PHOTOCATALYTIC ACTIVITY OF SCHIFF BASE BIOPOLYMER BASED METAL OXIDE NANOCOMPOSITE

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ABSTRACT

In recent years, Schiff bases are their unique applications in the photocatalytic process, the biopolymers of the Schiff base are becoming more widely recognized. These materials enhance the activity of metal oxide and are useful in the development of new photocatalysts. The synthesis and photocayalytic applications of the nanocomposites have much importance and concern in all aspects of chemistry and related fields such as biology and physics. As versatile ligands, Schiff bases are formed when carbonyl compounds (aldehydes or ketones) are condensed with amines. These reviews summarize the preparation and photocatalytic application of Schiff base biopolymer and their metal oxide nanocomposites.

Keywords— Schiff base, Biopolymer, Metal oxide, photocatalysis.

INTRODUCTION

Schiff bases are important chelating agent which offers great flexibility in the design of useful, interesting and commercial ligand system. They are derived from aromatic amine and carbonyl compound by nucleophilic addition and dehydration thereafter to generate imine [1]. Various studied have been conducted on the applications of Schiff's-base complex and reliable catalytic reactions. These include the reduction and reaction of carbonyl compounds, thionyl chlorination, hydrosilylation and epoxidation of ketones, as well as the application of corrosion inhibitors [2]. Schiff base complexes show catalytic activity towards electron-reduction of oxygen. Some metal and metal oxide complexes of a biopolymer bond Schiff base show catalytic activity on decomposition of hydrogen peroxide and oxidation of ascorbic acids [3].

Schiff base biopolymer and their metal oxide nanocomposites materials have gained a lot of attention due to their improved physical and chemical characteristics. Due to their improved properties i.e., good mechanical strength, porosity, toughness, electrical and thermal conductivities, dispersibility, and high mobility such materials are suitable for different functional and structural applications in science and technology [4]. They have be use to remediation inorganic and organic pollutant, gas sensing, electronic devices, biomedical fields, photocatalytic degradation of organic dyes, etc [5]. With advanced surface features of biopolymer (Schiff base) base metal oxide nanocomposites like, stability, controlled structural and surface features are feasible in the photochemical degradation of organic pollutants [6]. Owing to high photodegradation capability, control band gap, and resourceful synthetic approaches, these materials have been potentially utilized in thephotochemical degradation of organic dyes [7]. The common biopolymer like polysaccharides (Chitosan, Starch, Chitin, Cellulose etc.) and metal oxide such as CuO, MnO_2, SnO_2, TiO_2, ZnO, ZrO_2, and CeO_2 etc. [8] have been utilized in different fields of science and technology. In preparation to Schiff base biopolymer based metal oxide nanocomposites among a nanophase-separated structure, the homogeneous dispersion of metal oxide nanoparticles together with a reduction in the size of the polymer-metal oxide interfaces is extremely significant as it in essence alters the physical properties of the nanocomposite [9]. It is an essential to have a homogenously dispersion of metal oxide during the biopolymer matrix in order to form a homogeneous nanophase separated structure [10]. The property of biopolymer nanocomposite can be improved owing to the present of metal oxide nanoparticles [11]. Therefore nanocomposites are generally used in various applications, including structural materials from active surface coating to photocatalytic applications [12]. Due to immense number of publication on the synthesis of Schiff base biopolymer based metal oxide nanocomposites, it is complicated to cover up the topic totally; so this chapter will give a common overview of the basic strategy involved in the synthesis of biopolymer based metal oxide [13] nanocomposites, as well as their catalytic application.

PHOTOCATALYSIS AND ITS MECHANISM

Generally in the presence of ultra-violet (UV) and visible lights photocatalysts are utilized to speed up chemical reactions [14]. The photo catalytic activity of nanocomposites is characterized by stability, adequate morphology, adequate band gap, high surface region, and reusability [15]. The photocatalytic reactions are two types, i.e., homogeneous and heterogeneous photo catalytic reactions. In this process catalytic reagents are mostly used to degrade or mineralize hazardous materials into CO_2 and H_2O, decomposition of atmosphere pollutant, deactivation or destruction of microorganisms, and degradation of waste plastics [16]. The photocatalytic behavior of biopolymer and their metal oxide composite materials are well known in the presence of UV radiation [17]. The photocatalysis process on the surface of biopolymer and metal oxide composites are mediated by valence and conduction bands. These bands are regarded as holes and electrons [18]. In the presence of UV light electrons are shifted from valence to conduction band through a proper bandgap (Figure 1). Finally this procedure involved important to the formation of reactive oxygen species (ROS) [19]. In the photocatalytic mechanism degradation of dyes ROS is generally responsible (Figure 1).At last, photocatalysis mechanism is involved to oxidation and reduction process on the surface of several biopolymer based metal oxide and its composite nanomaterials. This procedure is mediate by conduction bands (CB) such as electrons (e^-) and valence bands (VB) such as holes (h^+) which is absorbed by ultra-violet light. The pairs of h^+ ion are accelerated to the formation of highly aggressive species, i.e., hydroxyl (OH^-) radicals or superoxide radicals from the wetness and atmospheric oxygen. These ions are adequate to oxidized and decomposed organic material or smell gases and destroy bacteria's [20].

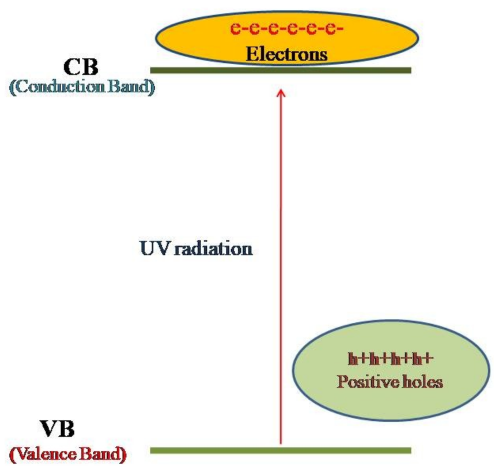

Figure1. Shifting of electrons from valence to conductance band.

Photocatalysis process is an efficient method for the degradation of organic pollutants, microbial disinfection and mineralization of hazardous compound owing to the formation of OH^- ion (strong oxidizing agent) [21]. But the reactions occur in the presence of O_2 and H_2O, the electrons in the conduction band is selected by oxygen and give increase to a superoxide radical anions; H_2O is oxidized into OH^- on the oxidation sites [22]. The generated reactive species results in the complete mineralization of organic pollutants and reactions e^-/h^+ ion pairs by different electron donor and acceptor. Further, the redox potential reaction of valence and conduction bands are satisfactorily positive and negative for the generation of OH^- and superoxide radicals [23].

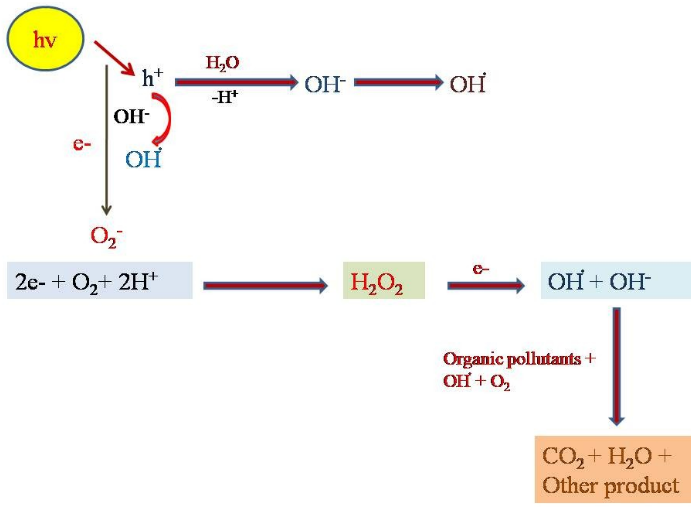

Figure 2. Schematic representation of photo degradation of organic dye.

PROCESSING OF BIOPOLYMER BASED METAL OXIDE NANOCOMPOSITES

There is great attention to the preparation method of biopolymer based metal oxide nanocomposite. There are three common techniques for the preparation of biopolymer based metal oxide nanocomposites. a) In situ polymerization of monomers, b) second is the direct mixing/blending of metal oxide nanoparticles and biopolymer via melt or solution mixing and c) sol-gel process.

In situ polymerization

In situ polymerization is a prevalent route for the preparation of biopolymer based nanocomposite on a larger scale and avoiding chain destruction. In situ on a nanoparticle layer has been used to prepare polyaniline, polypyrrole, and polymethyl-methacrylate [24]. Taking polyaniline as an example, aniline is used the distinctive precursor, which is then immersed in HCl solution with the addition of ammonium persulfate that acts as an oxidant [24]. ZnO and TiO_2 based PMMA nanocomposites were prepared using an in situ bulk polymerization process [25], where the surface of nanoparticles was used alkylphosponic acid for modifying. The benefit of a these method lies in the fact that the whole procedure is facile, controllable, and scalable, promoting the intercalation of monomer between the nanoparticles.

Direct mixing/blending method

The preparation of biopolymer based metal oxide nanocomposites, Blending/ex situ method is the simplest method and can normally be divided into solution blending and melts blending [26].

Sol-gel method

The Schiff base biopolymer based metal oxide nanocomposites was synthesized by sol gel method specially in the fabrication of self-cleaning film and glass coating. The fact that sol-gel resultant inorganic composite required a low synthesis temperature; the physical property of the doping element could be retain by controlling the composite material between the guest molecule and the host matrix [27].

DEGRADATION OF ORGANIC DYES BY NANOCOMPOSITE MATERIALS

Nanocomposites combine with different materials in which at least one of the materials has particle sizes 1-100 nm [28]. Due to their improved physical and chemical characteristics nanocomposite materials have gained a lot of attention. Some Schiff base biopolymer based metal oxides were successfully used in the photodegradation of different dyes from aqueous solutions (Table 1). Nanocomposite materials are suitable for different functional and structural applications in science and technology due to their improved properties, i.e., good mechanical strength, electrical and thermal conductivities, porosity, toughness, dispersibility, and high mobility [29]. They have been used to photocatalytic degradation of organic dyes and remediation inorganic and organic pollutants. The Schiff base biopolymer based metal oxide nanocomposites with superior surface features, stability; restricted structural and surface features are viable in the photochemical degradation of organic pollutants. Due to efficient synthetic approaches, controlled bandgap these nanomaterial's have been potentially utilized in the photochemical degradation of organic dyes [30].

Table 1. Some biopolymer based metal oxide nanocomposites are used in the photodegradation of dyes.

S. No.	Biopolymer	Metal oxide	Dye degraded	References
1.	Poly (vinyl alcohol g-acrylamide)	ZnO/SiO_2	Methylene blue, crystal violet, congo red	[31]
2.	Polyaniline	Cu_2O/ZnO	Congo red	[32]
3.	Polypyrrole	TiO_2/V_2O_5	Oxytetracyclineofloxaci	[33]

			n	
4.	Polyaniline	rGO/MnO_2	Methylene blue	[34]
1.	Alginate	CeO_2	Crystal violet	[35]
2.	sodiumalginate	ZnO	Methylene blue Congo red	[36]
3.	Polypyrrole	Bi_2MoO_6	Tetracycline	[37]
4.	Polymethyl methacrylate	TiO_2	Methylene blue	[38]
5.	Polythiophene	TiO_2	Rhodamine B	[39]
6.	Cellulose	ZnO	Rhodamine B	[40]

CHARACTERIZATION TECHNIQUES FOR NANOCOMPOSITES

The study of physical and chemical features of Schiff base biopolymer and their metal oxide composite materials by different characterization techniques. The resultant shows with surface, dispersion, aggregations, functional properties, shape, size, particle arrangement, basic elemental composition, etc. The various common techniques were used; X-ray diffraction spectroscopy (XRD), Fourier transform infrared spectroscopy (FTIR), UV-Visible spectroscopy, X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Zeta-potential, Dynamic light scattering (DLS), Atomic absorption spectroscopy (AAS), Energy dispersive X-ray spectroscopy (EDAX), and Atomic force microscopy (AFM). Concisely, these characterization techniques can be separated into three categories, i.e., surface morphology, functional property and other techniques (Table 2).

Table 2.Various characterization techniques were used to characterize composite nanomaterial.

Technique		**Application**
Analysis for functional properties	X-ray diffraction spectroscopy (XRD)	Crystallinity and amorphous behavior
	Energy dispersive x-ray spectroscopy (EDAX)	Elemental composition in the nanocomposites
	Atomic absorption spectroscopy (AAS)	Determination of elemental concentration
	X-ray photoelectron	Elemental Oxidation state

	spectroscopy (XPS)	
	UV-Visible spectroscopy	Light extinction properties
	Fourier transform infrared spectroscopy (FTIR)	Determination of functional groups
Analysis for surface morphology	Scanning electron microscopy (SEM)	Determination of Structural , surface features, surface area, and particle size
	Transmission electron microscopy (TEM)	
	Atomic force microscopy (AFM)	
Other analysis	Dynamic light scattering (DLS)	Surface charge and particle size
	Zeta potential	

CONCLUSION

A current review article has discussed the process of photocatalysis and utilization of various efficient Schiff base biopolymer based metal oxide nanocomposite using photocatalyst of different dyes from aqueous solution under appropriate irradiations. In this articles illustrated to the synthetic approaches. For the use of large-scale operation of wastewater treatments, costeffective, stable, and biodegradable, should be designed Schiff base biopolymer based metal oxide nanocomposite as photocatalysts. The choices of a appropriate photocatalyst should be based on their low-cost, safety, bandgap, high capacity to work under sunlight or other visible lights, efficiency, and simple recovery and reusability.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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