

## Identification of the three Isomers of Monochlorophenol: Application of Briggs-Rauscher Oscillation

Muhammad Yasir Nawabi<sup>1</sup>, Waqar Uddin<sup>2</sup> and Gang Hu<sup>1,\*</sup>

<sup>1</sup> School of Chemistry and Chemical Engineering, Anhui University, Hefei, 230601, People's Republic of China

<sup>2</sup> Office of Research Innovation and Commercialization, Bahria University, Karachi Campus, Pakistan

\*E-mail: [hugang@ustc.edu](mailto:hugang@ustc.edu)

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A Briggs-Rauscher oscillating system has been established for the identification of the isomers of monochlorophenol (MCPs). The samples were assessed, based on their different perturbations behavior's, in the reaction, over the concentration range of  $1.5 \times 10^{-8}$  to  $1.25 \times 10^{-3}$  molL<sup>-1</sup>. In the system; substrate malic acid, and a complex macrocyclic nickel [NiL](ClO<sub>4</sub>)<sub>2</sub> catalyst were used. The obtained data have shown that individually injected isomers at the same concentration, give distinct perturbation behaviors. 2-Chlorophenol (2-CP) caused a change in period of oscillation, at the lower concentration but 3-Chlorophenol (3-CP) and 4-chlorophenol (4-CP) did not show their reactivity, while at the higher concentration, 2-CP quenching the oscillation that could not be regenerated, 3-CP show stability in the system, However, 4-CP caused the change in the period of active oscillation. Linear regression analysis relationships were found, in the change of oscillation period and the decrease of oscillation number to the increases of concentration of 2-CP and 3-CP. The detection of limits was  $6.75 \times 10^{-8}$  molL<sup>-1</sup> and  $1 \times 10^{-3}$  molL<sup>-1</sup> for 2-CP, and 4-CP respectively. The oxidizing process of 2-CP and 3-CP, described on the base of the suggested FCA (Furrow-Cervellati-Amadori) model. The formation of product of 2-CP and 4-CP in reaction was identified by UV-spectroscopy.

**Keywords:** Briggs-Rauscher oscillator; Monochlorophenol; Identification; Isomers; Perturbation.

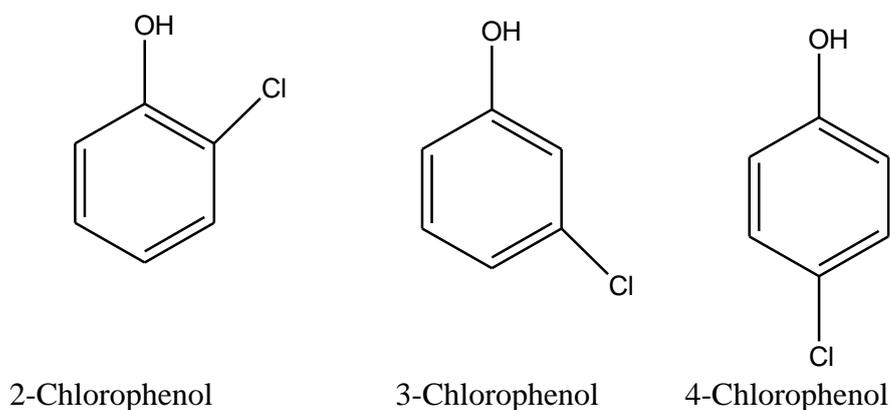
### 1. INTRODUCTION

The oscillating chemical system [1] is a prototypical phenomenon, consists of a complex mixture and shows nearly a periodic or temporally periodic variation in one or more than one intermediate species. A few decades, a hundred numbers of the chemical system have been discovered. Amide these the three oscillating systems, Belousova-Zhabotinsky (BZ) [2–6] Briggs-Rauscher (BR) [7–11] and Bray-Libefasky (BL) [12,13] were widely studied. Instead of these oscillating systems, two other kinds of oscillator, patterns [14,15] and waves[16] were used, in the field of quantitative technique such as

determination of ions [17,18] for analysis of organic reagent [8,19–21], antioxidant values [9,22,23] and exploring of energy conservation [24,25]. But in the area of analytical, these were rarely used for qualitative investigation. It is therefore exceptionally appreciated, the improving implementation of chemical oscillation in the field of qualitative analytical.

In analytical chemistry, an important task is to recognize the isomers that have a similar chemical formula but have distinct chemical reactivity. This is very necessary due to their critical role in medicinal chemistry and pharmacology [26–28]. Various reported analytical techniques have been used for the identification of the isomers such as gas chromatography-mass spectroscopy (GC-MS) [29] high-performance liquid chromatography (HPLC), mass spectroscopy (MS)[30] and liquid chromatography-mass spectroscopy (LC-MS) [31]. Although these techniques are more advanced and have a massive application, but they also have some specific limitations.

Mass-spectroscopy is an alternative analytical technique with high sensitivity and low detection limit but failed to identify the various geometrical, optical isomers, and positional isomers. Therefore mass-spectroscopy is often required combined with gas/liquid chromatography, chemical reactivity, ion traps, and ion-molecule collision [32,33]. LC-MS have higher sensitivity and selectivity as compared to MS for the selection of a suitable solvent which is assumed a difficult task. GC-MS has been played a critical role in chemical analysis, for a few decades, in the field of identification of drugs and isomers. The shortcomings of GC-MS include higher potential, which is easy to overload on a stage, the sample should be volatile or capable of derivatization and prevention it from the atmospheric gases such as CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, Ar, CO, H<sub>2</sub>O which is too difficult. The MS [34,35] and HPLC [36] techniques have been used for the identification monochlorophenol (identifying analytes in the current approach as well). The objective of this article is not only to introduce a simple, convenient, and lower limit of detection (LOD) analytical technique i.e., Briggs-Rauscher oscillating system for the identification of the three isomers of monochlorophenol (MCPs) but also aim to extend the application of the oscillating system in an area of analytical chemistry along with the work diverts the applications of the oscillating system towards the identification of chlorophenols as well. Recently, both oscillating techniques BR and BZ have been used to identification of two positional aliphatic isomers[37,38], aromatic isomers[5,39,40], four polynuclear aromatic isomers [41], ions [42,43] and hetero-aromatic isomers [44].



**Scheme 1.** The structures of Monochlorophenols (MCPs)

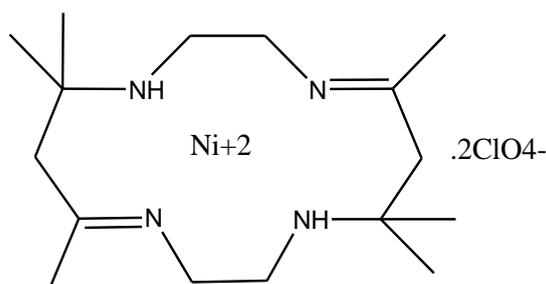
In the current work, we successfully demonstrate the differentiation of three isomers of MCPs (scheme 1) with the Briggs-Rauscher oscillating system. The concentrations of isomers that could be distinguished is over the range from  $2.0 \times 10^{-8}$  to  $9.0 \times 10^{-4} \text{ molL}^{-1}$  were classified in two portions; lower ( $2.0 \times 10^{-8}$  to  $6.0 \times 10^{-8} \text{ molL}^{-1}$ ) and higher ( $3.0 \times 10^{-4}$  to  $9.0 \times 10^{-4} \text{ molL}^{-1}$ ). At the concentration, injection of 2-chlorophenol (2-CP) caused the change in the potential, period of active oscillation also effects on the oscillation life and number of the cycles, while separately addition of 3-chlorophenol (3-CP) and 4-Chlorophenol (4-CP) could not show their reactivity with BR reaction. At the higher concentration, separate injections of MPCs isomers were given different behaviors than the lower concentrations. 2-CP completely terminated the oscillation. A 3-CP shown the same behavior as like low concentration. Addition of 4-CP perturb the oscillation and caused the change in a parameter of oscillation of period and decreased the oscillation number. The calibration curves of 2-CP and 4-CP, give a linear relationship between the increased concentrations of both vs. the change in the period and decreased of the oscillation.

Thus, the isomers of MCPs can be identified by using BR oscillator. BR analytical technique connecting with a container offers a fast qualitative method for recognition of three isomers MCPs (2-CP, 3-CP, and 4-CP) with simpler equipment. The other advantages of this method are that its various perturbation impacts could instantly identify the isomers, have a simpler setup, exceptional precision, and have a broad range of detections.

## 2. EXPERIMENTAL SECTION

### 2.1 Chemicals

MCPs Isomers; 2-CP (aladdin), 3-CP (Aladdin), 4-CP (aladdin) and chemical reagents of BR reaction i.e. malonic acid (Sinopharm chemical reagent, China), potassium iodate (Sinopharm chemical reagent, China), Hydrogen peroxide, (30%) (Sinopharm chemical reagent, China) sulphuric acid (Aldrich, 98 %) were obtained commercially and used into the experiment without any more additional purification while the reagent of BR, complex catalyst tetraazamacrocyclic Ni complex  $[\text{NiL}](\text{ClO}_4)_2$  (structure is given in scheme 2) was synthesized in the laboratory to reported literature [45] and the formation of the crystals was confirmed by the techniques of infrared-spectroscopy and elemental analysis.



**Scheme 2.** Structure of  $[\text{NiL}](\text{ClO}_4)_2$

The stock solution,  $2.0 \times 10^{-2} \text{ molL}^{-1}$  of  $\text{H}_2\text{SO}_4$  was prepared to double deionized water. However,  $2.1 \text{ molL}^{-1}$  stock solution of malonic acid,  $1.41 \times 10^{-1} \text{ molL}^{-1}$  of potassium iodate,  $1.741 \times 10^{-3} \text{ molL}^{-1}$  of Ni complex  $[\text{NiL}](\text{ClO}_4)_2$ , and  $4.1 \text{ molL}^{-1}$  of  $\text{H}_2\text{O}_2$  were prepared with  $2.5 \times 10^{-2} \text{ molL}^{-1}$  solutions of  $\text{H}_2\text{SO}_4$ . Apparatus were resin with double deionized water. The different concentrations of analyte (isomers), examined into the system, were prepared in solvent ethanol.

## 2.2 Apparatus

All identification experiments were carried at a temperature of  $4.0 \pm 0^\circ\text{C}$  in a 50 mL reactor. The temperature was maintained through thermostat, model DZCS-IIC, Nanjing Dazhankejiao institute of the instrument China. To keep stirring rate 550rpm of the mixture, a magnetic stirrer type 793, Jiangsu, and China was used. The potential changes were monitored by a platinum electrode type 213 (Shanghai, China) and a saturated calomel electrode (SCE) type 217 (Shanghai, China). Both electrodes were connected to an amplifier Shanghai, Chenhu CHI 832 China that has a potential measurement of  $\pm 20$ . SEC is associated with a salt bridge that has the function to neutralize the reaction that consists of the  $0.5\text{MNa}_2\text{SO}_4$  and crystals of KCl. The oscillation between potential and time was recorded with a programmer logger lite- acquisition software in PC, which indirectly connected to electrodes through the amplifier. Cyclic voltammogram were taken with a voltammeter model, CH1660, Shanghai, Chenhu instruments Ltd, China). The concentration of analytes was injected into reaction with the help of a micro-pipette model DR07820.

## 2.3. Procedure

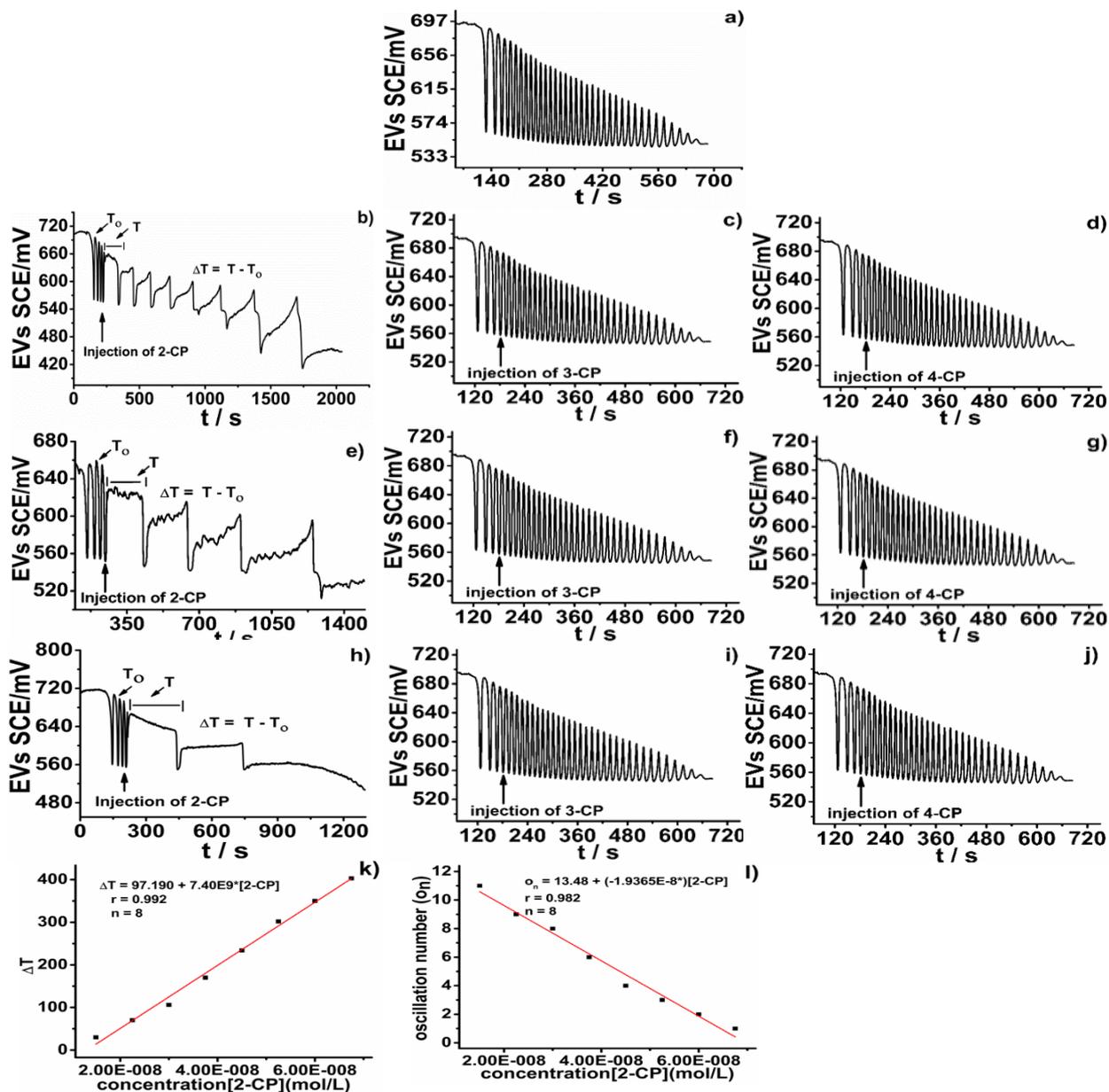
The prepared solutions of BR reagents with above-stated molarity were mixed directly into a 50 ml vessel and made its total volume of 40 ml. the volume of reagents was added with this ratio; 14.30 ml of  $\text{H}_2\text{SO}_4$ , 5.70 ml  $\text{KIO}_3$ , 3 ml  $[\text{NiL}](\text{ClO}_4)_2$ , 2.80 ml malonic acid, and 14.20 ml of  $\text{H}_2\text{O}_2$ . Both electrodes were dipped into the solution, after adding the last reagent, hydrogen peroxide into reaction reactor. The temperature of solution was kept constant at 305 K and stirred magnetically at a rate of 550 rpm. Oscillation signals were recorded in PC by the logger lite software which directly connected to an amplifier. After the stable oscillation analytes were analyzed. To ensure reproducibility of perturbation of samples, each was repeated three times.

## 3. RESULTS AND DISCUSSION

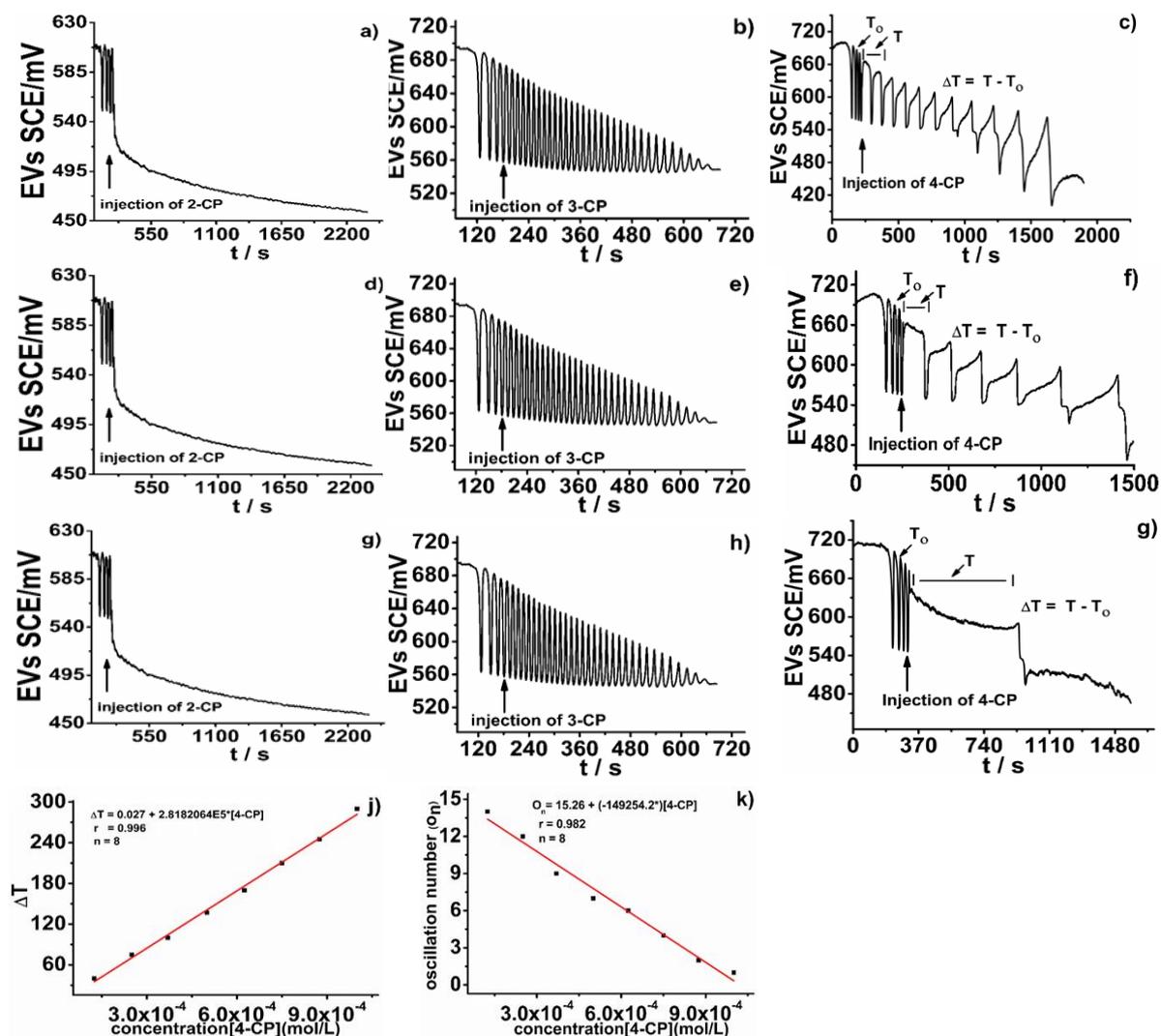
### 3.1. Perturbation action of three isomers (2-CP, 3-CP, 4-CP) of monochlorophenol

The BR typical oscillation as shown in Fig .1 (a) was obtained by mixing the reagents in above-stated procedure. To distinguish the three isomers, we were carried the perturbations experiments over the concentration range of  $2.0 \times 10^{-8}$  to  $9.0 \times 10^{-4} \text{ molL}^{-1}$ , classified into the two-parts, lower

concentration range  $2.0 \times 10^{-8}$  to  $6.0 \times 10^{-8}$  molL<sup>-1</sup> and higher concentration range range  $3.0 \times 10^{-4}$  to  $9.0 \times 10^{-4}$  molL<sup>-1</sup>.



**Figure 1.** (a) Typical oscillation profile for the proposed BR oscillation system; (b). Injection of  $2.25 \times 10^{-8}$  molL<sup>-1</sup> of perturb the active BR oscillation [2-CP]; (c). Injection of  $2.25 \times 10^{-8}$  molL<sup>-1</sup> [3-CP] didn't perturb the active BR oscillation; (d). Injection of  $2.25 \times 10^{-8}$  molL<sup>-1</sup> of [4-CP] perturb the active BR oscillation; (e). Injection of  $3.75 \times 10^{-8}$  molL<sup>-1</sup> of [2-CP] perturb the BR oscillation; (f). Injection  $3.75 \times 10^{-8}$  molL<sup>-1</sup> of [3-CP] didn't perturb the active BR oscillation (g). Injection of  $3.75 \times 10^{-5}$  molL<sup>-1</sup> of [3-CP] didn't perturb the active BR oscillation; (h) Injection of  $5.25 \times 10^{-8}$  molL<sup>-1</sup> of [2-CP] perturb the active BR oscillation; (I). Injection of  $5.25 \times 10^{-8}$  molL<sup>-1</sup> of [3-CP] didn't perturb the active BR oscillation; (j) Injection of  $5.25 \times 10^{-8}$  molL<sup>-1</sup> [4-CP] perturb the oscillation; (k) Calibration curve of concentration [2-CP] Vs. change in period (l) calibration curve of concentration [2-CP] VS decrease of oscillation number. Common Condition:  $[H_2SO_4] = 9.009 \times 10^{-3}$  molL<sup>-1</sup>;  $[MA] = 2.00925 \times 10^{-2}$  molL<sup>-1</sup>,  $[NiL](ClO_4)_2 = 1.3 \times 10^{-4}$  molL<sup>-1</sup>,  $[H_2O_2] = 1.349$  molL<sup>-1</sup>,  $T = 4 \pm 0.5$  °C.



**Figure 2.** (a). Injection of  $3.7 \times 10^{-4}$  molL<sup>-1</sup> of perturb the active BR oscillation [2-CP]; (b). Injection of  $3.7 \times 10^{-4}$  molL<sup>-1</sup> [3-CP] didn't perturb the active BR oscillation; (c) Injection of  $3.7 \times 10^{-4}$  molL<sup>-1</sup> of [4-CP] perturb the active BR oscillation; (d). Injection  $6.25 \times 10^{-4}$  molL<sup>-1</sup> of [2-CP] perturb the BR oscillation; (e). Injection  $6.25 \times 10^{-4}$  molL<sup>-1</sup> of [3-CP] didn't perturb the active BR oscillation (f). Injection of  $6.25 \times 10^{-4}$  molL<sup>-1</sup> of [4-CP] perturb the active BR oscillation; (g) Injection of  $8.75 \times 10^{-4}$  molL<sup>-1</sup> of [2-CP] perturb the active BR oscillation (h) Injection of  $8.75 \times 10^{-4}$  molL<sup>-1</sup> of [3-CP] didn't perturb the active BR oscillation; (i) Injection of  $8.75 \times 10^{-4}$  molL<sup>-1</sup> [4-CP] perturb the oscillation; (j) calibration curve of concentration [4-CP] Vs. change in period (k) calibration curve of concentration [4-CP] VS decrease of oscillation number ( $O_n$ ). Common Condition:  $[H_2SO_4] = 9.009 \times 10^{-3}$  molL<sup>-1</sup>;  $[MA] = 2.00925 \times 10^{-2}$  molL<sup>-1</sup>,  $[NiL](ClO_4)_2 = 1.3 \times 10^{-4}$  molL<sup>-1</sup>,  $[H_2O_2] = 1.349$  molL<sup>-1</sup>,  $T = 4 \pm 0.5$  °C.

First, we have examined the isomers into the system at the lower concentration, the obtained results were shown in Fig 1 (b, c, d; e, f, g; h, i, j). The addition of 2-CP of  $2.2 \times 10^{-8}$  molL<sup>-1</sup>,  $3.7 \times 10^{-8}$  molL<sup>-1</sup> and  $4.5 \times 10^{-8}$  molL<sup>-1</sup>, caused the change in the oscillation period ( $\Delta T$ ) ( $\Delta T = T - T_0$ ), (where  $T$  is the period of oscillation after injection while  $T_0$  is the period of active oscillation before addition of sample) of oscillation profile and also reduced its oscillation life ( $O_L$ ) and oscillation number ( $O_n$ ) (Fig 1. b, e, h) but separately injection of the same amount  $2.2 \times 10^{-8}$  molL<sup>-1</sup>,  $3.7 \times 10^{-8}$  molL<sup>-1</sup> and  $4.5 \times 10^{-8}$

molL<sup>-1</sup> of 3-CP and 4-CP could not show the interaction with the system (Fig 1. c, f, i and d, g, j). It was found a linear relationship between the increased concentration of the 2-CP with the increase of  $\Delta T$  and decrease of  $O_n$  with the correlation coefficients of (r) 0.992 and (r) 0.982 respectively (Fig1. k, l). Whereas at the higher concentration,  $5.0 \times 10^{-5}$  to  $2.5 \times 10^{-4}$  molL<sup>-1</sup>, the isomers are given the different perturbations action by perturbing the active oscillation (Fig 2 (a, b, c; e, f, g; I, j, k)). When 2-CP was injected into the system, oscillation ceased that could not regenerate and potential of reaction also was dropped (Fig 2. a, d, g). The injected 3-CP shown the same behaviors as that it is shown at the lower concentration (Fig 2. (b,e,h)). While, 4-CP, perturb the oscillation, caused the change in the oscillation period ( $\Delta T$ ) and also effects on the oscillation number ( $O_n$ ), and oscillation life ( $O_L$ ) of the active profile of reaction (Fig 2 (c, f, i)). The polynomial regression curves (Fig 2 (J, k)) show a linear relation between the increased concentration of 2-CP within the  $\Delta T$  and decrease of  $O_n$ .

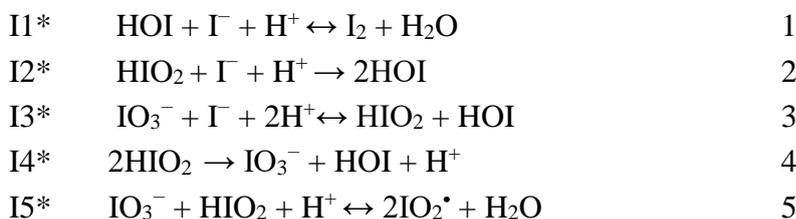
The perturbation of 2-CP at the lower concentration, involves a change in period, while 3-CP and 4-CP do not. But at the higher concentration, the perturbation of 2-CP permanently terminates the oscillation, 3-CP didn't show interaction with reaction, whereas 4-CP perturbation includes the change in period, hence three isomers of MCPs can be distinguished with their different perturbation effects by using the BR oscillator.

### 3.2. Mechanism of reaction

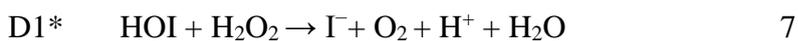
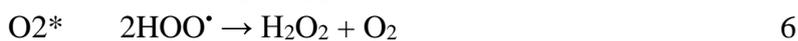
The oscillating reaction mechanism is a complex phenomenon, have the numbers of the kinetic steps and reactive and non-reactive in intermediate species [22,46] such as  $\cdot\text{OOH}$ ,  $\text{IO}_2\cdot$ ,  $\cdot\text{OH}$ ,  $\text{I}^-$  etc. It has been reported that the free radical played a very important role, in the determination and identification of the various compounds in the field of the oscillating system. The first explanation of the oscillating reaction was given by Noyes and Furrow 1982 [47] and developed an NF (Noyes-Furrow) model. After this, a new DE (De Kepper-Epstein) model was developed [48]. Later, in 1993 Sorensen and co-workers have presented the oscillating mechanism with a comprehensive explanation [49]. Lately, Furrow.et.al developed a summarized FCA (Furrow-Cervellati-Amadori) [50] model based on the models NF and DE. Original NF model consists 30-steps, 11 out of 30 are believed to be sufficient to generate oscillation. For  $[\text{NiL}]^{2+}$ -complex BR oscillator, we proposed 12-steps oscillatory mechanism in which 11 are taken from NF model and one from FCA model as mentioned below. For clarity, these 12 steps are divided into 5 groups kept asterisk (\*) on the basic steps of NF reactions as in reference [47].

The macrocyclic nickel complex catalyst-malonic acid-hydrogen peroxide-potassium iodate catalyzed oscillating is consisting of twelve steps, in which eleven belongs to the NF model and remaining one from the DF model. These reactions are given below from 1-12.

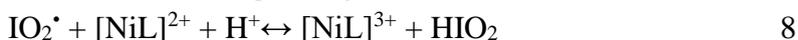
Reactions Involving Oxyiodine:



Reaction Involving Oxygen:



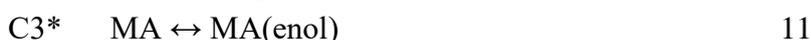
Reactions Involving Catalyst:



Reactions Involving Reduction of Oxyiodine:

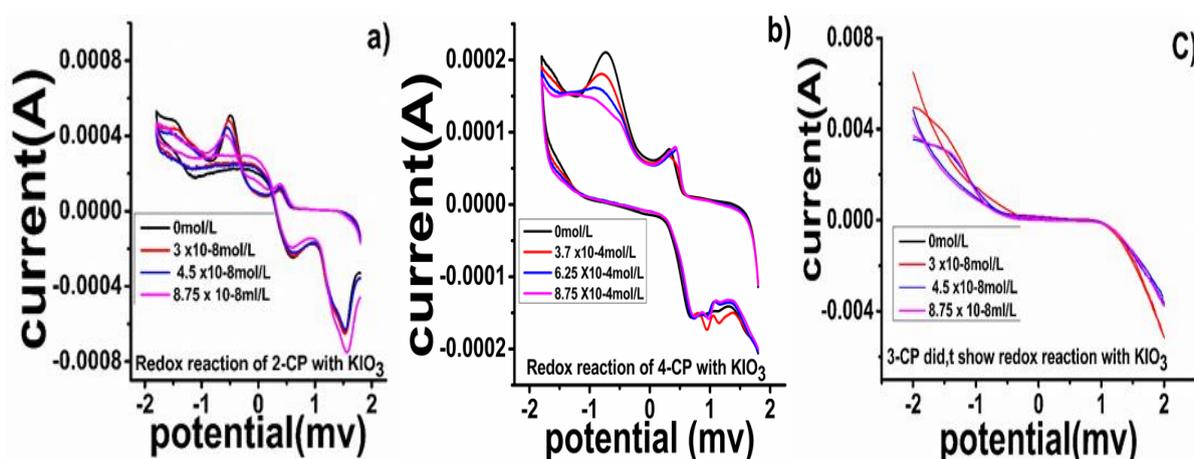


Reactions Involving Substrate – Iodine:



### 3.3. Cyclic voltammetry Experiment

We performed the cyclic voltammetry (CV) experiments to the confirmation of the existence of redox reactivity of MCPs with the reagents BR reaction. The experiments were carried into the system of  $2.1609 \times 10^{-2}$  [H<sub>2</sub>SO<sub>4</sub>] +  $1.995 \times 10^{-2}$  [KIO<sub>3</sub>],  $2.331 \times 10^{-2}$  [H<sub>2</sub>SO<sub>4</sub>] +  $1.30575 \times 10^{-4}$  [NiL](ClO<sub>4</sub>)<sub>2</sub>,  $1.625 \times 10^{-2}$  [H<sub>2</sub>SO<sub>4</sub>] + [H<sub>2</sub>O<sub>2</sub>] and  $2.3436 \times 10^{-2}$  [H<sub>2</sub>SO<sub>4</sub>] +  $1.47 \times 10^{-1}$  [MA][HOOCCH<sub>2</sub>COOH] with the presence and the absence of the MCPs analytes.



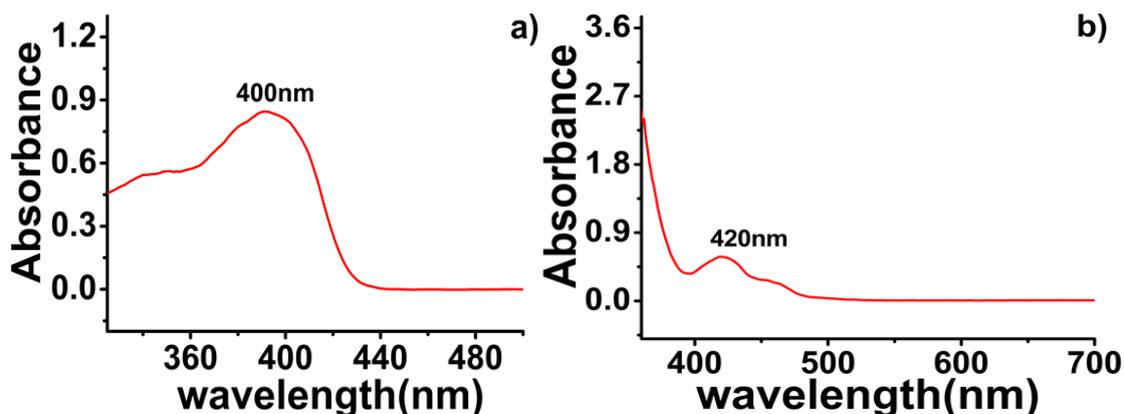
**Figure 3.** a) Cyclic voltammogram of 2-CP with KIO<sub>3</sub>; conditions; [2-CP] =  $3 \times 10^{-8}$  mol/L,  $4.5 \times 10^{-8}$  mol/L and  $6.0 \times 10^{-8}$  mol/L. [KIO<sub>3</sub>] =  $1.995 \times 10^{-2}$  mol/L, [H<sub>2</sub>SO<sub>4</sub>] =  $2.1609 \times 10^{-2}$  mol/L; b). Cyclic voltammogram of 4-CP with KIO<sub>3</sub>; condition's; [4-CP] =  $3.7 \times 10^{-4}$  mol/L,  $6.25 \times 10^{-4}$  mol/L and  $6.0 \times 10^{-4}$  mol/L. [KIO<sub>3</sub>] =  $1.995 \times 10^{-2}$  mol/L, [H<sub>2</sub>SO<sub>4</sub>] =  $2.1609 \times 10^{-2}$  mol/L. c) Cyclic voltammogram of 3-CP with KIO<sub>3</sub>; conditions; [3-CP] =  $3 \times 10^{-8}$  mol/L, [KIO<sub>3</sub>] =  $1.995 \times 10^{-2}$  mol/L, [H<sub>2</sub>SO<sub>4</sub>] =  $2.1609 \times 10^{-2}$  mol/L. d) cyclic voltammogram of 3-CP with H<sub>2</sub>O<sub>2</sub>; Conditions; [3-CP] =  $3 \times 10^{-8}$  mol/L, [H<sub>2</sub>SO<sub>4</sub>] =  $1.625 \times 10^{-2}$  mol/L, [H<sub>2</sub>O<sub>2</sub>] =  $2.3436 \times 10^{-2}$  mol/L. e) cyclic voltammogram 3-CP with the malic acid, conditions; [3-CP] =  $3 \times 10^{-8}$  mol/L, [H<sub>2</sub>SO<sub>4</sub>] =  $2.3436 \times 10^{-2}$  mol/L, [H<sub>2</sub>O<sub>2</sub>] =  $1.47 \times 10^{-1}$  mol/L. f) cyclic voltammogram of 3-CP with [NiL](ClO<sub>4</sub>)<sub>2</sub>; conditions; [3-CP] =  $3 \times 10^{-8}$  mol/L, [H<sub>2</sub>SO<sub>4</sub>] =  $2.331 \times 10^{-2}$  mol/L, [NiL](ClO<sub>4</sub>)<sub>2</sub> =  $1.30575 \times 10^{-4}$  mol/L.

The obtained data of cyclic voltammetry of isomers of 2-CP and 4-CP with  $\text{KIO}_3$  (Fig 3 (a, b)) shown the oxidation and reduction peaks, that were going to change with the respect to increase of concentrations of both isomers (Fig.3 (a,b)). It clarified to us that both isomers (2-CP, 4-CP) have redox reactivity with the BR reagent of  $\text{KIO}_3$ . Whereas the obtained cyclic voltammogram of the 3-CP with  $\text{KIO}_3$ , did not show the oxidation and reduction peaks (Fig 3c). It indicates that the 3-CP is not active in the reaction.

Although the CV experiments show that isomers were oxidized with  $\text{KIO}_3$  in acidic media, it is not possible to consider this reaction, into the BR system, because if it is assumed, then we cloud not noticed change in the period, due to the fast reaction of  $\text{KIO}_3$  with isomers. Therefore, we consider that the isomers in the reaction were reacted with the high oxidation potential free radical and oxidized into the products quinone.

### 3.4. Identification of the products of 2-CP and 4-CP isomers

According to the reported literature [51–53], 2-CP and 4-CP were reacted with hydrogen peroxide, manganese oxide in the dilute aqueous suspension, and potassium nitrosodisulfonate and oxidized into a product quinone. It has been in the published article [54], that, in the UV-spectroscopy, the absorbance peak of Quinone exists in the range of 350-450 nm.



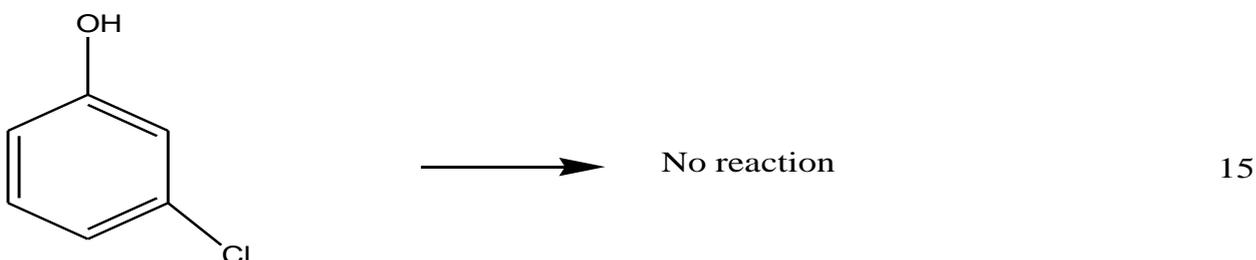
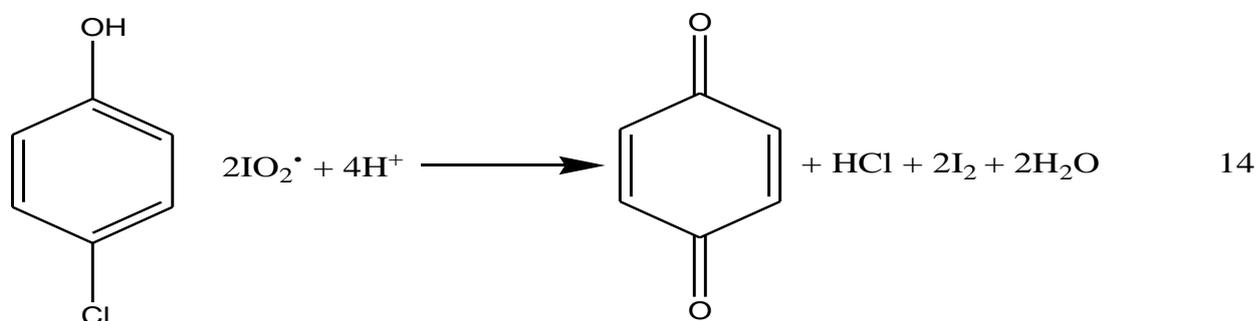
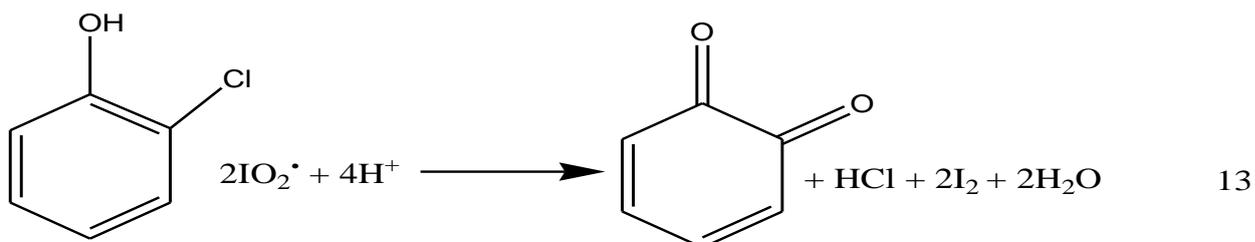
**Figure 4.** a) UV-Spectrum of 2-CP with  $\text{KIO}_3$  in acidic medium of sulfuric acid. Common conditions;  $[2\text{-CP}] = 6.0 \times 10^{-8} \text{ molL}^{-1}$ ;  $[\text{KIO}_3] = 1.995 \times 10^{-2} \text{ molL}^{-1}$ ,  $[\text{H}_2\text{SO}_4] = 2.1609 \times 10^{-2} \text{ molL}^{-1}$ ; b) UV-spectrum of 4-CP with  $\text{KIO}_3$  in acidic medium of  $\text{H}_2\text{SO}_4$ . Condition's;  $[4\text{-CP}] = 3.7 \times 10^{-4} \text{ molL}^{-1}$ .  $[\text{KIO}_3] = 1.995 \times 10^{-3} \text{ molL}^{-1}$ ,  $[\text{H}_2\text{SO}_4] = 2.1609 \times 10^{-2} \text{ molL}^{-1}$ .

To discover products of both isomers into the BR reaction, we performed UV experiments. For experiments, we prepared separately mixture of  $6.0 \times 10^{-8} \text{ molL}^{-1}$  of 2-CP and  $3.7 \times 10^{-4} \text{ molL}^{-1}$  of 3-CP with the solution of  $2.1609 \times 10^{-2} \text{ molL}^{-1}$  of  $\text{H}_2\text{SO}_4$  and  $1.995 \times 10^{-2} \text{ molL}^{-1}$  of  $\text{KIO}_3$ . Kept these for 40 ml mixtures for a half-hour, after this one 1ml of the solution of both samples was taken in the UV-cuvette respectively and run the experiments The obtained UV- spectrum (Fig 4 a,b) The obtained UV-spectrums (Fig 3 a, b) shows the absorbance peaks approximately at the 400 nm and 420 nm clarifies to

us with reported literature [51-53], that both were oxidized in products of quinone. The 2-CP was oxidized into 1, 2-quinone and while the 4-CP into 1, 4-quinone.

### 3.5. Explanation of the interpretation mechanism of isomers with intermediate $IO_2^{\bullet}$

The results of CV experiments confirmed the redox reaction of 2-CP and 4-CP with  $IO_2^{\bullet}$ -(see Fig 2). The spectrum of UV (see Fig 3), identified the product 1,2-quinone and 1,4-quinone into the system. Moreover, the involvement of  $IO_2^{\bullet}$  radical could cause  $\Delta T$  [40]. Based on literature, cyclic voltammogram and UV results, we added two more oscillatory reactions i.e. reactions 13 and 14 in the model of the FCA, for the explanation of the oscillating system response to the injection of the samples.



The added concentration of 2-CP reacts with the free radical  $IO_2^{\bullet}$  of the reaction and oxidized into product quinone and gives the  $I_2$  via reaction 13. The function of the  $IO_2^{\bullet}$  in reaction has the oxidation of  $NiL^{+2}$  into  $NiL^{+3}$ . The decreased concentration of the  $IO_2^{\bullet}$  by the consumption of reaction 8 affects the irreversible reaction 8 into reversible reaction and reduces the rate of oxidation of  $NiL^{+2}$  into the  $NiL^{+3}$ . Such a decrease in the rate of oxidation  $NiL^{+2}/NiL^{+3}$ , effects on the oscillation of active reaction and leads to decrease in its maximum potential and amplitude. The  $I_2$  generation by reaction 8 shifts reaction 9 and increase the concentration of  $I^-$  cause upsurge in the change of period and decrease of oscillation number of the active profile.

#### 4. CONCLUSION

First time, an efficient analytical technique BR oscillator was developed to distinguish the three aromatic isomers of MCPs. The suggested method shows satisfactory accuracy and acceptable limits of detection for the identification of isomers. The method was successfully applied to the determination of isomers and different behavior of isomers were noticed, over a range of the concentration of  $1.5 \times 10^{-8}$  mol/L to  $1.25 \times 10^{-3}$  mol/L, which can be utilized in qualitative examination. It was exposed by UV-spectroscopy that the 2-CP is oxidized into the 1-2 Quinone and 4-CP into the 1-4 Quinone via the  $\text{IO}_2^\bullet$  radical.

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#### CONFLICT OF INTEREST

The authors declare no conflict of interest.

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