DOI 10.7251/JEPM1901051C
UDC 628.1/.3:547.5/.6

Journal of
Engineering & Processing
Management

ORIGINAL SCIENTIFIC PAPER

Adsorption of phenol on polycrystalline gold from aqueous solutions

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Keywords:
Electrosorption, phenol, polycrystalline gold, natural water

Abstract
The presence of phenolic compounds as one of the most common organic pollutants in natural water (surface and ground waters) has been detected as a worldwide problem. Very small concentrations of phenols affect the quality of both environmental and household waters, and directly or indirectly impact lives in aquatic systems and humans, as well. Most of the organic compounds, containing certain functional groups, such as amino, amines, carbonyl, hydroxyl, groups containing sulfur and others, have shown ability of adsorption on metal surfaces from aqueous solutions. Cyclic voltammetry (dE/dt = 100 mV s^{-1}) with simultaneous monitoring of the double layer (dl) capacitance (at 100 Hz and 1 mV ac signal) was used for an adsorption study of phenol on polycrystalline gold from 0.5 mol dm^{-3} aqueous solutions of $NaHCO_3$. Thus, in this study an effort was made to establish a fast method, an electrochemical procedure for qualitative and quantitative determination of phenols in natural water systems.

1. INTRODUCTION

The presence of phenolic compounds as one of the most common organic pollutants in aquatic environments (surface and ground waters) has been detected as a worldwide problem. Very small concentrations of phenols affect the quality of both, environmental and household waters, and directly or indirectly impact lives in aquatic systems and humans, as well. Phenols have been recognized as toxic, mutagenic, carcinogenic, and have adverse short- and long-term effects on humans and animals. Toxicity of phenols is associated with the two main characteristics, its hydrophobicity and formation of free radicals. As soon as phenols diffuse into cells, they undertake active transformation into species of increased toxicity that may bind and damage DNA (Michałowicz and Duda, 2007). The entrance of phenolic compound in aquatic systems in wide concentration range (10 – 4000 mg dm^{-3}), is mostly related to the waste waters from different industries, such as petrochemical industry, pharmaceutical industry, chemical plants, production of rubber, pesticides, insecticides, glues, etc. (Patterson, 1977). In addition to the disposal of industrial and domestic wastes, the presence of phenols in environmental waters may be result of the degradation of natural organic substances present in water, and agricultural activities (Anku et al., 2017). Most of the organic compounds, containing certain functional groups, such as amino, amines, carbonyl, hydroxyl, groups containing sulfur and others, have shown ability of adsorption on metal surfaces from aqueous solutions (Lund and Hammerich, 1991, Chamovska et al., 2006). On the other hand, it is known that adsorption of organic molecules on metal surfaces, particularly those involving noble metals (Pt, Au, etc.), from natural waters, triggers significate changes in the double layer capacitance, double layer structure, and overall electrochemical behavior of these metals (Lund and Hammerich, 1991). Thus, in this study an effort was made to establish a fast method, an electrochemical procedure, for qualitative and quantitative determination of phenols in natural water systems.

2. MATERIAL AND METHODS

The measurements were carried out in the classical electrochemical cell using a gold wire ($d = 0.5$ mm, 0.26 cm^2) as a working electrode and a gold foil (10 cm^2) as an auxiliary electrode. The potentials were measured vs. saturated calomel electrode – reference electrode and referred to the standard hydrogen electrode (she).

Cyclic voltammetry ($dE/dt = 100$ mV s^{-1}) with simultaneous monitoring of the double layer (dl) capacity (at 100 Hz and 1 mV ac signal) was used for an adsorption study of phenol. The electric circuit used has been described elsewhere (Grchev et al., 1991).

0.5 mol dm^{-3} aqueous solutions of $NaHCO_3$ (MERCK, p.a. art. 6329) prepared using redistilled water, containing phenol (MERCK, p.a. art. 206), of certain concentrations (0-100 ppm), were used in this study.

The measurements were done at room temperature. Dissolved oxygen in the solutions was removed by agitation with purified nitrogen gas.

Electrochemical analyses were accomplished by the following instruments: Potentiostat (Institut fur Physikalishe Chemie und Electrochemie, Heinnrich Heine - University Duseldorf); Function generator, type 3300 A Hewlett-Packard; Lock-in-amplifier, type 5101 – EG&Princeton Applied Research and XYt recorder, type PM 8272, Philips.

3. RESULTS AND DISCUSSION

Electrochemical behavior of adsorbed phenol on Au electrode in redistilled water containing 0.5 mol dm^{-3} $NaHCO_3$ is presented in Fig.1. Measurements were done in a wide potential range, 0 – 1.45 V/she, i.e., from potentials at which reactions of reduction ($2H_2O + 2e^- = H_2O + 2OH^-$) occur (for potential lower than 0V), to potentials when reaction of oxidation starts at potentials more anodic than 1.4 V in aqueous systems of pH ~ 8. Experiments were performed in aqueous systems in absence (0) and presence of phenol of known concentrations (1, 5, 10 and 100 ppm).

j/E and *C/E* dependences for aqueous solutions in the absence of phenol clearly indicate the following:

1. In the range between 0 and 0.8 V/she, in the AB direction (anodic direction), relatively small anodic currents of around 10-15 μA cm^{-2} (independent on potential) were noticed. This potential range is characteristic in charging of the electrochemical double layer, when Faradaic processes of oxidation and reduction of some electrochemical active species are absent. On the other hand, the big changes in the capacitance noticed on *C/E* curves show a great change in the structure of the electrochemical double layer.
2. Electrochemical oxidation on the surface of the gold electrode occurs in the potential range from 0.8 to 1.35 V/she, resulting in appearance of the anodic current maximum at 0.95 V, and a dramatical decrease in capacitance. A very thin oxide film (0.65-0.8 nm) is created on the gold surface, mainly in accordance with the reaction: $2Au+3H_2O = Au_2O_3 + 6e^- + 6H^+$.
3. Potential range of 1.35 – 1.45 V/she, DE direction, as we have already mentioned, is characterized by a continuous oxidation reaction on the top of already formed thin Au_2O_3 film, that is in accordance to the *C/E* dependences.
4. In the cathodic direction of polarization (region EF), significant changes in the oxide film thickness, as well as in the capacitance at the Au / Au_2O_3 / solution interface, is not noticed. Electrochemical reduction of the oxide film occurs in the potential range labeled as FGH and it is characterized by appearance of significant maximum of the current, point G, at ~ 0.55 V/she, resulting in a fast, simultaneous increase in capacitance to values very close to those typical for the Au / solution interface. This observation confirms the reversibility of the processes of gold oxidation and reduction ($Au \rightarrow Au_2O_3 \rightarrow Au$).

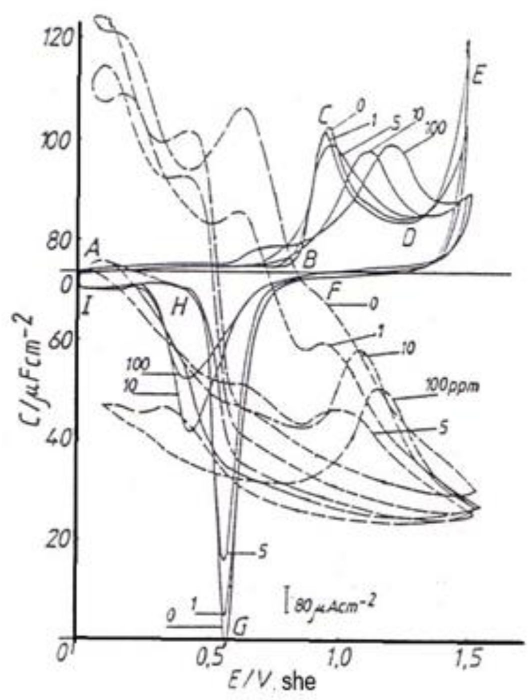

Figure 1. Voltammograms and capacitance spectra for gold without (0) and in the presence of phenol (1, 5, 10 and 100 ppm) in 0.5 mol dm^{-3} $NaHCO_3$ / redistilled water; 293 K, 100 mV/s.

It is obvious that the presence of phenol in redistilled water in concentrations 1-100 ppm affects the electrochemical behavior of gold in 0.5 mol dm^{-3} aqueous solutions of $NaHCO_3$, Fig. 1. The effect of phenol is noticeable in both, *C/E* and *j/E* dependences, particularly at higher concentrations (> 5 ppm). The influence of phenol on the electrochemical behavior of gold in the aqueous solutions of $NaHCO_3$ is described as follows:

Smaller concentrations of phenol in the solution (0 - 5 ppm) produce significant changes in the cathodic current maximum at 0.55 V/she (point G) and alterations in C/E dependences, too (Fig. 1 and Table 1). On the other hand, higher concentrations of phenol (5 – 100 ppm) assist a significant shift in the maximum of anodic current, point C, for 150 – 250 mV, as well as a shift in the maximum of cathodic current, point G, for about 100 – 130 mV and its further decrease (Table 1 and Fig. 1).

At the same time, it is worthy to be mentioned that the existence of phenol in the solution of 0.5 mol dm^{-3} in redistilled water, mainly, doesn't indicate electrochemical oxidation of phenol on gold surface, Fig. 1. All above mentioned effects of phenol on electrochemical behavior of gold in an aqueous solution of 0.5 mol dm^{-3} $NaHCO_3$, are generally explained by phenol adsorption on Au/solution and Au/Au_2O_3/ solution interfaces.

Adsorption of phenol molecules on gold surfaces initiates substitution of water molecules in the inner Helmholtz part of the electrochemical double layer, influencing an increase in the "thickness of this layer". In the absence of phenol, the thickness of the Helmholtz part mainly depends on the size of the water molecule (dH_2O ~ 0.4 nm), whereas, in the case of adsorbed phenol molecules, at full surface coverage (θ ~ 1), the thickness of the Helmholtz part is influenced by the dimensions of the phenol molecule, and its orientation on the metal surface (0.6 – 0.8 nm).

Table 1. Electrochemical parameters for adsorption of phenol in the system: Au / 0.5 mol dm^{-3} $NaHCO_3$ / redistilled water, at room temperature

***C* (ppm) (mol dm⁻³)**	**C_{min} (μF cm⁻²)**			**J_p^r (mA cm⁻²)**	**E_p^r (V/she)**
	~ 0 V/she	~ 0.85 V/she	~ 1.30 V/she		
0	121.21	70.62	28.99	1.144	0.560
0.1 $1.06 \cdot 10^{-6}$	118.05	67.46	27.14	1.112	0.555
0.5 $5.3 \cdot 10^{-6}$	114.36	62.71	26.35	1.064	0.555
1.0 $1.06 \cdot 10^{-5}$	107.51	57.97	25.3	1.048	0.555
5.0 $5.3 \cdot 10^{-5}$	73.8	43.21	24.24	0.876	0.550
10.0 $1.06 \cdot 10^{-4}$	73.8	42.42	24.24	0.424	0.420
50.0 $5.3 \cdot 10^{-4}$	54.02	39.26	23.2	0.372	0.410
100.0 $1.06 \cdot 10^{-3}$	46.9	31.09	23.2	0.328	0.400

Experimental data of minimal capacitance, at three characteristic potentials: 0 and 0.85 V/she (Au / 0.5 mol dm^{-3} $NaHCO_3$/redistilled water/phenol interface) and 1.3 V/she (Au / Au_2O_3 / 0.5 mol dm^{-3} $NaHCO_3$ / redistilled water / phenol interface); as well as those of cathodic current maximum (J_p^r, point G) at different concentration of phenol, are summarized in Table 1. Least squares regression analysis was used to find models as a best fit to the experimental data. Empirical equations of high correlation (~ 0.88), showing relationship between capacitance, C (μF cm^{-2}) and concentration of phenol in the solution, c (mol dm^{-3}), are given below:

C = -31.7 – 26.35 log c, μF cm^{-2} at 0 V/she (1)
C = -6.1 – 12.62 log c, μF cm^{-2} at 0.85 V/she (2)
C = 18.77 – 1.375 log c, μF cm-2 at 0 V/she (3)

This indicates the possibility for qualitative and quantitative determination of the concentration of phenol in a wide concentration range (0.1 – 100 ppm).

4. CONCLUSIONS

Based on the experimental results and discussions related to the electrochemical behavior of phenol in aqueous solutions (redistilled water) of 0.5 mol dm^{-3} $NaHCO_3$, it can be concluded the following:

- Phenol, present in the above-mentioned aqueous systems, is stable in the used potential range of 0 – 1.45 V/she, i.e., it doesn't show any Faradaic processes of oxidation and reduction on the gold surface.
- Significant influence of phenol in the concentration range 0 - $5.3 \cdot 10^{-3}$ mol dm^{-3} on electrochemical anodic oxidation of gold was noticed, as well as its pronounced adsorption on the Au/solution interface.
- Experimental data obtained by the use of cyclic voltammetry and simultaneous monitoring of the double layer capacitance of the system Au / 0.5 mol dm^{-3} $NaHCO_3$ aqueous solution, for both the absence and presence of phenol in the solutions, indicate the possibility of application of this technique in qualitative and quantitative determination of phenols in environmental aqueous systems.

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