Deactivation of Gold Electrode at Chlorophenols Electrooxidation

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Electrochemical impedance spectroscopy (EIS) was used as the main technique coupled with cycling voltammetry (CV) to characterize the surface fouling of a conventional gold electrode in chlorophenol aqueous solutions caused by the electropolymerization of chlorinated phenol on the electrode surface. Different chlorophenols show differences in the voltammetric responses and deactivation due to fouling process, depending on number of the chloro substituents on the aromatic ring. Results showed that the fouling extent at gold electrode present the following order 2 CP > 2,4,5 TCP > 2,4 DCP. In order to characterize the interface between Au electrode and solution before and after polymerization, the Mott Sckhotky technique was used. According to the Mott Schottky equation, positive slope of C^{-2} *vs. potential plots suggest an n-type semiconductor behaviour for polymeric films.*

Keywords: chlorophenol electrooxidation, gold electrode, EIS, differential capacitance

Chlorophenols (CPs) constitute a group of organic substances that are introduced into the environment as a result of several activities [1]. Because of their numerous origins, they can be found in industrial wastewaters, soils and surface waters, and several of them have been listed among the 65 priority pollutants by the US EPA [2].

From the 19 CPs existing, 2,4 dichlorophenol and 2,4,5 trichlorophenol are used for production of herbicides and pentachlorophenols (PCP) act as fungicides, herbicides and insecticides [3-4].

In general, the resistance of CPs to microbial degradation, their environmental persistence, and toxicity increase with increasing Cl substitution. It has also been reported that the position of the Cl atom in the aromating ring determines the rate of microbial degradation [5].

The removal of chlorophenols from wastewater is of environmental interest because CPs has negative effect on a number of aquatic life form. Consequently, reducing the concentration or total mineralization of chlorinated phenol is a necessary pretreatment prior to waste water discharge to a biological waste treatment facility.

Therefore, the degradation of CPs is of great interest in the environmental protection field as well as in industrial process control. The electrochemical oxidation of chlorophenols is a promising method for wastewater remediation.

The researchers [6] reported that phenols electro oxidation produces electrode fouling and that tars formed on the electrode by electropolymerization show a low rate of oxidation, low permeability and strong adhesion to the electrode [7].

A wide variety of electrodes such as platinum [8], modified platinum [9], gold [10-11], modified GC [12], tindioxide-coated titanium electrode [13] and boron-doped diamond electrode [14] have been used for oxidative removal of chlorophenols. Chlorophenols usually undergo oxidative polymerization on many electrodes even at low concentrations.

Deactivation of the electrode was usually found to be more evident in alkaline solutions, as compared to that in acidic phenolic solutions. Electrode potential is also an important parameter for electropolymerization of phenols. Electrode fouling is more likely to occur in the potential region of water stability, but slighter fouling is achieved in the oxygen evolution region, probably due to both the attacking of oxygen bubbles onto the polymeric films and the oxidation destruction of films by generated hydroxyl radicals [15].

Different methods have been used to investigate the electropolymerization behaviours of phenol and its derivations and to characterize the polymeric films formed, including cyclic voltammetry (CV) [16], electrochemical impedance spectroscopy (EIS) [17], gel permeation chromatograph (GPC) [18], Fourier transformed infrared (FTIR) spectroscopy [19], electrochemical quartz crystal microbalance (EQCM) [20], scanning electronic microscopy (SEM) [21], scanning tunneling microscopy (STM) and gas chromatography–mass spectrometry (GC–MS) [22].

In this work, the electrochemical oxidation of 2 chlorophenol (2 CP), 2,4 dichlorophenol (2,4 DCP) and 2,4,5 trichlorophenol (2,4,5 TCP) on Au stationary and rotating disk electrode was studied by CV, EIS and volatmmetry on rotating disc electrode (RDE).

In order to obtain information at the adhesive interface between the formed polymeric structure and metal, both the capacitance and resistance were measured at various concentrations.

Experimental part

The cyclic voltammetry and electrochemical impedance spectroscopy experiments were carried out for different concentrations of chlorophenols in 0.1M Na_2SO_4 as supporting electrolyte, at room temperature, using a three-electrode system. The working electrode was an Au disk (0.07 cm^2). Also, a platinum wire was used as counter electrode and all potentials were measured against a saturated calomel electrode.

Cyclic voltammetry measurements were performed using a GAMRY PC3 potentiostat. The investigation has been done in anodic direction from 0 to 1.1 V and before each scan the electrode was prepared to ensure a

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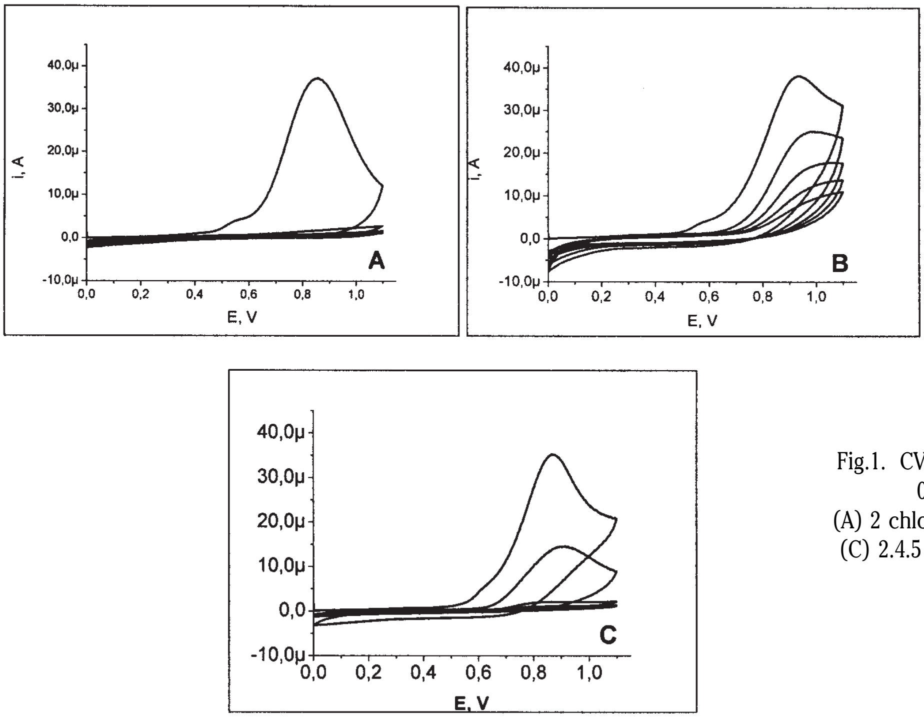

Fig.1. CV curves of Au electrode in Na_2SO_4 0.1 M, containing 4 mM of: (A) 2 chlorophenol, (B) 2,4 dichlorophenol, (C) 2.4.5 trichlorophenol; potential sweep rate 100 mV/s

reproducible surface by polishing, rinsing with distillated water and ultrasonic cleaning for 4 min in high purity water.

The impedance of working electrode interface was measured as a function of DC voltage. The capacitance vs. potential and resistance vs. potential curves were obtained at 100Hz frequency, and 10 mV amplitude, in the potential region corresponding to oxidation of chlorophenol, 0V ÷ 1.1V.

2 chlorophenol (2 CP) 2,4 dichlorophenol (2,4 DCP) and 2,4,5 trichlorophenol (2,4,5 TCP), were purchase from Aldrich and used as received.

For the *p*H study buffer solutions and H_2SO_4 and NaOH solutions were used in order to obtain desired *p*H values.

All the solutions were freshly prepared with double distillated water.

Results and discussions

Cyclic voltammetry

The first five consecutive cyclic voltammograms of the Au electrode in 4 mM solutions of chlorinated phenol in Na_2SO_4 0.1M at a potential sweep rate of 0.1 V/s are shown in figure 1 A,B,C.

Anodic oxidation of chlorophenols occurs during a positive-going potential scan in the range 0.6 ÷ 1.0 V. In the first CV scan, the peak currents are about 38µA for all studied chlorophenols and the peak potential is achieved at 0.85 V for 2CP, 0.94 V for 2,4DCP and 0.86 V for 2,4,5TCP.

The almost 100 mV potential difference in anodic direction can be observed for 2,4 DCP showing a slower oxidaxion of di-chlorophenol.

For 2CP oxidation curves, in the second cycle the maximum current drops drastically to a negligible value. This decrease of current is a well-known phenomenon for electrochemical oxidation both of phenol and its chlorinated derivates and may be explained by deactivation of the electrode due to polymerization process [23] which occurs on the electrode surface. The high molecular weight compounds formed on the electrode surface during electro-oxidation block of the chlorophenol molecules to enter to the electrode surface due to a low permeability of such film.

The CV curves recorded on the Au electrode in 2,4-dichlorophenol solution (fig. 1, B) differ considerably from those obtained in 2-chlorophenol. The maximum current from first positive-going potential sweep is almost the same as in the case of 2-chlorophenol but the current decay, with cycling, is slower compared to that of 2-chlorophenol. The deactivation of the electrode is not so clearly, a residual current can be observed and in the fifth cycle.

The CV curves in 4mM 2,4,5-trichlorophenol solution are shown in Figure 1, C. In this case the peak current decreases slowly with the number of cycle presenting a clear peak in the second cycle and then a current quickly drop in the subsequent cycles can be observed.

The reactivity of the CPs depends on the number of chlorine atoms, but also on their position in the aromatic ring, as was presented in other previous work [24, 25].

The obtained results are completely different of those obtained in [22] on platinum electrode in alkaline solution which have reported a faster deactivation of electrode surface at electrooxidation of 2,4DCP and 2,4,5TCP and a slower decreasing of the oxidation current after the first cycle for 2CP.

The value of the anodic peak potential of 2CP oxidation decreases linearly with increasing of *p*H in the region 2 – 9, with a slope of 59 ± 4 mV (*p*H unit)$^{-1}$. The results are in concordance with that reported in [3] on glassy carbon electrode and indicate an equal number of protons and electrons in reaction. On the range *p*H ≥ 9 the anodic peak potential presents only a little dependence on the *p*H.

The peak currents are proportional to the square root of the scan rate, which indicate control by mass transport for all studied concentrations of chlorophenol. The experimental slope of the plot of i_p versus $\upsilon^{1/2}$ is 1.016.10^{-4} A.V$^{-1/2}$ .s$^{1/2}$ for 2CP, 0.818.10^{-4} A. V$^{-1/2}$ .s$^{1/2}$ for 2,4 DCP and 0.844.10^{-4} A.V$^{-1/2}$ .s$^{1/2}$ for 2,4,5TCP, respectively.

Equation (1) predicts that log (i_p) is linear vs. E_p with a slope equal to $-(an_aF/(RT))$.

$$i_p = (0.227)nFAC_0k^0\exp\left[-\left(\frac{\alpha n_a F}{RT}\right)(E_p - E^0)\right] \qquad (1)$$

where:

i_p - the peak current (A);
n - number of exchanged electron;
E_p –peak potential (V);
A - the area of electrode (cm^2),;

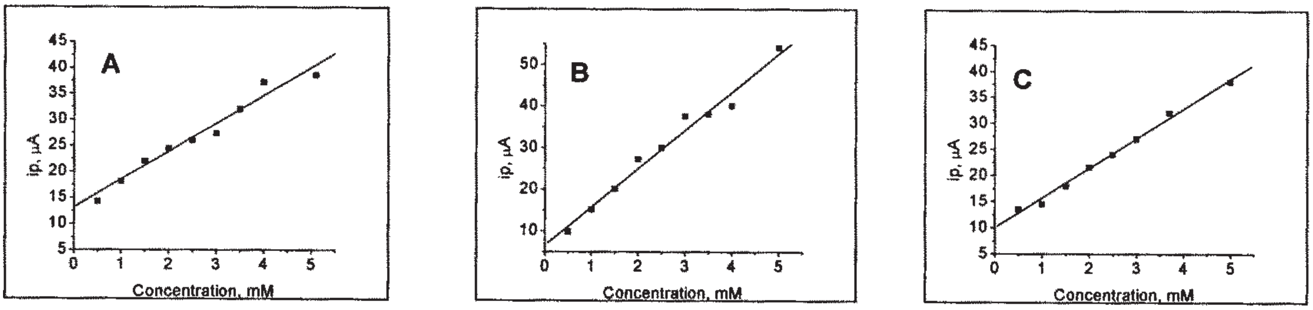

Fig.2. Variation of peak current with concentration of chlorophenols on Au electrode in Na_2SO_4 0.1 M solution, A) 2 chlorophenol, B) 2,4 dichlorophenol, C) 2,4,5 trichlorophenol

C - the concentration in the bulk solution (in mol/cm^3);
αn_a the apparent number of electrons transferred;
υ - the scan rate (mV s^{-1}).

The electron transfer rate constants (k^0) can be calculated from the intercept and present the following order 2 CP > 2,4,5 TCP > 2,4 DCP, table 1.

Table 1
THE ELECTRON TRANSFER RATE CONSTANT

Compound	k^0 (cm.s^{-1})
2-chlorophenol	2.17×10^{-8}
2,4 dichlorophenol	2.77×10^{-11}
2,4,5 trichlorophenol	1.63×10^{-9}

Additionally, the peak currents increase linearly with concentration of chlorophenols on the concentration range of 0.5 – 5 mM with a slope of 5.4 µA mM^{-1} for 2 CP, 9.2 µA µM^{-1} for 2,4 DCP and 5.7 µA mM^{-1} for 2,4,5 TCP, respectively (fig.2).

The results are in concordance with those observed in cyclic voltammetry curves, so that the highest slope value was obtained for 2,4 DCP who presented to resume the slow blocking of the electrode. Also, the smallest slope was obtained for 2CP who presented the fastest deactivation of the electrode even after the first CV cycle.

For concentrations higher than 5mM it was observed that the same i_p vs. conc. linearity was not kept and the slope decreases continuously with the concentration increasing. This behaviour can be also attributed to more rapid electrode blocking due to the fouling phenomena for higher concentrations of phenol.

Electrochemical impedance spectroscopy

In order to characterize the interface between Au electrode and solution before and after polymerization, the electrochemical impedance spectroscopy (EIS) was used. The potentiodynamic electrochemical impedance spectroscopy (EIS) technique was used to measure the changes that occur in the electrochemical interface during the chlorophenols oxidation, due to special characteristic of the polymeric films [26]. Figure 3 presents comparatively the resistive component of impedance vs. potentials curves for electrochemical oxidation of studied chlorophenols. The resistance was calculated assuming a simple parallel RC equivalent circuit of the interface.

All the curves are characterized by a sudden increase of the resistance when the electrooxidation processes are occurred. Such increase of the resistance is mainly attributed to the blocking of the electrode with the species obtained by electropolymerizarion processes.

For comparison we use the potential-resistance values corresponding to peak potentials from CV, such as 0.85 V for 2CP, 0.94 V for 2,4DCP and 0.86 V for 2,4,5TCP

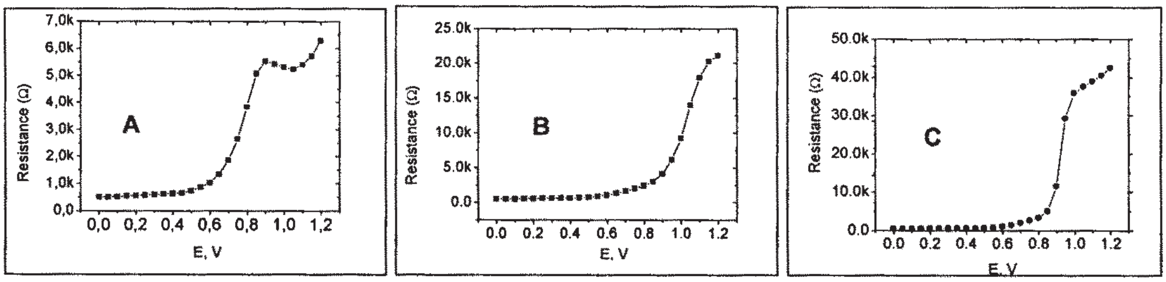

Fig.3. Resistance vs. potentials curves for 4 mM solutions of:
A) 2 chlorophenol, B) 2,4 dichlorophenol, C) 2,4,5 trichlorophenol on Au electrode in Na_2SO_4 0.1 M solution

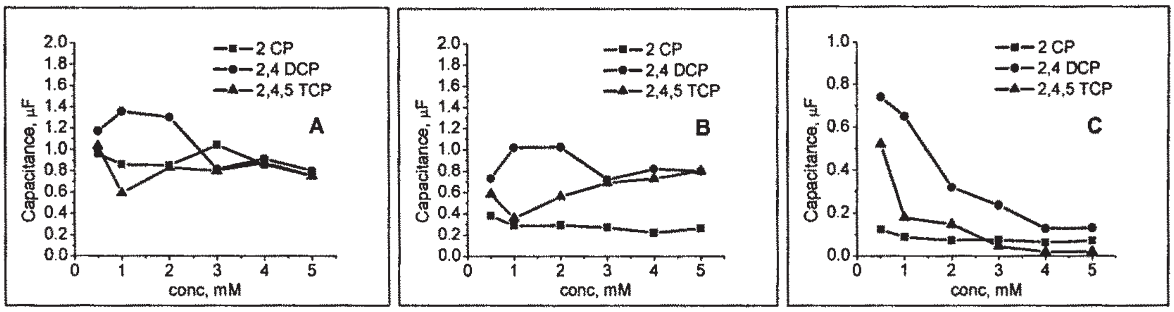

Fig.4. Capacitance vs. concentration of chlorophenols at: A) 0.4V, B) 0.8V, C) 1.1V on Au electrode in Na_2SO_4 0.1 M solution. Frequency applied 100 Hz of a.c. 10 mV potential

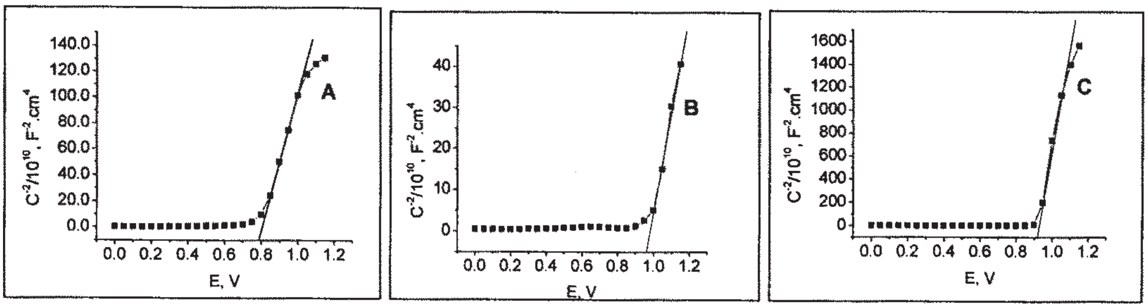

Fig. 5. C^{-2} vs. potential plots for 4 mM solutions of: A) 2 chlorophenol, B) 2,4 dichlorophenol, C) 2,4,5 trichlorophenol on Au electrode in Na_2SO_4 0.1 M solution. Frequency applied 100 Hz of a.c. 10 mV potential.

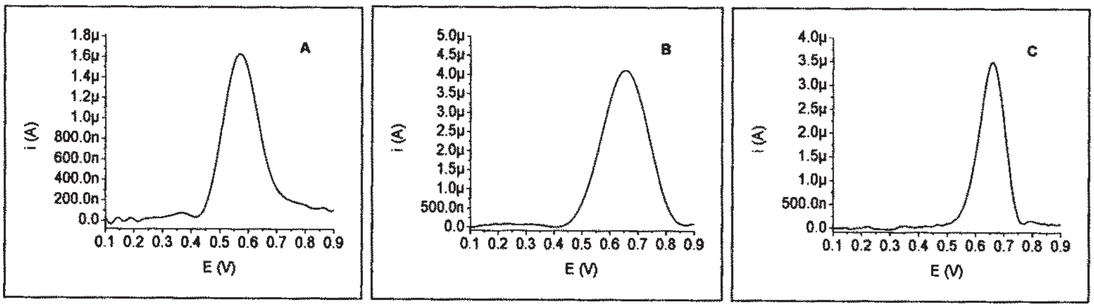

Fig. 6. Linear sweep voltammograms of RDE Au electrode at 500 rpm in Na_2SO_4 0.1M solution, containing 2 mM of: (A) 2 chlorophenol, (B) 2,4 dichlorophenol, (C) 2,4,5 trichlorophenol; potential sweep rate: 2 mV/s

The resistances corresponding to the peak potential are 2.4 k Ω for 2,4DCP, 3.3 kΩ for 2,4,5 TCP and 4.4 k Ω for 2CP which are in concordance with the results from cyclic voltammetry showing the same deactivation order 2 CP > 2,4,5 TCP > 2,4 DCP.

At 1.1V the values of the resistance are 5.5 Ω for 2CP, 20 Ω for 2,4DCP and 40 Ω for 2,4,5 TCP, respectively, showing a different resistive behaviour after peak potential.

The same observations can be made from the variation of the differential capacitance of the interface with concentration, (fig. 4). The values of capacitance remain almost constant with concentration at 0.4V and 0.8V, respectively (fig. 4, A, B). At 1.1V the evolution of the capacitance is contrarily with that observed at evolution of resistance, the capacitance decrease with concentration for 2,4DCP and 2,4,5 TCP, and remain almost constant for 2CP.

The voltage dependence of the space – change capacitance is well known from the model of metal semiconductor contact in electronic systems, which is widely used in the analysis of the Mott Schottky plots in semiconductors.

According to the Mott Schottky equation, C^{-2} is related to the electrode potential E by the equation (2) [27]:

$$\frac{1}{C^2}=\frac{2}{N\ e\varepsilon_r\varepsilon_0}\left(E-E_{FB}-\frac{kT}{e}\right) \qquad (2)$$

where:

C = capacitance of the space charge region;

E_{FB} = flat band potential;

ε_0 = permittivity of free space;

ε_r = dielectric constant;

e = elementary charge (+ e for electrons and – e for holes);

N = acceptor or donor concentration;

k = Boltzmann constant;

T= the absolute temperature.

The C^{-2} vs. potential plots recorded for all studied chlorophenols present a linear dependence at the value of potential, which the film is formed on the electrode surface, figure 5.

These dependences present a positive slope, which is according to Mott Schottky equation for an *n*-type semiconductor [28].

Electrooxidation of chlorophenols on Au RDE

In the attempt to avoid the electrode fouling, positive scans at 2 mV.s^{-1} were carried out with RDE for different concentration of chlorophenols in the range 0.5-5 mM. The RDE experiments were also performed in order to try to investigate the reaction mechanisms related to chlorophenol oxidation phenomena.

In CV the current increases as the potential reaches the oxidation potential of the analyte, but then falls off as the concentration of the analyte is depleted close to the electrode surface unlike RDE voltammograms when due to hydrodynamic regime would have to obtain a current plateau.

Unfortunately, for all studied angular velocities in the range 500-2500 rpm it was not obtained a limiting current and not different current wave was observed. The obtained curves are similarly with those obtained on stationary gold electrode.

The presence of the current peak on the linear sweep voltammograms (LSV) on RDE is not a common behaviour and suggests that the electrooxidation process occurs *via* deactivation of the electrode surface due to the polymerization process and the blocking of the electrode surface [24].

The figure 6 presents the linear sweep voltammograms recorded on RDE electrode.

As the peak current presence and the fall in the current observed on RDE voltammograms are attributed to deactivation of the electrode, the value of the peak current should give us some information about the process of the electrode blocking.

The values of the maximum current are 1.65 µA for CP, 3.5 µA for TCP and 4.2 µA for DCP suggesting the following deactivation order 2CP > 2,4,5TCP > 2,4DCP which is concordance with the results obtained from cyclic voltammetry.

The difference between peak potentials extracted from LSV and CV may be due to both different potential sweep rate used (100 mV/s for CV and 2 mV/s for LSV) and the system working of RDE under forced convection.

Conclusion

Both the polymerization degree and the electrode deactivation depend on the structure and the permeability of the polymer formed, determined by the degree of chlorination and the structure of the isomer, their reactivity and polymerization pathways.

The CV investigations of chlorophenols in neutral medium (0.1M Na_2SO_4 solution) show that their oxidation rate on Au electrode increases in the row: 2,4 chlorophenol >2,4,5 chlorophenols > 2 chlorophenol.

The results of EIS measurements are in concordance with the results from cyclic voltammetry showing the same deactivation order 2 CP > 2,4,5 TCP > 2,4 DCP.

The C^{-2} vs. potential plots recorded for all studied chlorophenols present a linear dependence at the value of potential, where the film is formed on the electrode surface. These dependences present a positive slope, which is according to Mott Schottky equation for an *n*-type semiconductor.

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