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Simultaneous Electrochemical Analysis of Ibuprofen and Paracetamol by Clay Modified Carbon Paste Electrode: Analytical Application in Human Blood

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Abstract- Cyclic voltammetry and differential pulse voltammetry techniques for the simultaneous analysis of ibuprofen (IBU) and paracetamol (PCT) at carbon paste electrode modified with clay (CPE-Clay) are reported. The surface characterization of the clay was realized by zero-point charge and electrochemical methods. The electrocatalytic activity of clay toward ibuprofen electro-oxidation and paracetamol redox were reported. The kinetic parameters for ibuprofen and paracetamol electro-analysis by the modified carbon paste electrode clay-CPE were calculated. Peak ibuprofen oxidation and peaks paracetamol redox were well presented onto modified electrode clay-CPE when compared with other electrodes in the literature. Peak oxidation of the ibuprofen and peaks paracetamol redox was well presented onto modified electrode clay-CPE compared with other electrodes in the literature. The high sensitivity of the clay-CPE is measured by the DPV method showed linear variation with ibuprofen and paracetamol concentration with respectively detection limit (LOD) of 3.23×10^{-8} mol L^{-1} and 1.04×10^{-8} mol L^{-1}. The applicability of the working electrode has been explored by the simultaneous electroanalysis of the ibuprofen and paracetamol in human blood samples.

Keywords- Clay; Electrochemical behaviour; Ibuprofen; Paracetamol; Electroanalysis; Human blood

1. INTRODUCTION

Ibuprofen is a non-steroidal anti-inflammatory drug (NSAID), it is greatly used as painkillers and antipyretic agents [1]. This drug is utilized to remedy mild suffering such as dysmenorrhea, headaches, dental pain, postoperative pain, and musculoskeletal/joint disorders, because of its anti-inflammatory properties [2,3]. IBU is the most frequently used NSAID in the U.S. and Europe, due to its good efficacy toward pain [4,5]. Paracetamol is a long-standing and widely used 'over-the-counter' drug in the world. It was first used in 1893 by Von Mering in medicine. Nevertheless, it was discovered in the 19th century for the first time that it had antipyretic and analgesic properties. It is not carcinogenic and effectively replaces aspirin for patients sensitive to aspirin [6]. Paracetamol is used to lower fever, colds, and pain from tension headaches, migraines, chronic pain, back pain, joint pain, and toothache [7-9]. It is also needed to treat osteoarthritis [10] and is sometimes utilized for the control of cancer pain. New research suggests that paracetamol helps protect against changes leading to cardiovascular disease [11].

The analytical techniques, such as high-performance liquid chromatography [12,13], gas chromatography [14], spectrophotometry [15,16], spectrofluorometry [17,18], infrared spectrometry [19], supercritical fluid chromatography [20], proton magnetic-resonance spectroscopy [21], conductometry [22] and capillary electrophoresis [23-25] were utilized to detect the ibuprofen concentration were reported. The methods previously were cited are costly and require expertise. Different electrochemical techniques in the literature have used silver-functionalized nano-carbon fiber composite electrode, an Ag-doped zeolite expanded graphite composite electrode, a bare boron-doped diamond electrode using CV and DPV, a paste of carbon modified palladium-montmorillonite (Mt) electrode using DPV, clay modified carbon paste electrode, natural phosphate modified carbon paste electrode, aluminum modified carbon paste electrode, zinc modified carbon paste electrode and heavy metals modified carbon paste electrode [26-35].

These methods have shown remarkable advantages in the detection of drugs in several matrices. The ibuprofen electrocatalysis at the montmorillonite-doped carbon paste electrode (Mt-CPE) was reported by Loudiki et al. [36]. From the literature survey, the oxidation peak of ibuprofen and redox peaks of paracetamol were observed at different modified electrodes that are not well presented. This clay was used to improve the redox peak shape of IBU and PCT, and a better signal-to-noise ratio.

This work aims to study electro-catalytic detection of IBU and CPE at modified electrode clay- CPE and to determine them in human blood and drug samples. The electrooxidation of the ibuprofen and the redox of the paracetamol at two electrodes (CPE, clay-CPE) were investigated using CV and DPV. Simultaneous peak oxidation of the ibuprofen and peaks redox of the paracetamol was well presented onto modified electrode clay-CPE compared with other electrodes in the literature. The electroanalysis method is simple, easy, fast, sensitive, and reproducible.

2. MATERIALS AND METHODS

2.1. Chemicals and Materials

The chemicals used in this work were of high purity. KH_2PO_4, Na_2HPO_4, HCl and NaOH, PCT, and IBU were purchased from Sigma-Aldrich. Clay [37], Carbon graphite has been supplied by Carbone, Lorraine, ref. 9900, France **.**

Paracetamol and Ibuprofen were dissolved in phosphate buffer (pH 6) to prepare the stock solution of 1.0×10^{-2} mol L^{-1}. Afterward, the working standard solutions have been prepared by successive dilution with phosphate buffer**.**

The CV and DPV methods were carried out by a Voltalab Potentiostat (model PGSTAT 100) driven by the electrochemical data processing software during analysis (Voltalab master 4 software). The electrochemical compartment was operated with three electrodes: a clay-CPE working electrode, a reference electrode (saturated Calomel electrode), and an auxiliary electrode (platinum electrode). The pH meter (Radiometer Copenhagen, PHM210, Tacussel, and French) was used to adjust the pH of the medium.

2.2. Procedure

Voltammetric simultaneous analysis of ibuprofen and paracetamol was performed using an unmodified and modified carbon-paste electrode (clay-CPE). The working electrode was placed in an electrochemical cell containing 20 mL of 0.1 mol L^{-1} phosphate buffer solution (pH 6) with the molecules of ibuprofen and paracetamol. The electrochemical cell containing 1.0×10^{-3} mol L^{-1} of ibuprofen and 1.0×10^{-3} mol L^{-1} of paracetamol were utilized to investigate the influence of all chemical and electrochemical parameters. The CV and DPV studies were performed in the potential going from 0 V to 1.4 V and from 0.2 V to +1.4 V, respectively. All measurements were obtained at 25 °C.

2.3. Samples preparation

To electrochemically determine the analytical performance of the clay-CPE, the simultaneous detection of IBU and PCT was performed in human blood samples. IBU and PCT were ground in a mortar and part of the powder equivalent to the average weight were dissolved in a phosphate buffer solution (PBS) (pH 6). The appropriate volume of human blood was enriched with ibuprofen and paracetamol and transferred to a 100 ml volumetric flask containing phosphate buffer (pH 6). The concentration of ibuprofen in the tablets and the blood was detected using DPV.

3. RESULTS AND DISCUSSION

3.1. Electrocatalytic performance testing

To determine the electrocatalytic activity of clay vis-à-vis simultaneous IBU and PCT electro-oxidation, the cyclic voltammogram of ibuprofen (1.0×10^{-3} mol L^{-1}) and paracetamol

(1.0×10^{-3} mol L^{-1}) in phosphate buffer solution (pH 6) at the carbon paste electrode (CPE) and clay-CPE is shown in Figure 1.

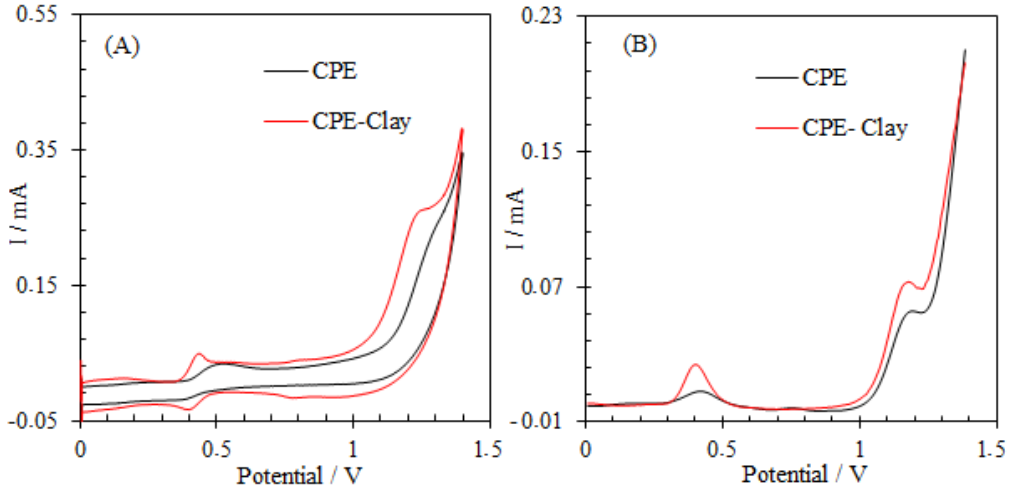

Figure 1. (A) CVs and (B) DPV of a mixture of 1.0×10^{-3} mol L^{-1} of IBU and PCT in 0.1 mol L^{-1} PBS (pH 6.0) at CPE and Clay-CPE at 100 mV s^{-1}

Figure 1A shows for CPE, an oxidation peak of the IBU is observed at E_{pa}=1.3 V with peak current 0.27 mA, and the PCT exhibit a pair of redox waves at E_{pa}=0.5V with peak current 0.01 mA and E_{pc}=0.4V with peak current -0.1 mA. With the incorporation of the clay, the oxidation potential of ibuprofen shifts to E_{pa}=1.2 V, with peak current 0.30 mA, the redox PCT waves at E_{pa}=0.42V with peak current 0.04 mA and E_{pc}=0.4V with peak current -0.04 mA. Figure 1B confirms the results of Figure 1A.

Modifier clay catalyzes ibuprofen oxidation and paracetamol redox by making the electron transfer faster. The surface characteristics such as (strong adsorptive competence, good chemical stability, and high oxides content) were responsible for such electrochemical behavior [38-40]. Also, there might be some interaction between clay particles and studied molecules electrostatically, which leads to the consignment of the drug toward clay-CPE.

3.2. Effect of scanning rates

The effect of scanning rates on the electroanalysis responses of PCT and IBU was investigated at the clay-CPE surface by CV. Figure 2A showed the CV plots with different scan rates (30-400 mV s^{-1}) in 1.0×10^{-3} mol L^{-1} ibuprofen and 1.0×10^{-3} mol L^{-1} paracetamol.

The current density of peaks increases linearly with the $\upsilon^{1/2}$ (Figure 2B). A linear correlation between the $\upsilon^{1/2}$ and I_{pa} demonstrates that the process is controlled by the diffusion phenomenon.

$$I_{pa}(\mu A)\ (IBU) = 20.5\ \upsilon^{1/2} - 34.5;\ R^2=0.9718 \quad (1)$$

$$I_{pa}(\mu A)\ (PCT) = 4.6\ \upsilon^{1/2} - 9.3;\ R^2 = 0.9064 \quad (2)$$

$$I_{pc}\ (\mu A)\ (PCT) = -\ 6\ \upsilon^{1/2} + 13.9;\ R^2 = 0.9111 \qquad (3)$$

In order to confirm if the diffusion is the rate-limiting step of the clay-CPE reaction ibuprofen and paracetamol, the linear fitting of Ep *vs.* log ν was also affected (second inset in Figure 2C). This indicates that the kinetics of the oxidation reaction of IBU and PCT is controlled by diffusion because the current is straight. The corresponding equation is as follows:

$$E_{pa}\ (IBU) = 0.1311 \log v + 0.9831;\ R^2 = 0.9688 \qquad (4)$$

$$E_{pa}\ (PCT) = 0.0245 \log v + 0.392;\ R^2 = 0.8452 \qquad (5)$$

$$E_{pc}\ (PCT) = -\ 0.037 \log v + 0.4877;\ R^2 = 0.89 \qquad (6)$$

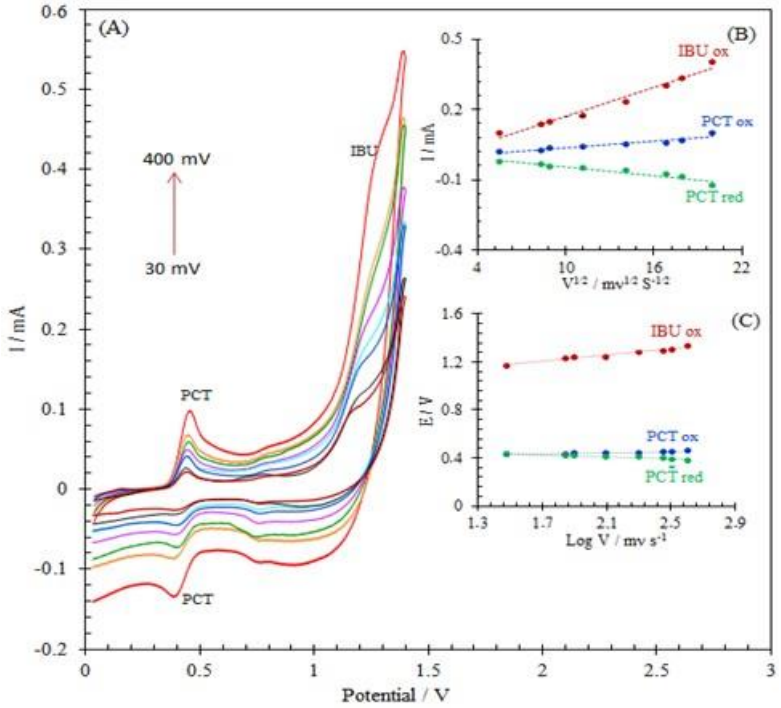

Figure 2. (A) CVs of a mixture of 1.0×10^{-3} mol L^{-1} of IBU and PCT in 0.1 mol L^{-1} PBS on clay-CPE at different scan rates (30-400 mV s^{-1}); (B) plot I *vs.* $v^{1/2}$; (C) plot E *vs.* Log υ

3.3. Analytical performance evaluation

3.3.1. Optimization of experimental parameters

In order to achieve the current response of a mixture containing ibuprofen (10^{-3} mol L^{-1}) and paracetamol (10^{-3} mol L^{-1}) with the highest magnitude and best shape, effect of the experimental parameters on the oxidation current of ibuprofen and the redox current of paracetamol were studied.

The step width influence on the current intensities of ibuprofen and paracetamol were evaluated in the range from 200 to 1000 ms (Figure 3A). The signals increase up to 600 ms,

then decrease due to peak broadening. In other experiments, a value of 600 ms for each step, was used to obtain the good diffusion of electroactive molecules on the surface of the electrode.

Pulse height influence (Figure 3B) was investigated in the range that varies from 20 to 200 mV/AgCl. As expected, an increase in signal intensity has been observed up to 60 mV/AgCl. From its values, the paracetamol signals remained stable. In this work, a value of 60 mV/AgCl was used.

Step height (Figure 3C) and pulse width (Figure 3D) were studied in the range from 5 to 50 mV/AgCl and 40 to 200 ms, respectively. The highest peaks intensity was obtained for step height and the pulse width was 8 mV/AgCl and 60 ms, respectively. A slight signal reduction has been noticed for higher values.

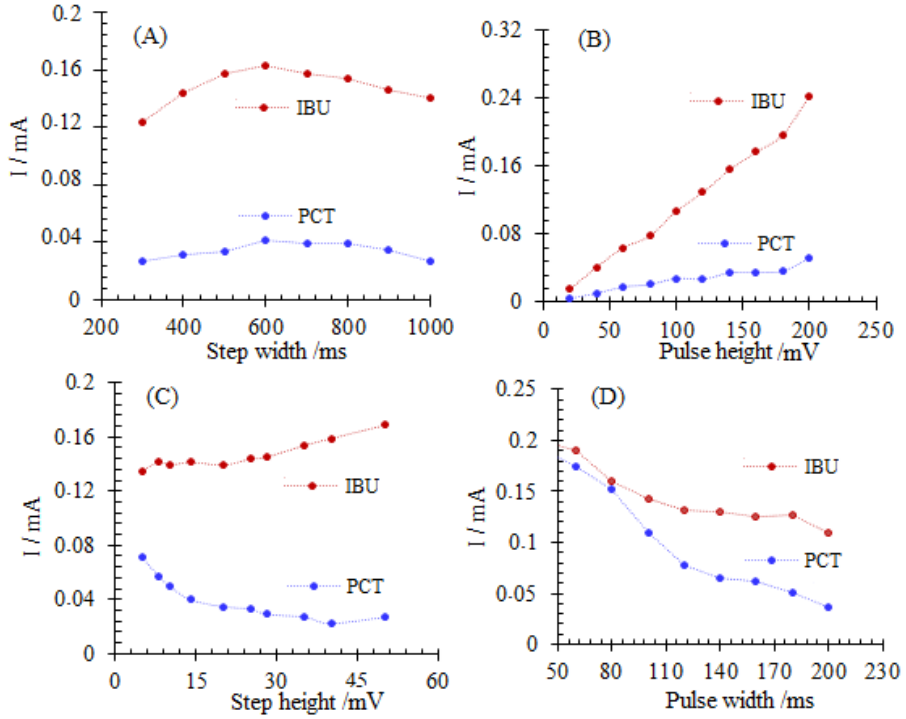

Figure 3. Effect of the variables (step width, pulse height, step height, pulse width) by the DPV technical, 1.0×10^{-3} mol L^{-1} IBU and PCT in PBS (pH 6.0) at clay-CPE

The pH influence was studied (Figure 4A) in phosphate buffer containing 10^{-3} mol L^{-1} IBU and PCT by varying pH values from 2 to 10. The responses of peak currents and potentials of IBU and PCT significantly change with increasing pH. The better signals of the peaks are obtained at pH = 6. The anodic peak potentials of PCT and IBU move towards low values of potential with the increase of pH. The linear relationship of the formal potential of IBU and PCT with pH (Figure 4B) can be expressed as the equations below:

$$\text{IBU: } E_{pa}\text{ (IBU)} = -0.0143\text{ pH} + 1.3202;\ R^2=0.9824 \quad (7)$$

$$\text{PCT: } E_{pa}\text{ (PCT)} = -0.0427\text{ pH} + 0.7385;\ R^2=0.9823 \quad (8)$$

The effect of the accumulation time on the voltammetric measurements was studied from 0 to 420 seconds in the presence of 10^{-3} mol L^{-1} of IBU and 10^{-3} mol L^{-1} of PCT. Figure 4C represents an increase in the current intensity as a function of accumulation time during the first 30 seconds. The current intensity of the anode peaks decreases after saturation of the active sites of the clay-CPE.

The increase of the modifier's loading affects the electroanalysis of the PCT and IBU at the clay-CPE surface (Figure 4D). The peak current of PCT and IBU increases with the increase of the clay until 7 %, after this value the current decreases. Hence a 7% of the ratio by weight has been used in this work.

Hence a 7% of the clay-CP ratio by weight, 30 s of the preconcentration time, and pH=6 were used throughout this work.

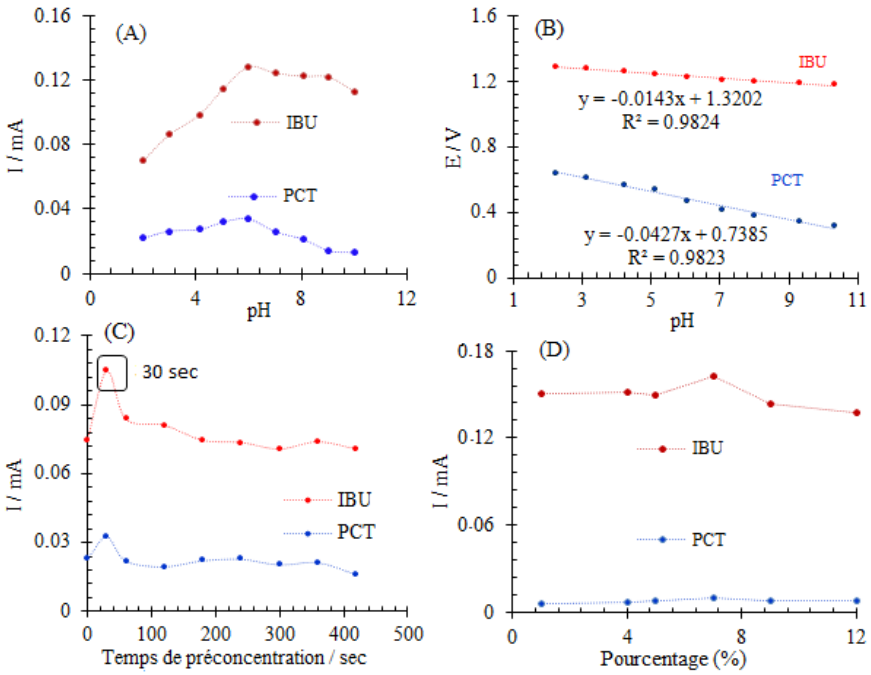

Figure 4. Influence of the experimental variables (pH, time preconcentration, and percentage of clay involved) using the DPV method, 1.0×10^{-3} mol L^{-1} IBU and PCT in PBS (pH 6.0) at clay-CPE

3.3.2. Simultaneous detection of IBU and PCT

DPV was found to be very sensitive in detecting low amounts of chemical species compared to when compared to VC. The influence of different chemical parameters on the response of electrodes using DPV was investigated. In our experience, the optimal chemical parameters chosen for these studies were as follows: accumulation time=30 s, pH=6, mass ratio of Clay = 7%, step width=600 ms, step height=8 mV, pulse width=60 ms, and pulse height=60 mV.

The selective determination of IBU and PCT at clay-CPE was carried out by increasing the concentration of one product while keeping the concentration of the other product constant.

Figure 5A indicates that the DPV signals of PCT oxidation increased remarkably with the increase of PCT concentration, and the coexisted IBU had no influence on the electroanalysis of PCT. As illustrated in Figure 5B, the increase of I_{pa} fits the linear equation of I_{pa}(mA)= 0.12[PCT]+0.0186 (R^2=0.9864) when the concentration of PCT increases from 1.0×10^{-6} to 1.0×10^{-3} mol L^{-1}.

The clay-CPE has a good limit of detection and quantification (LOQ) for PCT using Eq. (9) and (10) [41-43] and was found to be 8.4700×10^{-8} mol L^{-1} and 2.8218×10^{-7} mol L^{-1}, respectively. Where S is the standard deviation of the blank signal and M is the slope.

$$LOD = 3S/M \qquad (9)$$

$$LOQ = 10S/M \qquad (10)$$

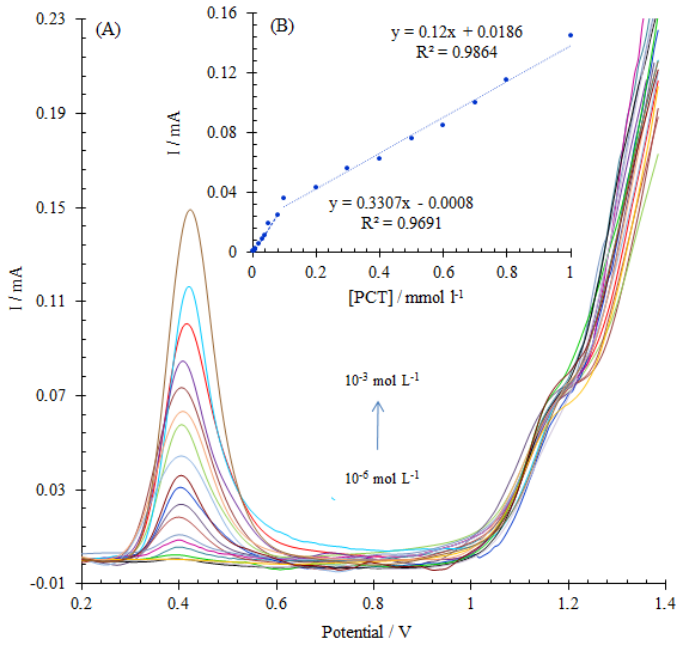

Figure 5. (A) DPVs of clay-CPE in 0.1 mol L^{-1} PBS (pH 6.0) containing various concentrations of PCT (1.0×10^{-6} to 1.0×10^{-3} mol L^{-1}) in the presence of 1.0×10^{-4} mol L^{-1} IBU; (B) plot of linearity between current and concentration

Similarly, as shown in figure 6A, in the coexistence of PCT, the linear range of IBU was from 1.0×10^{-6} to 1.0×10^{-3} mol L^{-1} with a regression equation of I_{pa}(mA =0.1177 [IBU]+ 0.0083 (R =0.9896) (Figure 6B). The calculated LOD and LOQ are 4.0925×10^{-8} mol L^{-1} and 1.3601×10^{-7} mol L^{-1}, respectively.

The below results indicate that the oxidation reactions of IBU and PCT at Clay-CPE take place independently.

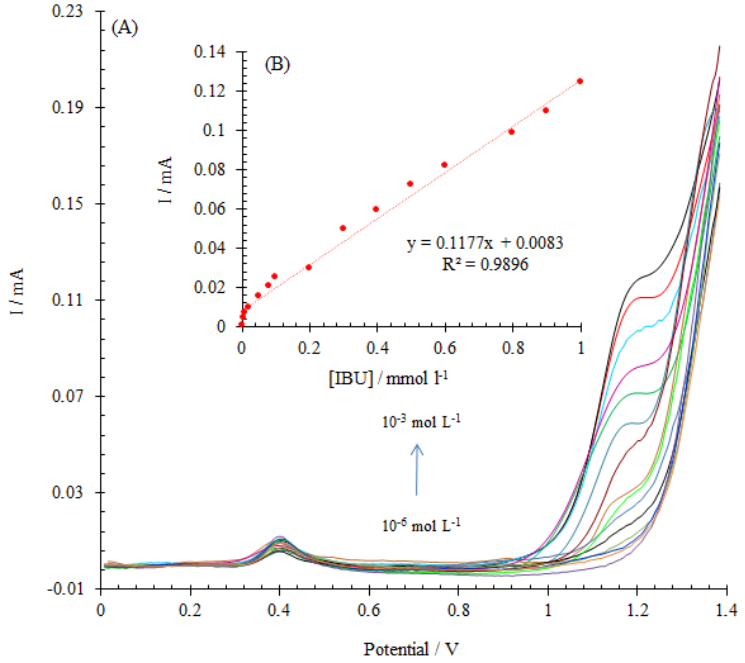

Figure 6. (A) DPVs of clay-CPE in 0.1 mol L^{-1} PBS (pH 6.0) containing various concentrations of IBU (1.0×10^{-6} to 1.0×10^{-3} mol L^{-1}) in the presence of 1.0×10^{-5} mol L^{-1} PCT; (B) plot of the relationship between the peak current and concentration

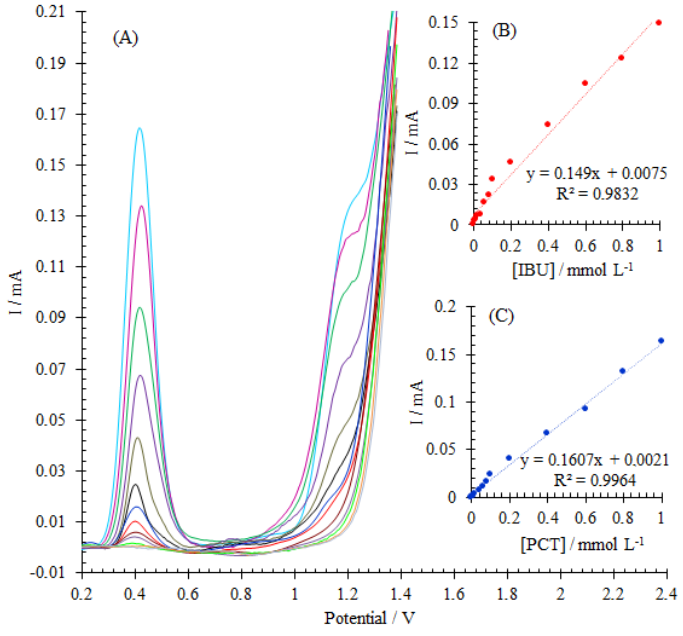

Figure 7. (A) DPVs of clay-CPE in 0.1 mol L^{-1} PBS (pH 6.0) containing various concentrations of IBU and PCT (1.0×10^{-6} to 1.0×10^{-3} mol L^{-1}); (B) and (C) plot of the relationship between the peak current and target concentration

The simultaneous analysis of IBU and PCT by clay-CPE was studied by synchronously changing the concentration of the two molecules in their mixture (Figure 7A). The oxidation

peak currents of IBU and PCT were linearly correlated with their concentrations (Figures 7B and 7C). The regression equations for PCT and IBU were I_{pa}(mA)=0.1607[PCT]+0.0021 (R^2=0.9964) and I_{pa}(mA)=0.149[IBU]+0.0075 (R^2=0.9832) and the LOD has been estimated to be 1.0401×10^{-8} mol L^{-1} and 3.2323×10^{-8} mol L^{-1}, respectively. These values are, respectively, by those obtained in their selective detection. It is confirmed that the fabricated clay-CPE is suitable for the simultaneous electroanalysis of IBU and PCT in mixed systems.

3.3.3. Interference of coexisting substances

The influence of several molecules likely to interfere with the detection of IBU and PCT has been studied under good conditions. For this fact, the interferences of some common molecules were evaluated. Experimental results show the effect of some common molecules including dopamine, resorcinol, hydroquinone, salicylic acid, (each of 1.0×10^{-4} mol L^{-1}) on the Recovery of 1.0×10^{-5} mol L^{-1} of IBU and PCT were represented in Table 1.

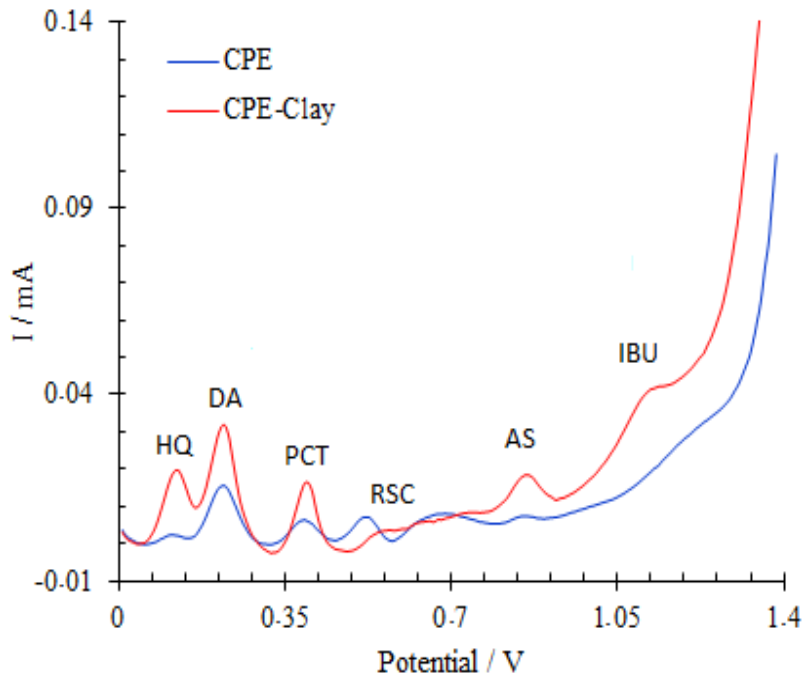

Figure 8. DPV curves after exposure to a solution containing 1.0×10^{-4} mol L^{-1} dopamine (DA), hydroquinone (HQ), resorcinol (RSC), and salicylic acid (AS) at CPE, and clay-CPE

The use of the clay-CPE for the simultaneous determination was demonstrated by the clean separation of the potential peaks compared with CPE (Figure 8). These results show that clay-CPE is characterized by excellent selectivity for the simultaneous determination of PCT and IBU without interference from other coexisting molecules.

Table 1. Influences of coexisting molecules on the electroanalysis of 1.0×10^{-5} mol L^{-1} IBU and PCT.

Interfering	**Concentration (1.0×10^{-5} mol L^{-1})**	**Recovery [PCT] (%)**	**Recovery [IBU](%)**
Dopamine	5	168.64±0.248	81.13±0.274
	10	139.24±0.025	85.67±0.106
	100	131.19±0.050	82.19±0.082
Catechol	5	108.55±0.015	114.68±0.035
	10	128.81±0.396	106.04±0.015
	100	155.59±0.115	100.52±0.434
Ascorbic acid	5	118.18±0.151	121.12±0.221
	10	116.75±0.075	156.41±0.139
	100	130.14±0.081	80.39±0.493
Phenol	5	104.62±0.097	94.75±0.046
	10	105.61±0.056	79.29±0.295
	100	107.92±0.115	6.06±0.020
Resorcinol	5	171.60±0.080	132.13±0.110
	10	82.65±0.214	82.99±0.286
	100	87.45±0.410	19.42±0.131
Hydroquinone	5	103.52±0.025	94.11±0.200
	10	79.97±0.085	92.57±0.361
	100	98.47±0.025	91.85±0.361
Salicylic acid	5	86.54±0.075	87.43±0.013
	10	79.81±0.095	121.36±0.040
	100	87.16±0.065	94.41±0.032

3.3.4. Analytical Application

To confirm the repeatability and reproducibility of the results, to verify the applicability of the analytical method, clay-CPE was used to simultaneously electroanalysis of IBU and PCT in human blood.

Human blood was prepared by adding 0.268 g of Na_2HPO_4 and 0.015 g of KH_2PO_4 (0.1 mol L^{-1} of phosphate buffer solution) to 20 mL of human blood, then enriched with appropriate amounts of simultaneous IBU and PCT (1.3×10^{-3} mol L^{-1}) and then we will dilute the solution up to 1.0×10^{-6} mol L^{-1}. The electroanalytical curves have been recorded by DPV.

The analytical plots were obtained by DPV experiments (Figure 9). Peak currents have been shown to increase linearly relative to the IBU and PCT added to the buffer solution:

$$I_{pa}\ (mA) = 0.0471\ [IBU] + 0.1034\ ;\ R^2 = 0.9475 \quad (11)$$

$$I_{pa}\ (mA) = 0.039\ [PCT] + 0.0085\ ;\ R^2 = 0.89 \quad (12)$$

The statistical results of the analytical application are shown in Table 2 with satisfactory results.

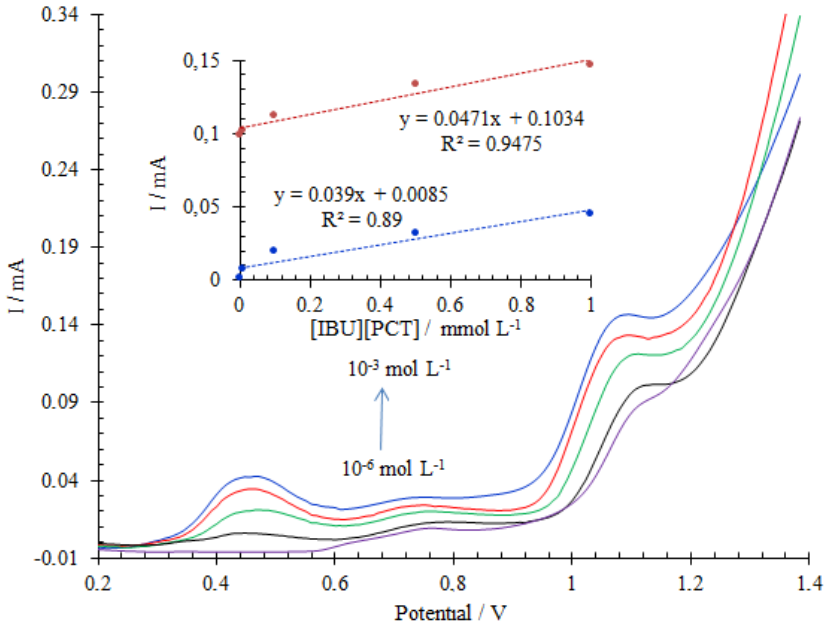

Figure 9. DPV of different concentrations of IBU and PCT (10^{-6} mol L^{-1} to 10^{-3} mol L^{-1}) at clay-CPE in the human blood

Table 2. The statistical results of the analytical application.

Settings	**IBU**	**PCT**
R^2	0.9475	0.8900
Standard deviation	2.5442×10^{-10}	1.7426×10^{-10}
LOD (mol L^{-1})	1.6214×10^{-8}	1.3404×10^{-8}
LOQ (mol L^{-1})	5.4049×10^{-8}	4.4682×10^{-8}
DSR (%)	2.2805	5.2042

4. CONCLUSION

In the present work, a simple, efficient, and sensitive electrochemical technique was combined with the clay-CPE to simultaneously detect IBU and PCT. Therefore, due to the excellent electrocatalytic activity of clay-CPE, it showed two well-defined voltammetric peaks with greatly enhanced peak currents compared to that at CPE, which provided high sensitivity for the oxidation of IBU and PCT. After optimization of the experimental parameters, the concentration ranges of IBU and PCT using DPV and clay-CPE, the detection limits are lower compared to previous electrochemical electrodes reported. Additionally, the proposed modified electrode was applicable to determine IBU and PCT in human blood with satisfying results. All the results showed that the proposed method is simple, low cost, and effective, which provides for the simultaneous detection of ibuprofen and paracetamol.

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