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Flow-injection chemiluminescence determination of cloxacillin in water samples and pharmaceutical preparation by using CuO nanosheets-enhanced luminol–hydrogen peroxide system

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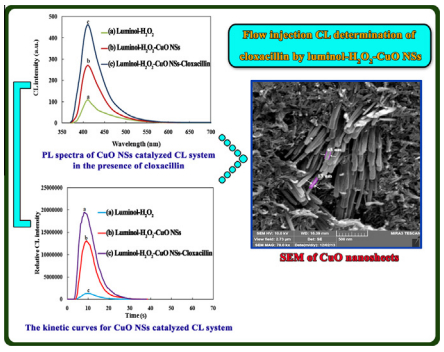
HIGHLIGHTS

- Well-crystalline CuO NSs by an ultrasonic assisted precipitation method.
- CuO NSs as an excellent catalyst for luminol–H_2O_2 CL system.
- Determination of cloxacillin using luminol–H_2O_2–CuO NSs flow injection CL system.
- Investigation of enhancement mechanism of cloxacillin on the CL mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, a rapid and sensitive flow-injection chemiluminescence (flow-CL) system was developed for the determination of cloxacillin sodium in environmental water samples and pharmaceutical preparations. The method was based on the enhancement effect of cloxacillin sodium on the CL reaction of luminal–H_2O_2–CuO nanosheets (NSs) in alkaline medium. The CuO nanosheets were synthesized using a green sonochemical method. The physical properties of the synthesized CuO nanosheets were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. The influences of various experimental factors such as H_2O_2, NaOH, luminol and CuO nanosheets concentrations were investigated. Under the optimum conditions, the enhanced CL intensity was linearly related to the concentration of cloxacillin sodium in the range of the 0.05–30.00 mg L^{-1} with a correlation coefficient of 0.995. The corresponding detection limit (3σ) was calculated to be 0.026 mg L^{-1}. The relative standard deviation (RSD) of the developed method was 2.21% with 11 repeated measurements of 4.00 mg L^{-1} cloxacillin sodium. Also, a total analysis time per sample was 30 s which confirmed the rapidity of the proposed method. The analytical applicability of the proposed CL system was assessed by determining cloxacillin sodium in spiked environmental water samples and pharmaceutical preparation. Furthermore, the possible mechanism of CL reaction was discussed.

Introduction

Cloxacillin sodium is a semi-synthetic penicillin synthesized in 1962 [1]. It is a ß-lactam antibiotic used for treatment of bacterial

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infections in human and animals because of its activity against various gram positive and gram negative bacteria [2]. The extensive presence of different drugs in the aquatic environment results from wide manufacturing of medical preparations, discharge of large quantity of expired drugs as well as exertion of residues of drugs and their metabolites by animals and humans [5]. This leads to the adverse effects in human health and encourages the emergence of bacterial resistance to these drugs in human. So, monitoring pharmaceuticals such as cloxacillin sodium in environmental water samples seems to be very important in order to avoid their hazards to human health [6,7]. Moreover, screening cloxacillin sodium in the pharmaceutical products is of importance to prevent its adverse effects in patients under treatment and to achieve optimum therapeutic doses.

Over the last years various analytical methods have been developed to determine the concentration of cloxacillin sodium including spectrophotometry [8], high-performance liquid chromatography (HPLC) [9–11], HPLC with ultraviolet detection (HPLC/UV) [12,13], HPLC with ultraviolet-diode array detection (DAD) [14], ultra performance liquid chromatography (UPLC) [15], capillary zone electrophoresis with diode array detection (CZE–DAD) [16] and chemiluminescence [17] in food, environmental water samples and biological fluids. These methods are very efficient for the determination of the cloxacillin sodium in various matrix; however, some of them suffer from different disadvantages such as time-consuming procedure, low sensitivity, high cost instrumentation and difficulties in sample preparation [18]. This has necessitated the development of simple and cheap method to monitor the presence of pharmaceuticals in different samples.

Flow-CL which combines flow-injection analysis technique with CL detection and possesses the advantages of the two methods is a simple, rapid, sensitive and low cost analytical technique [19–21]. Recently, it has been widely used in variety of fields including pharmaceutical analysis and environmental monitoring for determination of various substances in a large amount of samples. However, literature survey shows that some of the CL methods used for the determination of compounds have low sensitivity due to the relatively low CL intensity (low quantum yield) [22,23].

In recent years increasing attention has been paid to the utilization of nanomaterials in CL systems which allows using the novel characteristics of the nanomaterials including high surface areas, high activity and high selectivity in CL reactions [24]. Moreover, application of nanomaterials in CL reactions could enhance the CL signal and could offer very good stability for the CL methods. These lead to the lower limits of detection which is an essential factor for analytical applications [19,25].

Commonly, the catalysis of nanomaterials (NMs) for CL system was found to be dependent to their size, surface state, and morphology. In this context, different state of NMs including Au [26], CuO [27–29], Se [22] and magnetite [30] were used in different CL systems.

Among these NMs, synthesis of transition metal oxides such as CuO at nanoscale have received great attention in recent years for various catalytic applications including CL reactions due to its surface catalytic effect [28,31,32]. Therefore, different methods have been developed to synthesize CuO NMs with different structure morphology such as aqueous precipitation, hydrothermal, sonochemistry and so on [31,32]. To this range of methods, precipitation and sonochemistry have attracted increasing interest for preparing CuO nanomaterials with uniform crystallite size and high surface area [33,34]. Moreover, the both methods are simple, cost-effective and environmentally benign, which is a promising synthesis route for preparation of various nanomaterials [28,29,33]. So, in the present work, CuO nanosheets were synthesized by a green and quick precipitation method in the presence of ultrasonic irradiations. CL reaction of luminol–H_2O_2 is one of the most widely used systems in the field of CL, and it is frequently used for the determination of different substances [35–38]. In this study, the CuO nanosheets enhanced CL system of luminol–H_2O_2 was used to develop a more sensitive method to determine cloxacillin sodium in environmental water samples and pharmaceutical preparation. Cloxacillin sodium was subjected to some preliminary tests. It was found that cloxacillin sodium was able to increase the CL emission of luminol–H_2O_2–CuO nanosheets. The resultant increase in CL intensity was proportional to cloxacillin sodium concentration. The possible enhancement mechanism of the CuO nanosheets and cloxacillin sodium on the developed CL system was also investigated regarding the CL spectra.

Experimental

Reagents and solutions

All the chemicals and reagents used in this work were of analytical grade and purchased from Merck Co. (Germany), except for pure cloxacillin sodium, which was purchased from Jaber Ebne Hayyan pharmaceutical Co. Tehran, Iran. Table 1 illustrates the structure and some properties of the cloxacillin [3,4].

Distilled water was used throughout the experiments. A stock standard solution of 2×10^{-2} mol L^{-1} luminol was prepared by dissolving 0.354 g luminol in 100 mL of 0.1 mol L^{-1} NaOH in a brown volumetric flask. A stock solution of 1 mol L^{-1} sodium hydroxide was prepared by dissolving 4 g sodium hydroxide in 100 mL double distilled water. Working solutions of H_2O_2 were prepared fresh daily from 30% (w/w) H_2O_2 reagent. A 100 mg L^{-1} stock standard solution of cloxacillin sodium was prepared by dissolving 25 mg cloxacillin sodium in 250 mL distilled water and stored at 4 °C in refrigerator and protected from light. A 0.02 mol L^{-1} copper(II) acetate monohydrate solution was prepared by dissolving 0.998 g in 250 mL distilled water. Cloxacillin sodium capsules were purchased from Farabi pharmaceutical Co. Iran (Tabriz). All working solutions were prepared by diluting their related stock solutions.

Apparatus

The CL signals from the CL reaction in the flow cell were monitored by a FB12 luminometer (Berthold Detection Systems, Germany) and imported to the computer for data acquisition. Ultraviolet–visible (UV–Vis) spectra were recorded by UV–Vis spectrophotometer (WPA lightwave S2000, England) in the range of 200–800 nm. A bath type sonicator (Sonica, 2200 EP S3, Italy) with 50–60 Hz frequency was used to provide ultrasonic irradiations for synthesis of CuO nanosheets. To characterize the crystal structure and phase purity of as-prepared sample, XRD pattern was measured at room temperature by a Siemens X-ray diffraction D5000 (California, USA), with Cu Kα radiation. The accelerating voltage of 40 kV and emission current of 30 mA were utilized. The size and the morphology of the prepared nanosheets were characterized by SEM (S-4200, Hitachi, Japan). The photoluminescence spectra were recorded on a FP-6200 spectrofluorometer (Jasco, Japan).

CL instrumentation and procedure

The CL analysis was conducted on a laboratory-built flow-injection CL system. The schematic diagram of the flow system used is shown in Fig. 1. A peristaltic pump, labeled as *P*, was used to deliver all respective solutions into the flow cell at a flow rate of 2.0 mL min^{-1} for each channel. Polytetrafluoroethylene (1.0 mm i.d.) was used as a connection material in the flow system. A