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Simultaneous determination of paracetamol and 4-aminophenol based on poly(chromium Schiff base complex) modified electrode at nanomolar levels

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ABSTRACT

Highly selective and sensitive electrochemical method was developed for the simultaneous determination of paracetamol (PR) and 4-aminophenol (4-AP) present in the pharmaceutical samples. Poly(chromium Schiff base complex) was fabricated onto the glassy carbon electrode by cyclic voltammetry technique. The modified glassy carbon electrode (GCE) has exhibited better electrochemical response towards the simultaneous determination of paracetamol and 4-aminophenol than the GCE. Additionally, the chromium Schiff complex modified GCE exhibits quasireversible process for PR and reversible process for 4-AP, when compared to that of GCE, this response may be attributed to the presence of Cr(III) in the modified layer. The effect of pH and scan rate was evaluated for the fabricated sensor in order to know the optimum conditions at which better response can be achieved. Moreover the kinetic parameter of the fabricated sensor was calculated separately for both the analytes. From differential pulse voltammetric (DPV) technique, the peak separation between the PR and 4-AP was found to be 300 mV and the electrochemical responses of the both analytes fall in the linear range from 8 nM to 125 nM and 8 nM to 133 nM, with the detection limits of 6.8 nM and 5.6 nM for PR and 4-AP respectively. From these studies, the proposed method based on electropolymerized chromium Schiff base complex was simple, rapid, cost effective and convenient for the simultaneous determination of PR and 4-AP at nanomolar levels in pharmaceutical samples.

1. Introduction

Paracetamol, a worldwide known drug which is used to get rid of mild to moderate pain associated with headache, backache, arthritis, postoperative pain, and for reducing fevers of bacterial/viral origin. Simultaneous determination of paracetamol (PR) and 4-aminophenol (4-AP) is more important in the quality control of synthetic process of paracetamol [1,2], since the co-existing, 4-aminophenol is highly undesirable due to its nephrotoxic and teratogenic effects on human [3–5]. On exposure to light, paracetamol may undergo degradation to give 4-aminophenol as the undesired product. Over usage of paracetamol will lead to serious side effects such as hepatic toxicity, kidney damage, liver failure and finally may lead to death. Hence there is a necessity to determine the 4-AP and PR for industrial and clinical purposes. In literature, there are several methods available to determine 4-AP and PR separately, to name a few HPLC, titrimetry, capillary electrophoresis, spectrofluorometry and spectrophotometry [6–9]. However, these methods are more expensive, tedious, time consuming. Among all the reported techniques, electrochemical method is conducive because of its ease of handling, real time monitoring and compact size. 4-AP and PR can be simultaneously determined by electrochemical methods, since both the compounds have good electrochemical activity and provides distinct potential difference to detect. The use of bare glassy carbon electrode (GCE) for the determination of PR shows irreversible slow electron transfer, poor sensitivity, selectivity and poor reproducibility. To overcome this, researchers have modified GCE with appropriate layers to determine PR and 4-AP separately or simultaneously. Among the modified GCE, few reports were available for the simultaneous determination of PR and 4-AP based on poly(3,4-ethylenedioxythiophene) [10], gold nanoparticles and an organophillic layered double hydroxide [11], phenacetin on CdSe microspheres [12]. Even though there are reports for the

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simultaneous determination of PR and 4-AP, none of them have the detection limits in nanomolar level. In the present study we attempt to fabricate chromium Schiff base complex on to the GCE to detect 4-AP and PR simultaneously. Extensive literature survey reveal that no work has been reported so far on the simultaneous determination of PR and 4-AP based on Schiff base complex electrochemically polymerized-modified electrodes. Chromium Schiff base complex shows better electrochemical activity which can influence the electrochemical redox process of PR and 4-AP.

Schiff base ligands and their metal complexes have increasing interest in the area of research due to their various applications in different fields, such as antibacterial, antiviral, anticancer and antifungal agents [13–16]. Some other applications of Schiff base ligands and their metal complexes are in chemical analysis, catalysis, pesticides, transport of oxygen and sensors [17–20]. The salen type Schiff base ligands form more stable complexes with metal ions, through coordination of phenolic oxygen and imine nitrogen atoms. Chromium(III) forms stable complex with Schiff base ligands, due to the d^3 electronic configuration [21]. The chromium metal ion exhibit various oxidation states and good electrochemical redox properties, therefore chromium is an important metal for chemical and electrochemical catalytic reactions [22]. The chromium metal ion is an essential biological element, it involves in carbohydrate, lipid metabolism and insufficient quantity of chromium(III) leads to Type II diabetes and cardiovascular diseases [23–25]. In addition chromium Schiff base complexes are efficient electrode modifiers for electrocatalytic reactions and it can be used as better electrocatalytic sensors [26]. Electropolymerization method is an effective way to modify the electrode surface, it will be used in variety of applications in the fields of electrocatalysis and electroanalysis. Especially, the polynuclear Schiff base complexes show efficient electron transfer because of their important redox interaction [27]. We have already reported our work for the voltammetric determination of catechol by the chromium Schiff base complex modified GCE. In the present study we report the preparation of chromium Schiff base complex-modified GCE and its application for the simultaneous determination of PR and 4-AP.

2. Experimental

2.1. Materials

5-methylsalicylaldehyde and chromium Schiff base complex were synthesized by the previously reported method of our group [26]. Paracetamol was purchased from the commercially available drug as injection, 4-aminophenol was purchased from Alfa Aesar, disodium hydrogen phosphate, potassium chloride, sodium acetate, and sodium hydroxide were purchased from Qualigens and used without further purification. TBAP (Tetra(n-butyl) ammonium perchlorate) was purchased from Sigma Aldrich. All the chemicals were used as received. Doubly distilled water was used as the solvent throughout the experiment.

2.2. Instrumentation

Electrospray ionization mass spectrum of the complex was performed on a Quan-Tof (Q-Tof) mass spectrometer. Electrochemical Impedance Spectroscopy was carried out with the PGSTAT-12 electrochemical analyzer (AUTOLAB, The Netherlands BV). The morphology and EDX of the samples were analyzed by FE-SEM using HITACHI SU6600 high-resolution analytical field emission-scanning electron microscopy with variable pressure technology (AZO NANO, United Kingdom), FT-IR measurements (KBr Pellets) were carried out on a Bruker-Tensor27 FT-IR. Raman spectrum was recorded using laser Raman microscope, Raman-11 Nanophoton Corporation, Japan, XRD analysis were performed on Rich Siefert 3000 diffractometer with Cu-Kα_1 radiation (λ = 1.5406 Å). Photoluminescence spectrum was recorded using Perkin-Elmer LS-45 Fluorescence Spectrometer.

2.3. Electrochemical experiment

Cyclic voltammetry and differential pulse voltammetry (DPV) methods were utilized to determine the electrochemical sensing properties of chromium Schiff base complex towards paracetamol (PR) and 4-aminophenol (4-AP). All electrochemical sensing experiments were carried out using a CHI 1103A electrochemical instrument connected to a PC. The electrochemical experiments were carried out in 0.1 M phosphate buffer solution (PBS), pH 7 in a conventional three-electrode system using the bare and modified GCE as the working electrode. Platinum wire was used as an auxiliary electrode, saturated calomel electrode (SCE) was used as the reference electrode for sensing experiments and Ag/AgCl electrode as a reference for examine the electrochemical activity of chromium(III) Schiff base complex. For cyclic voltammetric measurements, the sensors were immersed in 30 mL of 0.1 M PBS containing 1×10^{-4} M PR and 4-AP, applying the potential in the range of −0.5 V to +1.2 V. Differential pulse voltammetry was carried out in the range of −0.4 to 0.8 V with an increment of 0.004 V, an amplitude of 0.025 V along with a pulse width of 0.05 s using 0.1 M disodium hydrogen phosphate and 0.1 M sodium dihydrogen phosphate (pH 7) as the background electrolyte. When a stable baseline was reached, 0.5 mL of 0.1 mM PR and 4-AP were added successively, followed by recording the steady-state current. All solutions used in these sensing experiments were prepared with double distilled water. All electrochemical experiments were carried out at room temperature and the potentials were referred to SCE.

2.4. Preparation of modified glassy carbon electrode

The working glassy carbon electrode was subjected for pre-treatment before it is applied for the electrochemical polymerization for the modification. The GCE was first polished with alumina slurries of different sizes like 0.03 μm and 0.1 μm to attain mirror finish. The polished GCE was employed for ultra-sonication in double distilled water for 20 min. After the mechanical pre-treatment the GCE was applied for electrochemical pre-treatment, it was carried out by applying a fixed potential of +0.5 V vs SCE for 300 s. Then a potential cycling was carried out between −1.5 and 1.5 V at a scan rate 50 mV s^{-1} for 20 cycles in 0.1 M sulphuric acid and acetonitrile solution. Finally the GCE was subjected for the electrochemical polymerization using the following procedure. 0.1 M chromium Schiff base complex in acetonitrile was taken in presence of tetrabutylammonium perchlorate (TBAP). TBAP was used as supporting electrolyte, in the electrochemical polymerization the potential cycling was carried out between 1.5 to −1.5 V at the scan rate 50 mVs^{-1} for 20 cycles. After the electrochemical polymerization chromium(III) Schiff base complex film was successfully generated on the surface of the clean GCE, then the film modified GCE was washed with double distilled water and used for the independent and simultaneous determination of paracetamol and 4-aminophenol in 0.1 M Phosphate buffer solution (PBS) at pH 7 as the background electrolyte. The electrochemically polymerized modified electrode was stored at 4 °C when it was not used.

2.5. Solution preparation

0.01 M Paracetamol solution was prepared by the following procedure, commercially available paracetamol injection was