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Bactericidal and catalytic performance of green nanocomposite based-on chitosan/carbon black fiber supported monometallic and bimetallic nanoparticles

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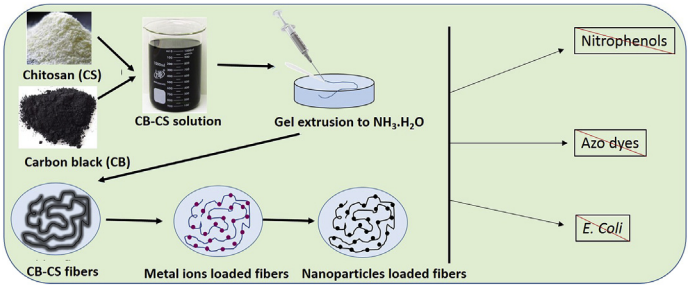
HIGHLIGHTS

- Carbon-black/chitosan fibers (CB–CS) supported mono- and bi-metallic nanoparticles (NPs) were prepared.
- The successful preparation of the material was confirmed by different characterization methods.
- CB-CS fibers supported metal NPs catalysed the reduction of toxic *para*-nitrophenol and azo dyes.
- The bimetallic Co + Cu/CB–CS showed highest catalytic performance among all the tested catalysts.
- All the CB-CS fibers supported metal NPs showed strong antimicrobial property.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanoparticles were synthesized on the surface of green nanocomposite based on carbon black dispersed in chitosan (CB–CS) fibres. The nanoparticles were monometallic Co, Ag and Cu and bimetallic Co + Cu and Co + Ag. The CB–CS fibres were prepared and introduced into separate metal salt solutions containing Co^{2+}, Ag^{+} and Cu^{2+} and mixed Co^{2+}+Cu^{2+} and Co^{2+}+Ag^{+} ions. The metal ions immobilized on the surface of CB–CS were reduced using sodium borohydride ($NaBH_4$) as reducing agent to synthesize the corresponding zero-valent metal nanoparticles-loaded CB–CS fibres. All the nanoparticles-loaded CB–CS samples were characterized using field emission-scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray diffraction techniques. When tested as catalysts, the nanoparticles-loaded CB–CS showed excellent catalytic ability for the reduction of toxic and environmentally unwanted pollutants of *para*-nitrophenol, congo red and methyl orange dyes. Afterwards, the antimicrobial activities of virgin and metal-loaded CB–CS fibres were tested and the metal-loaded CB–CS fibres were found to be effective against *Escherichia coli*. In addition, the catalyst can be recovered easily by simply

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Antibacterial
Escherchia coli

removing the fibres from the reaction mixture and can be recycled several times while maintaining high catalytic efficiency.

1. Introduction

Over the past decades, different noble metal nanoparticles have been used in catalysing different reactions, such as Au nanoparticles (Wu et al., 2015), Fe_3O_4@SiO_2–Ag (Du et al., 2012), Ag nanoparticles (Ahmad et al., 2016; Kamal et al., 2017a) and Pt/C (Vaidya et al., 2003) in the catalytic reduction of *para*-nitrophenol (*p*NP) to *para*-aminophenol (*p*AP) using $NaBH_4$. As alternatives to noble metal nanoparticles, some other transition-metal nanoparticles have proven to be similar in catalytic activity and a few have claimed them to have better performance in catalysing various reactions (Zhou et al., 2013; Datta et al., 2014; Kamal et al., 2016b). Bimetallic nanoparticles were more effective in catalysis. However, major concerns of using transition-metal nanoparticles as catalysts are their instability, self-aggregation, high cost and separation. The instability of metal nanoparticles (self-aggregation) is due to their high surface energy. Such an aggregation results in a decrement of both the selectivity and the catalytic activity of the nanoparticles. The next most challenging task in using metal nanoparticles as a catalyst is their separation from the mixture after completion of the reaction. It is reported that nanoparticles supported on high surface area substrates such as polymer spheres, carbon materials and metal oxides show good distributions and fine structure, and are easier for separation and recycling (Pacławski and Wojnicki, 2009; Lin and Doong, 2011; Khan et al., 2016b; Kamal et al., 2017b). To avoid the sintering of metal nanoparticles, diverse types of solid immobilizers have been used, such as polymers (Liang et al., 2013), alumina (Chen et al., 2015), zeolites (He et al., 2012), silica (Chen et al., 2010) and carbon (Yeung and Wolf, 1991), which showed excellent catalytic performance in a wide range of reactions. High conversion efficiency and rate of nitrophenol conversion were shown by all immobilized nanoparticles. In addition, the potential risk produced by nanoparticles could be reduced as well because the loss of nanoparticles could be avoided by their immobilization (Zhou et al., 2014).

Among the candidates for support, polymers are most frequently used because of their flexible nature and easy processing. Polymer nanocomposites are materials that are formed by the combination of polymers with nanofillers, and generally increase different properties of the polymer (Khan et al., 2011; Kim et al., 2013; Tahseen et al., 2016). Several works have been published for the preparation of nanocomposite using different biopolymers, like cellulose (Morawski et al., 2013), methylcellulose (Habibi et al., 2007) and chitosan (Khan et al., 2016b) as the main matrix. The most promising polymer is chitosan, which provides some favourable characteristics, like low cost, easy availability and having good chemical and environmental stability(Shahid Ali et al., 2016). Chitosan (CS) (ranks second most abundant natural polymer to cellulose) is a hydrolysed product of chitin. It is biocompatible, biodegradable and environmentally friendly. Recently, we prepared CuO-embedded chitosan spheres, which showed antibacterial activity and promising results in the adsorption of methyl orange (Khan et al., 2016b). Similarly, surface imprinted chitosan–TiO_2 and chitosan–ZnO composite has been reported for photocatalytic degradation of methyl orange (Kamal et al., 2015; Xiao et al., 2015). Hence, the nanocomposite is the best route to enhance the properties of polymer with the addition of inorganic nanomaterials.

Nitroaromatics such as nitrophenols are important building blocks to produce pesticides, pharmaceuticals, dyes, explosives and other chemicals used in industry (Emmanuel et al., 2014). However, the US Environmental Protection Agency (EPA) has considered nitrophenols as one of the main concern pollutants due to their hazardous and toxic nature (Guo et al., 2016). In addition to nitrophenols, coloured organic compounds were also reported as hazardous, toxic and carcinogenic, which pose a risk to humanity (Dong et al., 2007). Similarly, the presence of biological microorganisms such as bacteria in water badly affects its quality (Kamal et al., 2016a). Therefore, it is of utmost importance to detoxify water by killing the harmful bacteria. Different methods have been put forward to remove bacteria from water resources, such as electrochemical treatment, adsorption and microbial degradation (Chang and Chen, 2009; Chiou et al., 2013). However, these treatment processes have some limitations, which must be overcome by employing efficient new materials (Liu et al., 2012).

In the present work, carbon black (CB) nanomaterial was blended with CS by a simple one-step solution-based process to prepare green nanocomposite. CB was chosen as the dispersant material as it has high surface area and is known to have high adsorption capacity for different dyes (Bansal and Goyal, 2005; Sharififard et al., 2013). Moreover, chitosan shows poor mechanical properties. Therefore, CB was added to make a nanocomposite for better mechanical properties of the fibres. Next, we choose transition metals (Co, Cu), and their combination with Ag for the synthesis of nanoparticles. The bimetallic form of the nanoparticles was chosen because some recent studies described that it shows better catalytic performance (Fan et al., 2016; Nivethaa et al., 2017; Li et al., 2017). The CB–CS composite fibres were produced by pushing its gel from a syringe into a coagulation bath. After treating with different metal salt solutions, CB–CS composite fibres were treated with $NaBH_4$ for the synthesis of corresponding nanoparticles. Different metal-loaded CB–CS nanoparticles were characterized and applied for reduction of nitrophenol and azo dyes. In addition, comparative antibacterial studies of CB–CS and metal-loaded nanocomposite were performed against *E. coli*.

2. Experimental

2.1. Chemicals and reagents

Salts of silver nitrate, cobalt(II) nitrate and copper(II) sulphate, chitosan, ethanol, sodium borohydride and ammonium hydroxide were bought from Sigma-Aldrich. Deionized water was obtained from the departmental Millipore-Q water purification system. Other required reagents like nitrophenols and the dyes congo red and methyl orange were purchased from BDH Chemicals, Poole, England.

2.2. Preparation of carbon black–chitosan nanocomposite

CB–CS nanocomposite was prepared from the stock solution of chitosan containing 5.0 g chitosan polymer in 20 mL acetic acid and 80 mL deionized water. The CB nanomaterials with 5 wt% of chitosan were added and well dispersed in the solution through continuous stirring. Then, composite fibres were prepared from this