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Synthesis, characterization and application of zinc oxide nanocomposite for dye removal from textile industrial wastewater

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Dye effluents from textile units with azo compounds, heavy metals viz., Cu, Cd, Zn, Ni and Pb and other highly suspended solids contaminate the environment by releasing toxic and potential carcinogenic substances into the water bodies. Though there are various chemical and physical processes available for removal of such contaminants, their efficiency still needs improvement. In this study, we explored the efficiency of zinc oxide (ZnO) nanocomposites on the removal of dyes from synthetic and textile industrial effluents. ZnO nanoparticles were synthesized by chemical reduction method using zinc nitrate and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD results have shown the average size of nanoparticles to be ~20 nm. Size and shape of ZnO nanoparticles were confirmed by SEM. ZnO nanocomposite was prepared by incorporating ZnO nanoparticles with chitosan. Under optimum process conditions of initial dye concentration of 600 ppm, the ZnO nanocomposite dosage of 0.9 mg/mL at 30°C and pH 6, ZnO nanocomposite exhibited 99% of dye removal from synthetic and textile industrial effluent. However, process conditions were slightly differed when industrial effluent was used. The results suggested that ZnO nanocomposite could be used as an adsorbent for removal of dyes from industrial wastewater.

Keywords: Adsorbent, Chitosan, Nanoparticles, Pollution, Process optimization, Textile dye effluents (TDE), Textile industry

In industrial pollution, textile industries play a major role since they consume considerable quantity of water and chemicals and discharge large amounts of coloured dye effluents, which are toxic and non-biodegradable[1]. Dyes are extensively used in several textile-based industries because of their favorable characteristics, such as bright colour, water-fastness and simple application[2]. Synthetic dyes are exhibited in two forms, such as chromophores for determining the dye colour and auxochromes for determining the colour intensity[3]. Different types of dyes are used in textile industries; about 50% of reactive dyes are lost through hydrolysis during dyeing process. Hence, a large quantity of dyes appears in wastewater[4].

Textile dye effluents (TDE) contain 60-70% of azo compounds, which pollutes the environment by releasing toxic and potential carcinogenic substances into the waterbodies[5]. The dye industrial effluent comprises of highly suspended solids, chemical oxygen demand (COD), dye and chemicals in addition to heavy metals like Cu, Cd, Zn, Ni and Pb implies high toxicity to the environment. The TDE contaminates the water and land resources; thereby makes it unusable for human survival and growth[6,7].

As per the current statistics, nearly one lakh types of commercial dyes are available. In volume, 0.7-1.0 million tonnes of dyes are produced globally every year. It is estimated that about 90% of total dyes are used in fabric production and 0.28metric tonnes of TDE is discharged into the environment[8]. Dye stuffs are designed to resist biodegradation, and hence are barely removed from effluents using conventional treatment methods such as activated sludge treatments[9]. Biological treatments on TDE removal are hardly effective in complete removal of dye stuffs; rather they convert waste from one toxic form to another. However, their removal from the textile effluents before their discharge into the environment is inevitable not only for aesthetic reasons but also to secure water resources in water scarce regions[10]. The long term effects of dye toxicity through continuous TDE discharge on plants, animal and human is still not extensively studied.

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Various chemical and physical processes, such as chemical precipitation and separation of pollutants, coagulation, electro-coagulation, elimination by adsorption on activated carbon are employed for TDE removal[11]. Conventional water treatment aids in removal of harmful chemicals before the effluent is discharged into the environment, however, has practical complications and reduced efficiency[12]. Adsorption process is a simple and convincing process and need to be improved by developing more effective and cheaper adsorbents with higher adsorption capacities[13]. Chitosan has been reported as a potential adsorbent for removal of dyes[14]. The advantages of inorganic adsorbents over organic adsorbents are superior durability, less toxicity and greater selectivity and heat resistance[15].

Chitosan (CS) is a biopolymer derived from shrimp and crab shells with the characteristics of nontoxification, biodegradation and possess high efficiency rate in TDE removal[16]. It is an important substrate in various applications on environment treatment and drug delivery strategies. Several chitosan composites such as CS-TiO_2 (Titanium dioxide), CS-cuprous oxide, CS-CdS and CS-ZnO (Zinc oxide) are used to remove organic constituents. Adsorption of TDE on ZnO nancomposites is simple and charge guided process. The charges present on the surface of nanoparticles assist the adsorption process. ZnO nanoparticles are economically cheaper to prepare and possess better semiconducting properties than TiO_2[7-19].

Zinc oxide is n-type semiconductor with many attractive features. Zinc oxide with wide band gap of 3.17 eV as compared to TiO_2 is capable to generate hydroxyl radicals. Heterogeneous photocatalysis is a very promising method among advanced oxidation processes (AOPs), which can be applied for the degradation of pollutants. Heterogeneous photocatalysis with semiconductors such as TiO_2, ZnO, Fe_2O_3, CdS, and ZnS are used for removal of various contaminants[15]. The main advantage of ZnO over TiO_2 is the adsorption of larger fraction of UV spectrum and the corresponding threshold of ZnO is 425 nm[20]. It has also been reported that ZnO exhibited higher activity than TiO_2. Photocatalytic degradation of TDE with ZnO-Fe_3O_4-CS exhibited 70% removal after third recycle compared to COD treated samples[21]. The binary ZnO-Glass films are employed in photocatalytic decolourization of direct yellow 86 in aqueous solutions[22]. Photocatalytic adsorption exhibited 99% organic TDE removal of methylene blue and malachite green dyes with minimal dosage of ZnO-Polyaniline nanocomposite[23].

The incorporation of ZnO nanoparticles into polymers like chitosan has an advantage of recycling. ZnO-CS nanocomposites can easily be retained over ZnO nanoparticles. In this study, we have focused on preparation of ZnO-chitosan nanocomposites and their efficacy in removal of dyes from synthetic and textile industrial wastewater.

Materials and Methods

Materials

Zinc nitrate, polyvinyl pyrrolidone (PVP), H_2O_2, NaCl, chitosan flakes and sodium hydrosulphite were purchased from M/s. Himedia Laboratories Pvt. Ltd. India. Congo red and brown BR dye powder were procured from M/s. Merck Chemicals and M/s. Indokem Chemicals, India, respectively. All other chemicals used were of analytical grade.

Collection of industrial effluent

Textile industrial dye effluents were collected in and around Arcot (12°56´N, 79°24´E), Vellore District, Tamil Nadu, India.

Synthesis of ZnO nanoparticles

ZnO nanoparticles (NPs) were synthesized by following the modified method[19]. Using 100 mL of deionized water (Millipore, Mill-Q), 0.1 M Zn $(NO_3)_2$ was hydrolyzed with 250 mL of 0.2 M of NaOH and 1% PVP was added and stirred continuous for 2 h. The suspension was centrifuged at 3000 rpm for 5 min at 4°C and pellet was obtained. About 1 M of H_2O_2 was added at 75°C and stirred for 1 h. Further, the sample was dried for 3 h in an oven at 65°C and subjected to calcination at 350°C for 6 h.

Preparation of ZnO-CS nanocomposite

About 2.5 g chitosan in 300 mL of 0.1 M acetic acid with 40 mL of 0.2 M sodium chloride was mixed and incubated for 12 h. Along with 50 mL of 0.1 M acetic acid, 1.25 g of ZnO NPs were added and stirred for 24 h. A transparent solution was obtained and dried in an oven at 65°C.

Characterization studies

Estimation of Dye concentration

Dye concentration and removal efficiency of ZnO-CS nanocomposite was estimated using UV-Vis spectrophotometer (Schimadzu UV-Spectrophotometer, Model UV-1800). For estimation of dye in synthetic effluent, absorbance was measured at 460 nm against blank and congo red was used as standard. For industrial effluent, the absorbance was measured at λ_{max} 465 nm against blank.

X-ray diffraction analysis

The structure of prepared ZnO nanoparticles and ZnO-CS nanocomposites was investigated by X-ray diffraction analysis (Advance Powder X-ray diffractometer, Bruker, Germany, Model D8). The sample was lyophilized and made to powdered form for XRD analysis. The sample was scanned through a range of 2θ angles in which all possible diffraction directions of the lattice was attained due to the random orientation of the powdered material. Using Eq. (1), interaction of the incident X-rays with the sample produced constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda$=2$d$sinθ). These diffracted X-rays were detected, processed and counted for analysis of particle size in nanometer regime.

$$\mathrm{P} = \frac{K\lambda}{\beta\,\mathrm{Cos}\theta} \quad (1)$$

where, P = particle size, k = Scherrer's constant (0.94), λ value can be derived from Bragg's equation ($2dSin\theta = n\lambda$), λ = wave length, β = full maxima half width, θ = diffraction angle.

Scanning Electron Microscopy (SEM) *analysis*

ZnO nanoparticles and ZnO-CS nanocomposites were sprinkled on scotch tape fixed to a metal stub and gold coated (~100Å). The gold coated samples were scanned in scanning electron microscopy (Model: Leo 435 VP, M/s Leo Electron Microscopy, Cambridge, UK) at 20000X resolution and different positions depicting distinct morphological features were photographed.

Dye removal using ZnO-CS nanocomposites

The synthesized chitosan mediated nanocomposites were used for adsorption of synthetic and industrial textile dye effluents. Synthetic effluent of 1000 ppm was prepared using congo red and concentration of collected industrial textile dye effluent was found as 850 ppm. Adsorption of textile dye effluent was carried out with ZnO-CS nanocomposite using batch process and the effect of initial dye concentration (200-1000 ppm), nanocomposite dosage (3-11 mg), pH (4-9), temperature (4-60°C) and contact time (30-150 min) were optimized. About 6 mg of ZnO-CS nanocomposite was added to 10 mL of synthetic effluent of known concentration and subjected to stirring at 150 rpm for 1 h at room temperature (37°C). To separate the treated effluent and nanocmposite containing dye, the mixture was centrifuged at 5000 rpm for 10 min at room temperature. The supernatant was collected for residual dye estimation by UV-vis spectrometer.

Results and Discussion

Morphology and size distribution

XRD pattern of synthesized ZnO-CS nanocomposites

Synthesized ZnO and ZnO-CS nanocomposites evaluated with XRD studies and confirmed the presence of crystalline pattern of Zinc oxide nanoparticles, which was matched with JCPDS (Joint committee on powder diffraction standards) data[24]. The data obtained from the research experimentation exhibited the presence of nano sized ZnO and ZnO-CS form as shown in Fig. 1 A and B. The analysis revealed the peak value of ZnO-NPs to be 31.76˚, 34.41˚, 36.23˚, 47.62˚ and 56.67˚; and that of ZnO-CS nanocomposite at 12.48˚, 16.44˚, 20.05˚, 22.34˚, 27.60˚ and 25.20˚. The average particle size was derived using Scherrer equation and the average particle size was found as 20 nm.

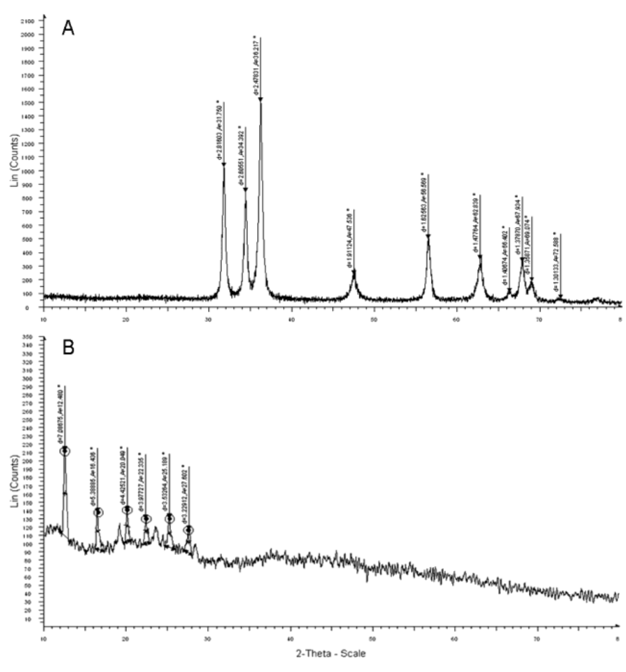

Fig. 1—XRD analysis. (A) ZnO Nanoparticles; and (B) ZnO-CS nanocomposites

SEM analysis

Size and morphology of ZnO-NPs and ZnO-CS nanocomposites were studied using SEM analysis (Fig. 2 A and B). The SEM image showed that the size and shape of the synthesized ZnO-NPs was ~75 nm and spherical, respectively. ZnO-CS nanocomposite was crystalline with the average particle size range of 75-200 nm. The coating of chitosan particles over the surface of ZnO nanoparticles was confirmed by SEM analysis. The average particle size of the ZnO-CS nanocomposite is influenced by the coating of chitosan particles[25].

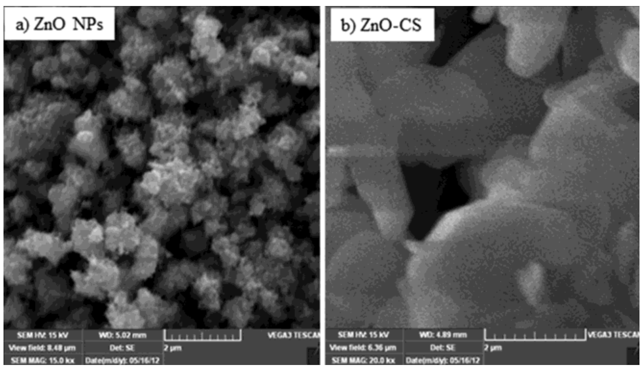

Fig. 2—SEM analysis. (A) ZnO Nanoparticles; and (B) ZnO-CS nanocomposites

Effect of process parameters for dye removal using ZnO-CS nanocomposites

Effect of initial dye concentration

The initial dye concentration was optimized against the efficiency of dye removal from synthetic effluent. It influences the absorption of photons by the catalyst surface, thereby, affect the degradation precentage[26]. The dye removal efficiency decreased slightly when the initial dye concentration was increased from 200 to 600 ppm and decreased thereafter rapidly with increase in initial dye concentration (Fig. 3A). At 600 ppm of initial dye concentration, the removal efficiency was 94%. Hence, it was construed as optimum.

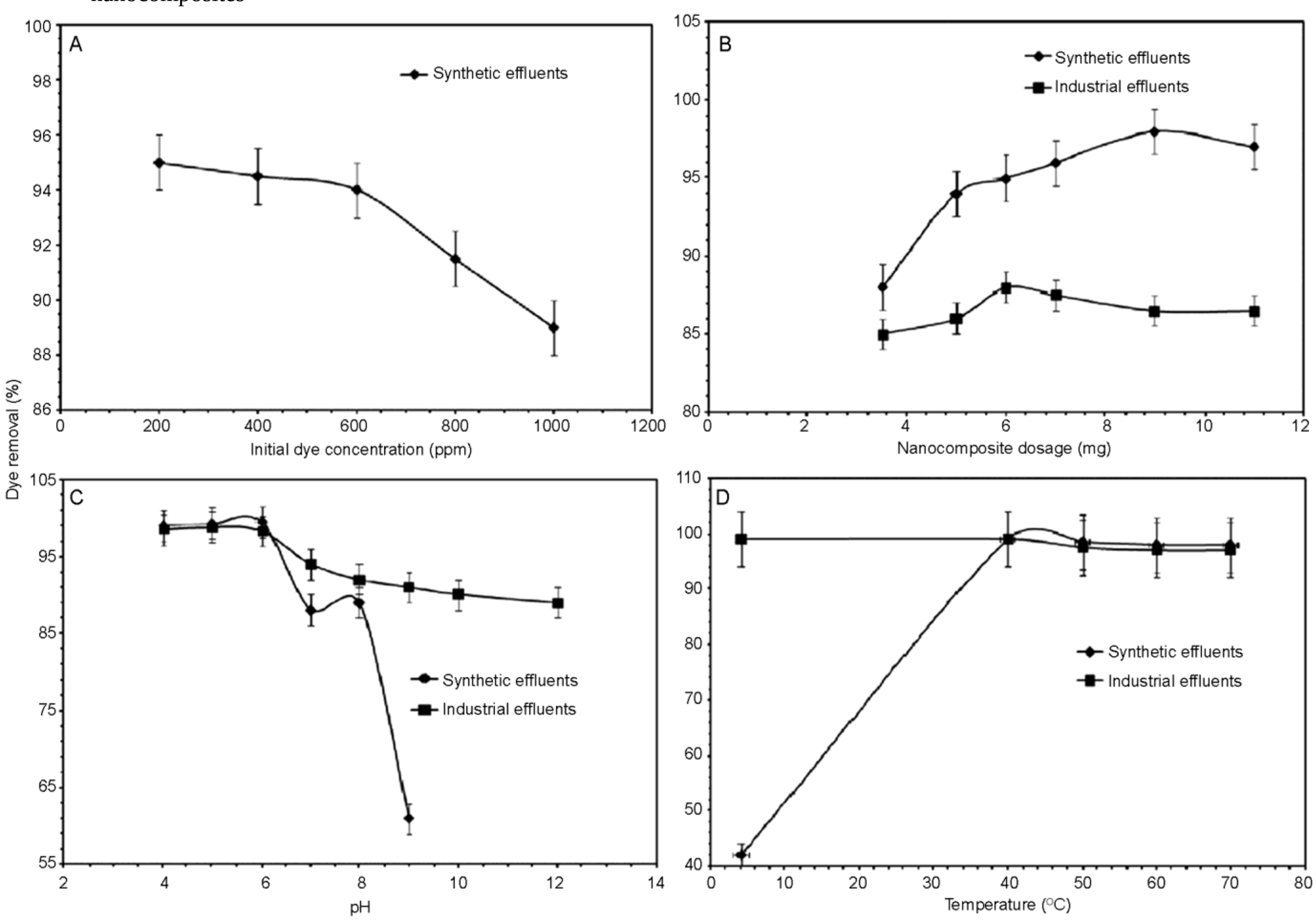

Fig. 3—Effect of process parameters for dye removal using ZnO-CS nanocomposites. (A) Initial concentration of synthetic dye; (B) Nanocomposite dosage; (C) pH; and (D) Temperature

Effect of ZnO-CS nanocomposite dosage

The optimized initial dye concentration of 600 ppm was maintained as constant by varying the dosage of ZnO-CS nanocomposite from 3-11 mg. The dye removal efficiency increased with increase in dosage of nanocomposite as adsorption was high and remains constant. Maximum dye removal of 98% was obtained with nanocomposite dosage of 9 mg. Similarly, in the case of industrial effluent, the dye removal efficiency increased with increase of nanocomposite dosage. Maximum dye removal of 88% was obtained at 6 mg of dosage and remained constant (Fig. 3B). The lower removal efficiency obtained with industrial effluent could be due to the presence of other impurities.

Effect of pH

The optimized initial dye concentration and nanocomposite dosage level are maintained constant; pH was optimized for synthetic and industrial effluent and varied from 4-9. At low pH, zinc becomes more positively charged and adsorption of dye was increased. The dye removal efficiency was remained same and decreased with increase in pH from 6.0 to 9.0 (Fig. 3C). Nanocomposite exhibited the dye removal efficiency of 99% when synthetic effluent was processed at pH 6. Similarly, it exhibited the dye removal efficiency of 98% while industrial effluent was processed at pH 6. Hence, pH 6 was construed as optimum.

Effect of temperature

The dye removal efficiency of synthetic and industrial effluent was optimized by varying the temperatures from 4 to 70°C (Fig. 3D). Increase in temperature activated ZnO-CS nanocomposite and resulted in increased adsorption of dye; thereby increased the dye removal efficiency. The dye removal efficiency was increased with increase in temperature. The maximum dye removal efficiency of 99% was obtained at 40°C. Hence, the process temperature of 40°C was construed as optimum.

Effect of contact time

The maximum dye removal efficiency of synthetic and industrial effluent was studied by varying the contact time from 15 to 150 min with optimized nanocomposite dosage, pH, and temperature. The dye removal efficiency was increased rapidly with increase in contact time from 15 to 60 min and thereafter remained same. The dye removal efficiency of 98.5% was obtained with synthetic and industrial effluent for 1 h. Hence, the contact time of 1 h was construed as optimum (Fig. 4).

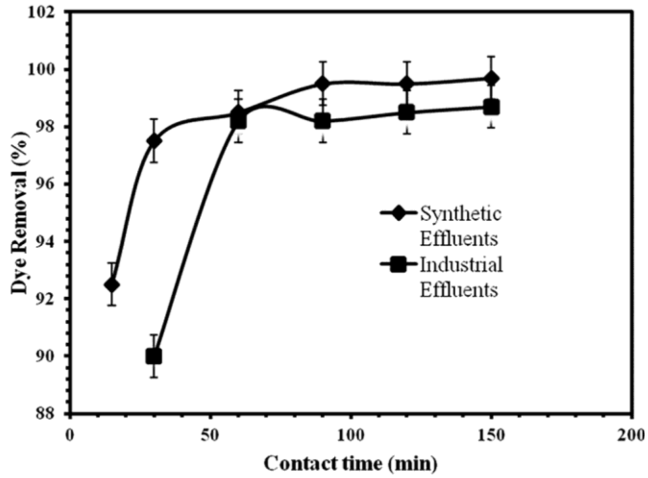

Fig. 4—Effect of contact time on dye removal efficiency

Conclusion

Synthesis of bio-mediated chitosan based zinc oxide nanocomposite exhibited the particle size range as 75-200 nm. SEM results revealed the size and morphology of synthesized ZnO-NPs as ~75 nm and spherical and ZnO-CS nanocomposite was crystalline with size range of 75-200 nm. The coating of chitosan particles was confirmed over the surface of ZnO nanoparticles by SEM analysis. The results suggested that the synthesized ZnO-CS nanocomposite could be used as an effective adsorbent for the removal of carcinogenic dye from textile industrial wastewater. Further, ZnO-CS nanocomposite could be reused for subsequent studies.

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