Application of Enzyme-Nanoparticle-Polymer Composites in Wastewater Treatment

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Different water treatment technologies such as photochemical degradation, biodegradation, electrochemical degradation, reverse osmosis, and membrane separation have been used to get rid of water pollutants. Enzymatic treatments have received great attention due to several advantages compared to physical and chemical treatments, such as mild operating conditions and high catalytic efficiency without harsh side effects. Oxidase and peroxidase enzymes from different sources have been immobilized on metal and metal oxide-polymer composites and used in the degradation of pollutants.

enzyme-nanoparticle-polymer composites wastewater pollutants

1. Introduction

In recent decades, the global community has increasingly recognized the formidable challenge posed by water pollution arising from the unregulated release of municipal and industrial waste [1][2]. Many industries including petrochemical, paints and explosives, food, pharmaceutical, leather and textile, pulp and paper, and cosmetics have contributed to this cause [3][4]. These discharges cause serious problems to aquatic life due to their high biochemical oxygen demand (BOD), chemical oxygen demand, and blockage of sunlight [5][6].

One of the industries producing the highest level of toxic chemicals from dyeing, printing, and finishing is the leather and textile industry [1]. The conversion of skin into leather in textile industries generates huge amounts of wastewater containing a variety of organic and inorganic chemicals such as dyes, neutral salts, phenols, and biogenic matter of skins [7][8]. The complex aromatic structures of these chemicals, especially the dyes, make them highly soluble in water and stable against light, aerobic decomposition, and oxidizing reagents [9]. Therefore, their accumulation leads to serious environmental concerns for aquatic life and human beings due to their adverse effects of toxicity, carcinogenicity, and mutagenicity [10]. Another industrial sector that has developed rapidly in the last century is the pesticide industry, as it is an important component of modern global agricultural systems for controlling pests and increasing crop yield [11]. These pesticides are applied in much higher doses than those required to kill the pests, and end up accumulating in water bodies via run off and percolation [12]. Unfortunately, these agrochemical residues not only pollute the aquatic systems and damage biodiversity, they cause serious health hazards to humans and may even directly or indirectly lead to death [13][14]. Moreover, these compounds have very long half-lives and can remain in the environment for several decades [15][16].

The growth of the pharmaceutical industry (veterinary and human medicines) in the past years has also led to rising amounts of drugs, antibiotics, and hormones. These medicines are not fully metabolized by living organisms and when these end up in wastewater treatment plants, they are difficult to biodegrade, since most of them are fat soluble [17][18][19]. For example a study conducted by Joss et al. [20] indicated that biological degradation of pharmaceuticals using activated sewage sludge from municipal wastewater could only degrade 4 out of 35 compounds by over 90% and 17 compounds by less than 50%. These compounds have increased in the environment due to their increased consumption and direct discharge into the environment. The presence of pharmaceuticals, cosmetics, and their metabolites in municipal waste and industrial effluents presents a significant challenge, as these compounds cannot be effectively eliminated using conventional techniques, and consequently are released to the receiving environment [21][22]. While in the environment, they accumulate or transform into metabolites under certain environmental conditions, and these secondary metabolites may even be more toxic than the parent compounds [12][23]. These make pathogenic organisms develop resistance against them over time, which is a high risk to human health [24].

The continued release, spread, and accumulation of persistent organic pollutants in the water environment from these industries, including polychlorinated biphenyls and polycyclic aromatic hydrocarbons from the petrochemical industries, have become a major threat to human health due to their toxic, mutagenic, and carcinogenic properties [25][26][27]. The emission of these pollutants occurs at the manufacturing stage, after consumption and disposal of unused products. These products are hard to be tracked or controlled in most situations and are resistant to natural biodegradation [12][28]. Most of these compounds are phenolic and, therefore, bio-recalcitrant, carcinogenic, and easily accumulate in plants and animals. They should, therefore, be removed prior to wastewater discharge [17][29][30].

Different water treatment technologies such as photochemical degradation, biodegradation, electrochemical degradation, reverse osmosis, and membrane separation have been used to get rid of these pollutants. However, these techniques are costly, consist of complicated procedures, do not entirely remove the pollutants, and lead to secondary contaminants that also need to be redisposed of [31][32]. Enzymatic treatments of these pollutants have received great attention due to several advantages compared to physical and chemical treatments, such as mild operating conditions and high catalytic efficiency without harsh side effects [33][34]. Hence, the use of biocatalysts in wastewater treatment has gained momentum due to their ability to target a wide range of pollutants [35]. Enzymes immobilized onto supports are often used in the treatment of wastewaters to ensure improved thermal and pH stability and repeatability, which is rarely achieved with free enzymes [36]. Various pollutants including drugs, dyes, pesticides, polycyclic aromatic hydrocarbons (PAHs), and even heavy metals have been degraded using enzyme/metal-polymer biocatalysts, as demonstrated in **Figure 1**. Oxidase and peroxidase enzymes from different sources have been immobilized on metal and metal oxide-polymer composites and used in the degradation of pollutants, as observed in **Figure 1**.

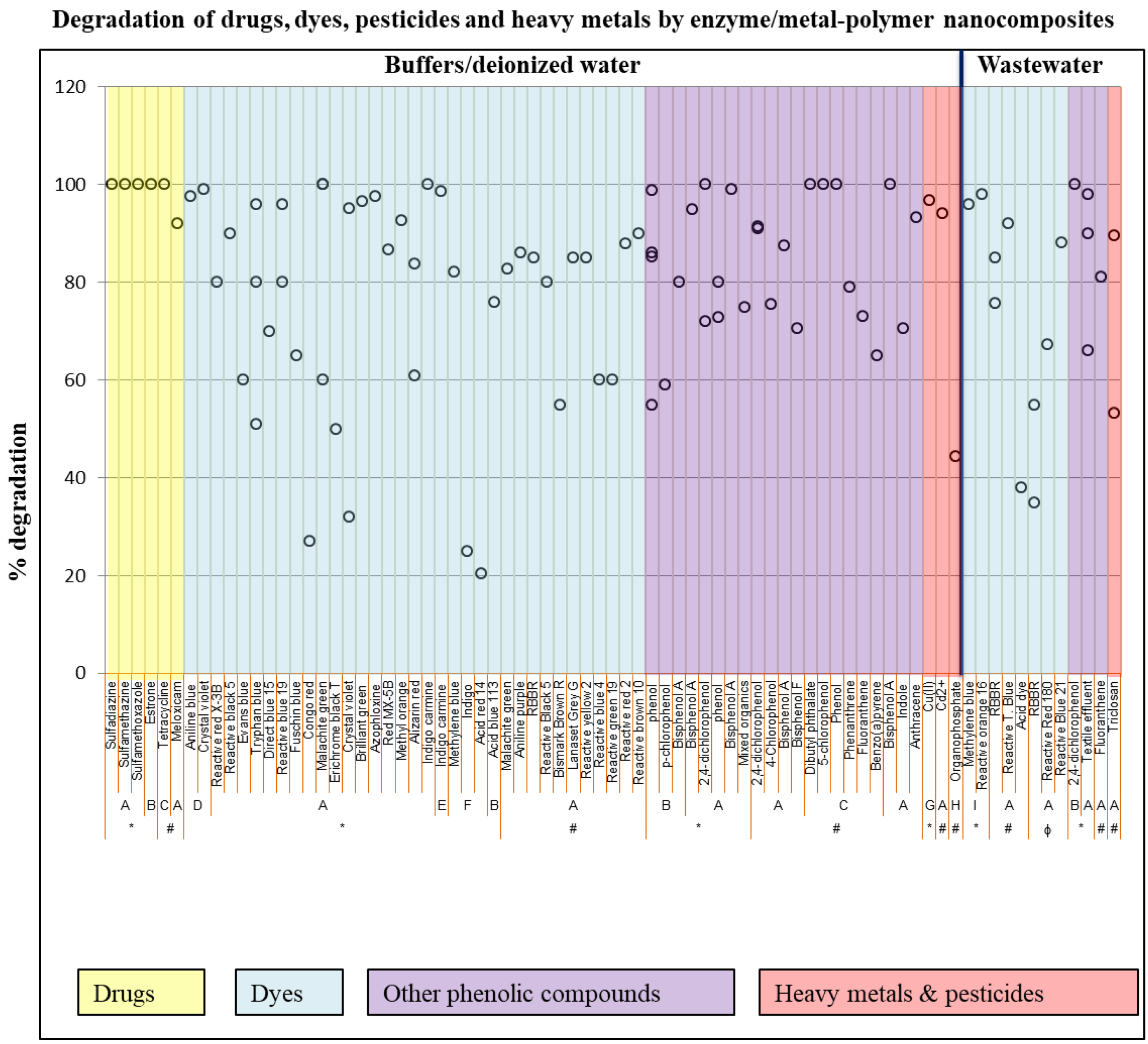

Figure 1. Different pollutants that have been degraded by enzyme-nanoparticle-polymer composites. A—Laccase, B—Horse radish peroxidase, C—Lignin peroxidase, D—Chloroperoxidase, E—Glucose oxidase, F—Glucose oxidase/laccase, G—*S. cerevisiae* enzyme, H—Glycerophosphodiesterase, I—Manganese peroxidase, * 0–6 h, # 6–24 h, ϕ over 24 h.

2. Laccase-Based Nanocomposite Biocatalysts for Degradation of Pollutants

Laccase is the most explored enzyme in wastewater treatment due to its ability to degrade a wide range of micro pollutants including dyes, pharmaceuticals, and endocrine-disrupting chemicals [37][38][39]. Unlike other oxidoreductases, laccase does not require hydrogen peroxide or other cofactors for substrate cleavage [40][41][42] and its range of compounds for oxidation can be increased with redox mediators [43][44]. Laccase-based composite

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biocatalysts show great potential in wastewater treatment as they have demonstrated high pollutant degradation rates with high reusability (**Table 1**). For example, Laccase/Fe_2O_3/PEI biocatalyst completely degraded sulfa drugs (Sulfadiazine, Sulfamethazine and Sulfamethoxazole) within 30 min and could still degrade 82.8% after 10 cycles in the same time frame [24]. Laccase/Ca-alginate beads degraded 99% bisphenol A [19] and dyes (aniline purple–86%, lanset grey G–85%, and reactive black 5–80%) [45] in 2 h and 24 h, respectively.

Table 1. Application of enzyme-nanoparticle-polymer composites in degradation of organic pollutants for application in wastewater treatment.

Nanocomposite (NC)	Immobilization Method	Pollutants Removed	Degradation (%)	Degradation Time	Reusability	Ref.
TiO_2/polyvinylidene fluoride (PVDF)	Crosslinking of TiO_2/PVDF membrane using APTES and glutaraldehyde followed by immersion in laccase solution	Bisphenol A	95	5 h	91.7% (96 h of continuous use)	[46]
TiO_2/bacterial cellulose (BC)	Physical adsorption of TiO_2 on BC followed by crosslinking with glutaraldehyde and immersion in laccase solution	Reactive red X-3B in presence of ABTS	80	60 min	70% and 57% (6 and 10 cycles, respectively)	[1]
Calcium alginate	Physical entrapment of enzyme in nanocomposite	Fluoranthene in a fluidized bed reactor	81.06	8 h	66.845% (60 days of storage)	[27]
Fe_2O_3/poly(ethylene glycol)/concovalin A	Chemical co-precipitation followed by crosslinking with glutaraldehyde and immersion in laccase solution	Sulfadiazine Sulfamethazine Sulfamethoxazole (all in presence of syringaldehyde mediator)	100	30 min	82.8% (10 consecutive cycles)	[24]
MNPs/chitosan	Physical mixing of NPs and chitosan followed by	Reactive black 5	90	30 min	47% (10 cycles)	[47]
		Evans blue	60	30 min		

Nanocomposite (NC)	Immobilization Method	Pollutants Removed	Degradation (%)	Degradation Time	Reusability	Ref.
	crosslinking with glutaraldehyde and immersion in laccase solution	Tryphan blue	80	40 min		
		Direct blue 15	70	60 min		
MNPs/polydopamine	Functionalized MNP-polydopamine NC with dialdehyde starch followed by immersion in laccase solution	2,4-dichlorophenol	72	3 h	77% (8 cycles)	[48]
			91	12 h		
Fe_2O_3/Cu-alginate	Physical entrapment of enzyme in nanocomposite	Triclosan	89.6	8 h	86.9% (3 cycles in acetate buffer)	[4]
			53.2	8 h (wastewater)		
		Remazol Brilliant Blue R (RBBR)	75.8	8 h		
			55	25 h (wastewater)		
			35	25 h (waste water)		
Cu (II)-chitosan-graft-poly (glycidyl methacrylate)/poly (ethylene imine)	Physical adsorption of laccase on nanocomposites	Phenol in presence of ABTS	80	4 h	50% (8 cycles)	[30]
MNPs/chitosan	Crosslinking with glutaraldehyde followed by immersion in laccase solution	2,4-Dichlorophenol	91.4	12 h	75.8% and 57.4% (2,4-DCP and 4-CP after 10 cycles)	[33]
		4-Chlorophenol	75.5			
MNPs/SiO_2/poly (glycidyl methacrylate)-S-SH	Physical adsorption of enzyme on the nanocomposite	Meloxicam	92	48 h	82.3%, 88.9%, and 87.5% (meloxicam, piroxicam and Cd^{2+}, respectively, after 5 cycles)	[21]
		Piroxicam	95			
		Cd^{2+}	94			

Nanocomposite (NC)	Immobilization Method	Pollutants Removed	Degradation (%)	Degradation Time	Reusability	Ref.
MNPs/Poly(p-Phenylenediamine)	Covalent immobilization using glutaraldehyde for crosslinking	Reactive blue 19	80	1 h	43% (8 cycles)	[6]
MNPs@MoS$_2$/polyethyleneimine	Physical adsorption of laccase on nanocomposite	Malachite green	82.7	Overnight	62% (10 cycles)	[25]
		Bisphenol A	87.6			
		Bisphenol F (all in presence of ABTS)	70.6			
Cu-alginate	Physical entrapment of enzyme in nanocomposite	Fuschin blue	65 (HOBT)	4 h	100% and 95% (120 h continuous use and 15 days storage, respectively)	[8]
		Congo red	27 (ABTS)			
		Tryphan blue	51(syringaldehyde)			
		Malachite green	60 (ABTS)			
		Erichrome black T	50 (HOBT)			
		Crystal violet (all in different mediators)	32 (HOBT)			
		Textile effluent in a continuous flow packed bed bioreactor	66 (colour) 90 (BOD) 98 (COD)			
MNPs/chitosan	Physical entrapment of enzyme in presence of ionic liquid and ABTS	2,4-dichlorophenol	100	4 h	93.2% (for 2,4-DCP after 6 cycles)	[49]
		Bisphenol A	100	72 h		
		Indole	70.5	72 h		
		Anthracene	93.3	72 h		
MNPs/polyethylenimine	Crosslinking of NPs with PEI using glutaraldehyde followed by chelation of	Phenol in a fixed bed reactor	72.93% at a flowrate of 25 μL/min	-	-	[34]

Nanocomposite (NC)	Immobilization Method	Pollutants Removed	Degradation (%)	Degradation Time	Reusability	Ref.
	laccase with Cu(II)					
MNPs/Cu^{2+}-PEG	In situ oxidation of metal salt using PEG followed by physical adsorption of laccase	Malachite green	100 (ABTS)	120 min	99.9, 90.1, 89.4, 94.6, 76.5, 80.1, 74.6, and 66.1% (respectively, for the dyes after 10 cycles)	[10]
		Brilliant green	96.5 (ABTS)			
		Crystal violet	95.2 (ABTS)			
		Azophloxine	97.7 (TEMPO)			
		Red MX-5B	86.6 (ABTS)			
		Methyl orange	92.7 (VLA)			
		Reactive blue 19	96 (TEMPO)			
		Alizarin red	83.7 (TEMPO)			
TiO_2/Zn-alginate	Physical entrapment of enzyme in nanocomposite	Alizarin red	61	5 h	100% (14 cycles)	[50]
		Tryphan blue	96			
		Malachite green	100			
		Indigo carmine	100			
Ca-alginate	Physical entrapment with crosslinking of enzyme prior to entrapment	Bisphenol A	99	2 h	70% (10 successive cycles)	[19]
Ca-alginate	Physical entrapment of enzyme in nanocomposite	Aniline purple	86.1	24 h	-	[51]
Ca-alginate	Physical entrapment of enzyme in nanocomposite	Reactive Red 180	67.2	11 days	-	[52]
		Reactive Blue 21	88.05			
Ca-alginate	Physical entrapment of enzyme in nanocomposite	Reactive T. Blue	92	72 h	22.3% (6 cycles)	[53]
Ca-alginate	Physical entrapment of	RBBR	85	2 h	52.1% and 70%	[45]

roxidase (HRP), due to its ability to oxidize a wide range of phenolic compounds in the presence of hydrogen peroxide [59]. It oxidizes phenolic compounds by adding hydrogen peroxide to form corresponding radicals which spontaneously interact to form insoluble polymers that can be easily removed from the wastewater [60]. HRP/nanoparticle-polymer composite biocatalysts have been explored in the degradation of phenols, dyes, and endocrine-disrupting compounds, as illustrated in **Table 2**. For example, HRP/MNPs/polyvinyl alcohol/poly acrylic acid could completely degrade estrone after 40 min [18], and HRP/TiO_2/polydopamine completely removed 2,4-dicholorphenol in Zhaohe wastewater samples in only 30 min [61]. Interestingly, the HRP/TiO_2/polydopamine biocatalyst retained 100% and 90% degradation activity after 15 and 25 reuses, respectively.

Nanocomposite (NC)	Immobilization Method	Pollutants Removed	Degradation (%)	Degradation Time	Reusability	Ref.
	enzyme in nanocomposite	Reactive Black 5	80	24 h	(Bismarck brown and all the	

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Nanocomposite (NC)	Immobilization Method	Pollutants Removed	Degradation (%)	Degradation Time	Reusability	Ref.
TiO_2/polydopamine	In situ polymerization of dopamine on TiO_2NPs followed by covalent crosslinking of enzyme with glutaraldehyde	2,4-dichlorophenol	100	30 min	100%, 90%, and 63.6% (15, 25, and 40 reuses, respectively)	[61]
MNPs/poly(glycidylmethacrylate-co-methylmethacrylate) (poly(GMA-MMA))	Crosslinking of enzyme and nanocomposite beads using glutaraldehyde	phenol	86	2 h	84% (8 weeks), 92%, and 79% (phenol and p-chlorophenol, respectively, after 48 h of continuous use)	[3]
		p-chlorophenol (in the presence of H_2O_2)	59			
Fe_2O_3/poly (amido amine) (PAMAM)/silk fibroin	Crosslinking of enzyme with nanocomposites using glutaraldehyde	Bisphenol A in presence of H_2O_2	80	120 min	-	[62]
Calcium alginate	Physical entrapment of enzyme in nanocomposite	Acid blue 113	76	240 min	Can be recycled up to 3 times	[7]
Aluminosilicate halloysite nanotubes/chitosan	Crosslinking of enzyme with nanocomposites using glutaraldehyde	Phenol in presence of hydrogen peroxide	98.8	30 min	60% (4 cycles)	[63]
MNPs/polyacrylonitrile	Crosslinking of enzyme with nanocomposites using glutaraldehyde	Phenol	85.2	-	52% (5 cycles)	[29]
MNPs/poly(vinyl alcohol)/poly(acrylic acid)	Physical adsorption of	Estrone	100	40 min	56.2% (7 cycles)	[18]

Nanocomposite (NC)	Immobilization Method	Pollutants Removed	Degradation (%)	Degradation Time	Reusability	Ref.
	enzyme on nanocomposites					
MNPs/polymethyl methacrylate	Physical entrapment of enzyme in nanocomposite	Phenol in presence of hydrogen peroxide	55	50 min	-	[64]
MNPs/poly(glycidylmethacrylate-co-methylmethacrylate) (poly(GMA-MMA))	Crosslinking of enzyme with nanocomposite beads using glutaraldehyde	Phenol	86	2 h	91% and 79% (phenol and chlorophenol, respectively, after 48 h of continuous operation)	[3]
		p-Chlorophenol (in presence of hydrogen peroxide in a fluidized bed reactor)	59			

lized on pollutant amine, it phthalate [32] ethylene blue in synthetic wastewater in just 50 min [2], glucose oxidase immobilized on NiFe2O4/tannin could degrade 98.6% of indigo carmine in presence of UV light within 90 min [31], and chloroperoxidase/TiO_2/polydopamine nanocomposites degraded over 95% of aniline blue and crystal violet in 2 min [61].

Table 3. Application of enzyme-nanoparticle-polymer composites in degradation of organic pollutants for application in wastewater treatment.

Nanocomposite (NC)	Enzyme	Immobilization Method	Pollutants Removed	Degradation (%)	Degradation Time	Reusability	Ref.
iO_2/polydopamine	Chloroperoxidase (CPO)	Covalent crosslinking of enzyme with nanocomposites using glutaraldehyde	Aniline blue	97.58	2 min	90.3%, 78.2%, and 53.71% (10, 15, and 20 reuses, respectively)	[61]
			Crystal violet	98.98	2 min		
$NiFe_2O_4$/tannin	Glucose oxidase	Physical adsorption of enzyme on nanocomposite	Indigo carmine in presence of UV light	98.6	90 min	85.57% (5 cycles)	[31]
$MnFe_2O_4$/calcium alginate	Glucose oxidase and Laccase	Physical adsorption of enzymes on the nanocomposite	Methylene blue	82.13	1 h	-	[9]
			Indigo	25.09			
			Acid red 14	20.42			
MNPs/PAMAM	Glycerophosphodiesterase (GpdQ)	Crosslinking of enzyme with nanocomposites using glutaraldehyde	Organophosphate pesticide	44.5	120 days	Used as a filter in a Pasteur pipette between two	[14]

Nanocomposite (NC)	Enzyme	Immobilization Method	Pollutants Removed	Degradation (%)	Degradation Time	Reusability	Ref.
						layers of sand	
MNPs@SiO$_2$/polydopamine	Lignin peroxidase	Physical adsorption of enzymes on the nanocomposite	Tetracycline	100	24 h	80.3% and 67.5% (7 and 14 days of storage), 70% and 30% (4 and 8 cycles, respectively)	[32]
			Dibutyl phthalate	100	24 h		
			5-chlorophenol	100	24 h		
			Phenol	100	24 h		
			Phenanthrene	79	24 h		
			Fluoranthene	73	24 h		
			Benzo(a)pyrene	65	24 h		
MNPs/chitosan	Manganese peroxidase	Crosslinking of enzyme with nanocomposites using glutaraldehyde	Methylene blue	96	50 min	91.7% and 86.7% (5 cycles-methylene blue and reactive orange, respectively)	[2]
			Reactive orange 16	98			
Fe$_2$O$_3$/chitosan	*Saccharomyces cerevisiae* enzyme	Adsorption of chitosan on the NPs surface followed by crosslinking with enzyme using glutaraldehyde	Cu(II)	96.8	60 min	-	[65]

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