wastewater treatment. This kind of material can remove more toxic molecules from polluted water by trapping more pollutant particles onto their porous surface area. Several research groups are focusing their work on the fabrication of more smart and useful material for the development of more advanced techniques. They used different types of synthesis methods to prepare more efficient nanoadsorbent material. Mesoporous ZnO, TiO2, CuO, Fe2O3, Ag2O, MgO, MnO2, SnO2 are examples of some promising adsorbent materials. They show excellent efficiency as a chemical adsorbent in accordance to their high surface area and presence of more active sites for adsorption in their interface. From the study of literature it can be concluded that in the near future, by controlling the mesoporous structure and electronic structure, more efficient and advanced metal oxide recycling devices for purification and recycling of wastewater will be developed.

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