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Sonochemical-assisted synthesis of $CuO/Cu_2O/Cu$ nanoparticles as efficient photocatalyst for simultaneous degradation of pollutant dyes in rotating packed bed reactor: LED illumination and central composite design optimization

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ABSTRACT

$CuO/CuO_2/Cu$ nanoparticles were prepared by sonochemical combined thermal synthesis method and used as new photocatalyst for simultaneous photocatalytic degradation of safranin O (SO) and methylene blue (MB) dyes in rotating packed bed reactor equipped to blue light emitting diode (LED). The physicochemical properties of the synthesized $CuO/Cu_2O/Cu$ nanoparticles were investigated by XRD, SEM and DRS analysis. The band-gap of the prepared $CuO/Cu_2O/Cu$-NPs was estimated to be about 1.42 eV which is appropriate for photodegradation process under blue light irradiation. In rotating packed bed reactors, two key parameters are very important, one high centrifugal field and other porous media, which intensify mass transfer operation leads to photodegradation improvement. The maximum photodegradation efficiency was obtained at pH of 6 and subsequently the effects of $CuO/Cu_2O/Cu$-NPs dosage, rotational speed, initial dyes concentration, flow rate and reaction time were studied by central composite design (CCD) and optimized values were found to be 0.3 g/L, 900 rpm, 10 mg/L of both dyes, 0.3 L/min and 90 min, respectively. Finally, results showed that synergistic effects induced by forming Cu_2O/CuO heterojunction containing Cu-NPs co-cocatalyst greatly accelerate electron transfer and effectively retard the reduction of CuO by photo-generated electrons.

1. Introduction

The toxic organic dyes due to development of industrials generates problems and hazards for different ecosystems. The contamination removal as essential issue in environmental systems were carried out by adsorption, coagulation, ozonation, electrochemical method and photocatalytic degradation. Amongst, photocatalytic degradation compare to the conventional purification methods causes directly conversion of pollutant to carbon dioxide and water and in this regard is superior to other methods and lead to the pollutants separation or transfer to another phase. This method, is innovative and effective approach for removal and degradation of dyes [1]. In the photocatalytic degradation process, irradiation sources have an extensive contribution in enhancing the activity of catalysts. In this case, conventional photocatalytic reactors widely are based on application of UV lamps for irradiation source which are expensive [2]. These source, due to the consumption of high energy (high voltage to operate), toxic materials, instability due to overheating, low mechanical stability and short lifetime considered as not economic. Therefore, the using of sunlight or near UV light can be considerable economic savings especially for large-scale operations. Furthermore, in this work, light emitting diodes (LEDs) based on light source have several advantages such as high photon efficiency, low voltage electrical power source, power stability, emission in broader spectral wavelength and no need for cooling during long time operation for complete photocatalytic reactions [3]. As well as, the search and design of new visible-light-driven photocatalysts for organic transformation has importance role in this method. These photocatalysts due to their narrow band gap are activated under sunlight irradiation [4–6].

Cupric oxide (CuO) and cuprous oxide (Cu_2O) are low cost, abundant resources, nontoxicity, chemical stability and easy preparation in

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diverse shapes of nanosized dimension P-type semiconductor with a narrow band gap of 1.2 eV and 2 eV, respectively, while they have to meet high requirements, i.e. good charge separation, visible light absorption, available reaction sites accessibility and earth-abundance as well as environment benignity [7,8]. However, their photocatalytic activity and stability still need to be much improved. One strategy for refine these problems is to form by combining them together in presence of one surface plasmon resonance (SPR) cocatalyst [9]. Therefore, several thermochemical, sol–gel, chemical vapor deposition, sonochemical and hydrothermal methods were developed to synthesize CuO/Cu_2O [10–12]. The enhancement in catalytic activity has been explained on the basis of synergism between CuO and Cu_2O and the surface plasmon resonance effect of Cu which also acts as a co-catalyst present on the surface of CuO/Cu_2O photocatalysts. Amongst, sonochemical approach for CuO/Cu_2O preparation possible for procedure intensification based on the important cavitational effects induced in the liquid medium [13,14]. The creation of cavitational events and the subsequent release of energy at microscopic level mean that the energy is made at the specific point of conversion or at the controlling active locations which can certainly enhance the energy productivities and also yield improved processing rates [15,16]. Also the acoustic cavitation of ultrasonic in liquid provides a high localized pressures and temperatures in effect of development, growth and collapse of bubbles. These conditions lead to increase mass transfer, shorten reaction cycles, and homogeneity of the prepared nanomaterial [17].

In other hand, the advantages of the sonochemistry method over conventional approaches for the synthesis of $CuO/Cu_2O/Cu$ nanoparticles, is including more uniform size distribution, higher surface area, faster reaction time, and improved phase purity, which was proven by many researchers [18–21]. The reaction times required in conventional methods are often several days, ultrasonic irradiation significantly shortens the reaction time to a few hours [22]. This great benefit is due to acoustic cavitation phenomenon resulting from the continuous formation, growth and implosive collapse of bubbles in the aqueous solution. When solutions are exposed to strong ultrasound irradiation, sufficient sound energy can drive the formation of novel nanostructures to occur under ultrasonic irradiation [23,24].

Conventional reactors due to low liquid – solid interfacial area and sedimentation of contaminants at the surface and blocking the activated sites of photocatalysts have low mass transfer. As well as, poor light distribution due to the thick film of liquid (short light penetration on the surface of catalyst) cause significant decrease in photocatalytic efficiency [25–28]. In this work, the above limitations simply can be overcome by construction of photocatalytic reactor via centrifugal field to intensify photocatalytic degradation of methylene blue and safranin O. In this reactor, blue LED and $CuO/Cu_2O/Cu$-NPs were used as light sources and photocatalyst, respectively. For achieve to the maximum photodegradation efficiency, the effects of important variables were investigated using central composite design under response surface methodology.

2. Experimental

2.1. Materials and apparatus

All reagent was purchased from Merck Company (Darmstadt Germany). The pH was adjusted and measured using pH/Ion meter model 686 (Metrohm, Switzerland, Swiss). The concentration of each dye was determined using Jasco UV–Vis spectrophotometer model V-530 (Jasco, Japan). X-ray diffraction (XRD, Philips PW 1800) was recorded using Cu kα radiation (40 kV and 40 mA). The morphology of $CuO/Cu_2O/Cu$-NPs was studied by scanning electron microscopy (SEM: KYKY-EM3200) under an acceleration voltage of 26 kV. Diffuse reflectance spectra (DRS) were collected with an Avantes spectrophotometer (Avaspec-2048-TEC). The ultrasonic processor UP200S (200 watts, 50/60 kHz, Hielscher Ultrasonics Germany) was used for sonication during the synthesis of $CuO/Cu_2O/Cu$ nanoparticles. Other material and equipment was used according to our previous report [29–32].

2.2. Synthesis of $CuO/Cu_2O/Cu$-NPs nanoparticles

The $CuO/Cu_2O/Cu$-NPs nanoparticles were prepared as follow: 2.0 g copper acetate monohydrate was dissolved in 50 ml deionized water. Subsequently, ammonia solution (25% w/w) was added to adjust pH at 8 and the resultant blue suspension was irradiated with high intensity ultrasonic horn (Ultrasonic processor UP200S, 200 watts, 50/60 kHz, Hielscher Ultrasonics, Germany) in ambient air for 3 h (6 * 30 min). On completion of sonication, the suspension turned dark blue in color and pH of the initial solution increases to 11.0. The dark blue precipitate was centrifuged and washed with distilled water for several times. The resultant product was dried at 120 °C for about 12 h and the dry black powder sample obtained as $Cu/Cu(OH)/Cu(OH_2)$ nanoparticles was used for further sample preparation. To promote the formation of $CuO/Cu_2O/Cu$ nanoparticles thermal annealing of the $Cu/Cu(OH)/Cu(OH_2)$ powder was carried out in an electrical tubular furnace at 500 °C for 2 h in the presence of N_2 gas atmosphere. It has been observed that during the calcination process, $CuO/Cu_2O/Cu$ nanoparticles were prepared. The following equations present the possible formation mechanism for $CuO/Cu_2O/Cu$ [33]:

$$H_2O + \text{ultrasonication} \rightarrow {}^{\cdot}OH + H^{\cdot} \quad (1)$$

$$2OH^{\cdot} \rightarrow H_2O + O^{\cdot} \quad (2)$$

$$Cu(CH_3COOH)_2{\cdot}H_2O + H_2O \rightarrow Cu^{2+} + CH_3COO^{-} \quad (3)$$

$$^{\cdot}H\,(O^{\cdot}) + Cu^{2+} \rightarrow Cu^{+} \quad (4)$$

$$^{\cdot}H\,(O^{\cdot}) + Cu^{+} \rightarrow Cu^{0} \quad (5)$$

$$Cu^{2+} + OH^{-} \rightarrow Cu(OH)_2 \quad (6)$$

$$Cu^{+} + OH^{-} \rightarrow Cu(OH) \quad (7)$$

$$Cu(OH)_2 + Cu(OH) \rightarrow CuO/Cu_2O\ (\Delta\ 400\ ^{\circ}C\ \text{under}\ N2) \quad (8)$$

2.3. Experimental set-up

The reactor system (Fig. 1) is composed of several parts: rotating porous packed bed, motor, strip blue LED, storage tank equipped with a stirrer and an air pump, flowmeter, sampling points and control box. The mixture of dyes solution including photocatalyst enters and sprays onto the inner edge of the packed bed by a distributor. The distributor is a nozzle with four vertical sets of holes. Inside the bed (the bed can be rotated in the range of 400–1200 rpm) dyes solution moves outward through the packing due to centrifugal force, the liquid is splashed on the stationary housing (The stationary housing made of Plexiglas, encircles the rotational section) and thinner liquid films and smaller droplets could be created. This design lead to increasing the mass-transfer coefficient and dramatically reduces the reactor size compared to conventional photocatalytic reactor [34]. The strip blue LED is installed around the stationary housing to supply the light of process. The reactor has a control system for regulation of the rotational speed of the motor; the blue LED sources, switching on the pump, motor, stirrer and air pump. The dimensions of rotating packed bed reactor are specified in Table 1.

2.4. Experimental procedures

The experimental procedures were carried out according to the runs of central composite design (CCD). Typically, certain amount of $CuO/Cu_2O/Cu$-NPs were added to distilled water and stirred to ensure a uniform dispersion of the photocatalyst particles. A certain amount of