Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 166 (2016) 49–55

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Graphene oxide supported copper oxide nanoneedles: An efficient hybrid material for removal of toxic azo dyes

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ARTICLE INFO

Article history:
Received 28 November 2015
Received in revised form 5 April 2016
Accepted 2 May 2016
Available online 4 May 2016

Keywords:
Graphene oxide
Copper oxide nanoneedles
Adsorption
azo dyes

ABSTRACT

Herein, we report a simple, one step synthesis of hybrid copper oxide nanoneedles on graphene oxide sheets (GO-CuONNs) through sonochemical method. The present method affords a facile mean for controlling effective concentration of the active CuO nanoneedles on the graphene oxide sheets, and also offers the necessary stability to the resulting GO-CuONNs structure for adsorption transformations.Furthermore, this hybrid GO-CuONNs is successfully employed in the removal of a series of hazardous ionic organic dyes namely coomassie brilliant blue, methylene blue, congo red and amidoblack 10B. Through careful investigation of the material, we found that the synergetic effect between CuONNs and GO play a significant role in the adsorption of all the dyes studied. The prepared hybrid material contains both hydrophobic and hydrophilic environment which is expected to enhance the electrostatic interaction between the adsorbent and the dye molecules, consequently favouring the adsorption process.

1. Introduction

Dyes used in the industries are generally classified as (a) anionic (direct, acid and reactive dyes), (b) cationic (all basic dyes) and (c) non-ionic (dispersed dyes) [1–4]. Basic and reactive dyes are widely used in the textile industry because of their favourable characteristics of bright colour, being easily water soluble, cheaper to produce and easier to apply on fabric [5–7]. These ionic organic dyes present in the effluents are of serious concern because of their adverse effects to human beings and environment [8–10].

Numerous physical, chemical and biological methods are actively attempted for efficient treatment of dyes in the effluents. One of the well-known and simple chemical methods for dye degradation is based on Fenton like reactions, where effective degradation is achieved through –•OH radical. However, larger consumption of H_2O_2 and subsequent treatment of ferrous slurry makes this process more tedious [11]. Chemical degradation of dyes through photocatalysis is believed to be a viable alternate. The most commonly utilized photocatalyst is TiO_2, which is active only in the ultraviolet light range due to its wide band gap (3.2 eV for anatase). Many reports have appeared on modification of TiO_2 with variety of materials whereas the quantum yield is still not satisfactory to meet the demand for practical applications [12–15]. Similarly physical adsorption of dyes on charcoals [16], activated carbons [17], polymers [18] and chemically modified cellulose [19] have also been tried enormously and the regeneration of the adsorbents still remain complicated.

In contrast to the conventional physical/chemical methods, biological treatment of the dye effluents offers few benefits owing to its low operating cost, versatility of the active microbial species and the range of metabolic pathways for effective dye degradation [20–23]. Through the past few years a number of microorganisms, including *S. Lentus*, have been documented which are able to transform azo dyes to non-coloured, non-toxic products under aerobic ecological conditions or even completely mineralize them [24]. Irrespective of these advantages, the industrial application of this process is limited due to the low rate of the degradation and the high rate of the biomass residue production.

In this regard, several investigators have developed various platforms for dye degradation based on interesting strategies using diversified materials. Li et al., have reported a recyclable photocatalyst based on Fe_3O_4@C@Cu_2O magnetic core-shell composite [25]. Zhang et al.,have utilized superparamagnetic Fe_3O_4 nanocomposite for the oxidation of phenolic and aniline based compounds in aqueous solution [26]. Panda et al., have demonstrated the catalytic activity of the Fenton like mesoporous Fe_2O_3-SiO_2 composite towards the complete degradation of methyl orange [27]. Likewise, Fe_3O-poly (3.4-ethylene dioxythiophene) core shell nanocomposite was also used as Fenton like heterogeneous catalyst for the degradation of reactive black 5 and orange II dyes [28]. All the above mentioned literatures have come

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http://dx.doi.org/10.1016/j.saa.2016.05.002
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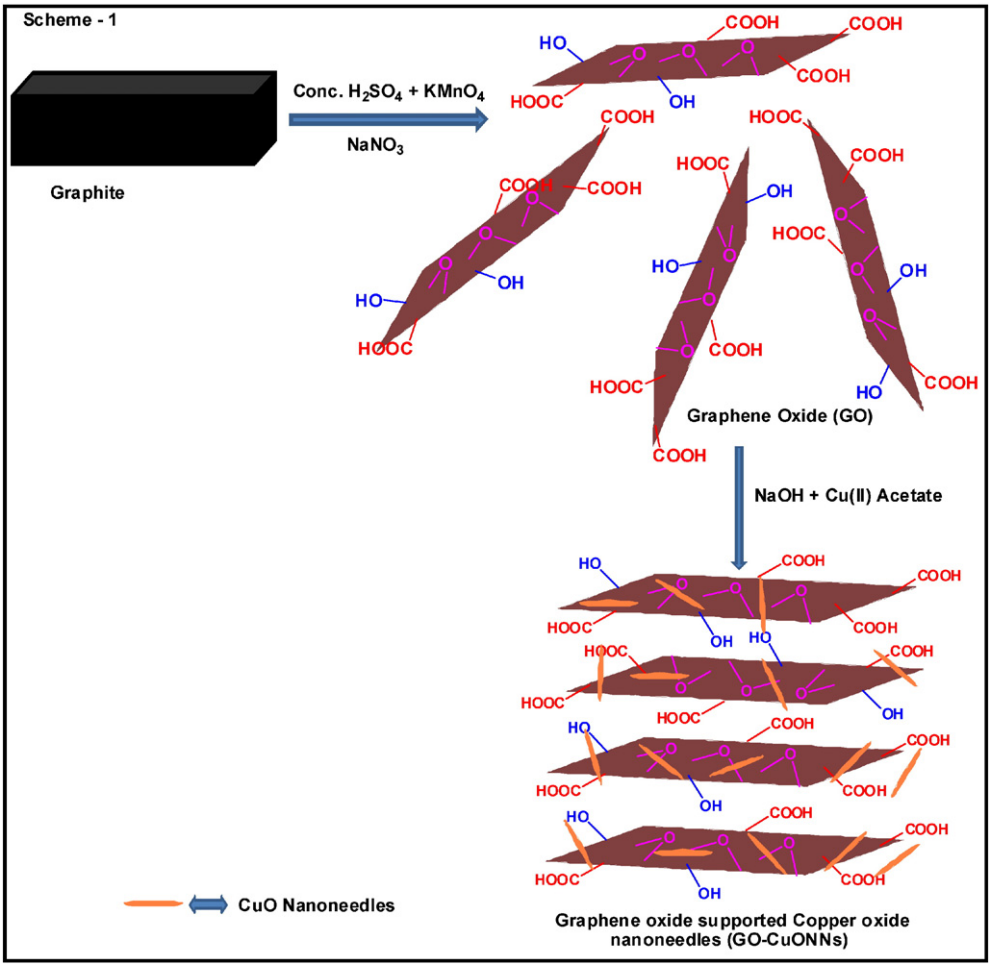

Scheme 1. Schematic illustration of synthesis of graphene oxide (GO) stabilized copper oxide nanoneedles (GO-CuONNs).

up with few or more advantages in the process of dye removal, which also emphasises the need for developing new and efficient nanomaterials for dye degradation with increased reaction rate without generation of secondary pollutants in the environment.

Based on the above discussions, it is obvious that the ideal material for the removal of dyes should possess, (i) large surface area, (ii) easy adaptability towards variety of dyes, (iii) in the event of any additional chemical reaction with external reagents, the resultant product must also be adsorbed on the surface and (iv) preferably heterogeneous type with hydrophilic and hydrophobic functionalities for better availability to provide strong physical adsorption in aqueous medium.

Graphene oxide (GO) has continuously proven to be a material of high interest because of its high surface area, porous structure and special reactivity [29–32]. In particular, the composites of GO with the low cost copper based metal oxides (CuO) are gaining large interest because of their potential towards diversified applications that include photocatalytic conversion of CO_2 to methanol [33], non-enzymatic glucose sensing [34] and so on. Owing to the promising characteristics of GO and CuO, our focus here is to utlize GO along with copper oxide nanoneedles (CuONNs) as a tool for the removal of synthetic ionic organic dyes. Incorporation of CuONNs onto GO is expected to introduce hydrophilic environment over GO and thus enhancing the electrostatic interaction between dye molecules and GO.In the present investigation, we have prepared copper oxide nanoneedles on graphene oxide sheets (GO-CuONNs) see Scheme 1 and demonstrated a simple and environment friendly methodology to remove the hazardous ionic fabric dyes using heterogeneous GO-CuONNs hybrid material as adsorbent.

2. Experimental

2.1. Chemicals

Graphite, fine powder of particle size 150 μm was purchased from Sigma Aldrich. Sulfuric acid, potassium permanganate, hydrogen peroxide, sodium nitrate, sodium hydroxide, cupric(II) acetate, congo red (CR), amidoblack 10B (AB), coomassie brilliant blue (CBB) and methylene blue (MB) were obtained from Merck, India. All chemicals were used without further purification. Double distilled water was used throughout the experiment.

2.2. Synthesis of graphene oxide supported copper oxide nanoneedles (GO-CuONNs)

The improved Hummers method was employed in the synthesis of GO [31,35]. The oxidation procedure used in this report could prepare GO with fewer defects in the basal plane. Cupric acetate monohydrate (0.33 g) was dissolved in the mixture of 250 mL of ethanol and 500 mL of distilled water in a 1 L beaker. Then 0.74 g of NaOH pellets was slowly added to the mixture and was sonicated for 10 min until the colour of the reaction mixture changed from blue-green to brownish black. Subsequently, 0.5 g of GO was added to the reaction mixture and the solution was kept under sonication for further 1 h. The resultant solid suspension was filtered using Buchner funnel and dried under vacuum at room temperature.