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Original Scientific Paper

A Voltammetric Study on the Aqueous Electrochemistry of Acid Red 1 (Azophloxine)

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Abstract. Aqueous electrochemistry of Acid Red 1 (AR 1) was studied using cyclic voltammetry and square-wave voltammetry in Britton-Robinson buffers (pH = 2–12). The recorded cyclic voltamograms of AR 1 displayed one-irreversible peak which was attributed to reduction of the azo group in the entire pH values. However, two adsorption peaks on the square-wave voltamograms were also seen except for the reduction peak of azo group in the AR 1 molecule. In the pH range from 3.0 to 11.5, the first adsorption peak was observed at more positive potential from that of the azo group, and its potential depended on the pH of electrolyte solution. As the contrary to the first adsorption peak, the second one at more negative potential from that of the azo group was observed over the pH range from 2.0 to 6.5, and its potential was not practically dependent on the pH. According to the obtained voltammetric data, a plausible mechanism for the reduction of AR 1 was suggested. Moreover, the adsorption of AR 1 at the mercury-electrolyte interface was also investigated at different pH values. The peak current variations with the deposition time and AR 1 concentration were present. The Henry isotherm was employed for adjusting the experimental results at pH = 4.0 while the Langmuir isotherm was used for the data at pH = 7.0 and 10.0, and the values of the Gibbs free energy of adsorption were calculated. Nevertheless, the adsorption isotherm at pH = 10.0 showed that small repulsive interactions between the adsorbed AR 1 molecules on mercury electrode were present at longer deposition times. The pH of the supporting electrolyte played an important role on the adsorption behaviour of AR 1.

Keywords: Acid Red 1, cyclic and square-wave voltammetry, adsorption, mechanism

INTRODUCTION

Azo compounds are well-known and highly important substances widely used in dye chemistry and pharmacy. They are also of great importance as intermediary products in organic synthesis and as initiators in polymer chemistry.[1] Azo dyes have been the subject of many polarographic and voltammetric investigations.[2–5]

Benzeneazo-8-acetylamino-1-naphthol-3,6-disulfonic acid sodium salt (Red 2G, Food Red 10, Amidonaphthol red G, azogeranine, azophloxine, azofloxin, C.I. 18050, Acid Red 1, AR 1) is a synthetic red azo dye[6] (Scheme 1) and also used in light and fluorescence microscopy as a real acid counterstain.[7] The photodegradation[8,9] and thermal degradation[10] of AR 1, and the effect of high-energy radiation[11] on it have been reported. Also, AR 1 has been used in the determination of proteins[12] and peptides.[13] Some papers in the literature have reported the determination of AR 1 by using of polarography[14–17] and linear sweep voltammetry.[18] Wong and Wieland[19] have investigated its electrochemical analysis in textile effluents. However, the electrochemical behaviour of AR 1 at mercury electrodes has still required more clarification. The exact reduction mechanism of AR 1 is not completely understood. And also its adsorption at the mercury-electrolyte interface has not been studied systematically so far. In addition, no square-wave voltammetry and cyclic voltammetry methods are reported in the literature for the electrochemical behaviour of AR 1.

Amongst several voltammetric procedures for the analysis, square-wave voltammetry (SWV)[20–22] appears as the most interesting one. The main advantage of SWV is the fast scan rate that can be applied, often the order of 1 V s^{-1} instead of the 1–10 mV s^{-1} used in other pulse techniques.[22] Moreover, the mathematical interpretation of SWV data provides several important parameters that are useful for the discussion of the reduction mechanism at the elecrode surface of such complex molecules.[22] This is an important and almost unique feature of this electrochemical technique.[22] On the other hand, cyclic voltammetry (CV) is the most effective and

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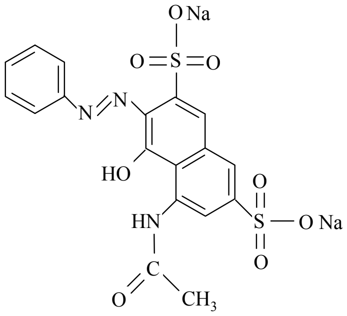


Scheme 1. The molecular structure of AR 1.

versatile electroanalytical technique available for the mechanistic study of redox system.[23]

In the present investigation, we report the voltammetric behaviour of AR 1 in aqueous buffer solutions as well as an attempt made to clarify its reduction mechanism on the mercury electrode by using of SWV and CV techniques. Also, the adsorption process of AR 1 onto the mercury layer at different pHs has investigated by means of square-wave adsorptive stripping voltammetry.

Adsorption phenomena

The mercury electrode adsorbs from the solution certain components and depolarization products. This adsorption is due to surface forces, the range of which usually does not exceed molecular dimensions, so that, as a rule, the adsorbed particles form a monomolecular layer.[24] When the depolarizer or its electrode reaction product is adsorbed, a separate wave, the so-called adsorption wave, is formed.[24] At a given temperature, the quantity of adsorbed substance depends on concentration (the dependence is given by an adsorption isotherm).[24]

The surface coverage, Θ, depends on the solvent, electrolyte, adsorbate structure and concentration and the concentration of any other species in the system as well as the nature of the electrode.[25]

Various isotherms have been used for analysis of adsorption on the phase boundary between mercury electrodes and electrolyte solution. The linear relation between electrode coverage (Θ) and the adsorbate concentration (c) in the bulk solution has been expressed by the Henry isotherm:

$$\Theta = \beta\, c$$

where β is the adsorption equilibrium constant.[24,26]

In this case, the interactions between the adsorbed molecules are neglected.[26] They are also neglected by the Langmuir isotherm:[26]

$$[\Theta / (1 - \Theta)] = \beta\, c$$

Langmuir isotherm is assumed that there are no interactions between adsorbed species, that the surface is smooth, and that eventually surface saturation occurs.[27] In the Langmuir isotherm, Θ is the degree of surface saturation defined as the ratio $\Gamma/\Gamma_{\max}$, where $\Gamma_{\max}$ is the maximum value of Γ corresponding to the maximum number of molecules or ions completely covering one square centimeter of the surface.[26] As can be seen from the above equations, Henry isotherm is also a special case of Langmuir isotherm. This linear adsorption isotherm may be used for small coverages.[24]

EXPERIMENTAL

Chemicals

AR 1 was purchased from MP Biomedicals, LLC and was used as received. All the chemicals used were of analytical-reagent grade and used without further purification. All solutions were prepared by deionized and triply distilled water.

Apparatus

A three-electrode potentiostatic control system (EG&G PARC 303A SMDE) with a hanging mercury drop (HMDE as working electrode), a $\mathrm{Ag|AgCl|KCl_{sat}}$ reference electrode and a platinum auxiliary electrode was used in all experiments. The potential scan was generated by means of an EG&G PAR 384B Polarographic Analyzer. The recording of current-potential curves was obtained by means of a Houston Instrument DMP-40 plotter connected to the polarograph. In the adsorptive stripping square-wave voltammetry (AdSWV) experiments, a PAR 305 stirrer was used.

Procedure

Before voltammetric experiments, a 10mL of the supporting electrolyte solution within the electrochemical cell was deareted by purging with pure nitrogen gas for 5 min, and the background voltamogram (blank) was obtained. Cyclic and square-wave voltamograms of AR 1 at Britton-Robinson (B-R) buffer solution were recorded after deaeration with oxygen-free nitrogen gas for a further 60 s. The experiments were performed by using equilibrium time of 5 s; scan rate of 200 mV s^{-1} (500 mV s^{-1} for CV); scan increment of 2 mV; drop size, medium (unless stated otherwise). In AdSWV technique, preconcentration was achieved on a new mercury drop, while the solution was stirred at 400 rpm (slow mode). The stirring was then stopped, and after the equilibrium time of 5 s a negative going scan was initiated using the following parameters: scan rate, 200 mV s^{-1}; pulse height, 0.020 V and medium drop size. All measurements were made in the nitrogen gas atmosphere at room temperature.

RESULTS AND DISCUSSION

No detailed voltammetric data concerning the adsorption process and the reduction behaviour of AR 1 were available, except for its determination at 0.1 mol dm^{-3} NaCl solution by linear sweep voltammetry.[18] Therefore, several voltammetric measurements with two different electrochemical techniques (cyclic and square wave voltammetry) were performed in B-R buffer solution covering the pH range between 2.0 and 12.0 in order to obtain such detailed informations.

Cyclic Voltammetry (CV)

A typical cyclic voltamogram of 2.44×10^{-5} mol dm^{-3} AR 1 in B-R buffer (pH = 5.0) has been shown in Figure 1. As can be seen in Figure 1, in the cathodic scan a reduction peak at –0.534 V was observed. However, the cathodic peak of AR 1 was not accompanied by an anodic peak, which indicates that its redox reaction was totally irreversible. As observed at pH = 5.0, only one irreversible peak was also observed for other pH values in the pH range of 2.0 – 12.0.

For the reduction peak of AR 1, the E_p *vs.* pH and i_p *vs.* pH curves at scan rate of 500 mV s^{-1} have been shown in Figure 2. With increasing pH, the reduction peak potential is shifted towards more negative potentials and the peak current is varied as well. The plot of the reduction peak potential *vs.* pH showed three linear segments. These linear segments can be expressed by the following equations:

$E_p / \text{V} = -0.0771\ \text{pH} - 0.1335$ $\qquad r = 0.9963$
(segment 1 in the pH range 2.0–7.5)

$E_p / \text{V} = -0.0514\ \text{pH} - 0.312$ $\qquad r = 0.9977$
(segment 2 in the pH range 7.5–10.0)

while the effect of pH on the peak potential in the pH range from 10 to 12 (segment 3) is almost negligible. These results indicate the participation of hydrogen ions in the electrode process of AR 1. The i_p *vs.* pH plot (Figure 2) has showed that the peak current reaches maximum values in the pH ranges 2.0–3.5, 4.0–7.5 and 8.0–12.0, respectively.

Examination of cyclic voltamograms of AR 1 at different potential scan rate range of 50–1000 mV s^{-1} at pH = 4.0, 7.0 and 10.0 reveals that the peak potential does shift to more negative potentials on increasing the scan rate (v). At each of the three pHs, the linear relationships between peak potential and the logarithm of scan rate have been obtained (Figure 3). The regression data obtained are given in Table 1. The number of protons involved per molecule, p, of the reactant in the rate determining step is calculated from the rate change of $E_{1/2}$ *vs.* pH by means of the following equation:[28]

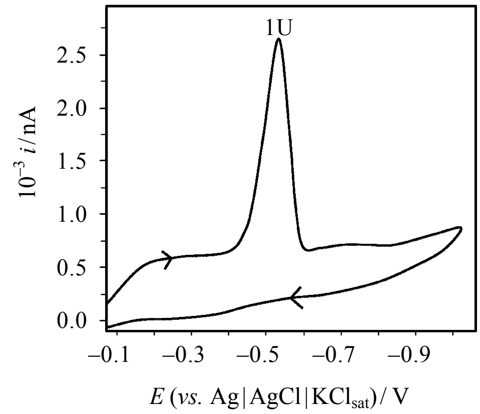


Figure 1. Cyclic voltamogram for 2.44×10^{-5} mol dm^{-3} AR 1 in Britton-Robinson buffer at pH = 5. Experimental conditions: scan rate (v) = 500 mV s^{-1}, equilibrium time = 5 s, drop size medium. 1U is the main reduction peak of AR 1.

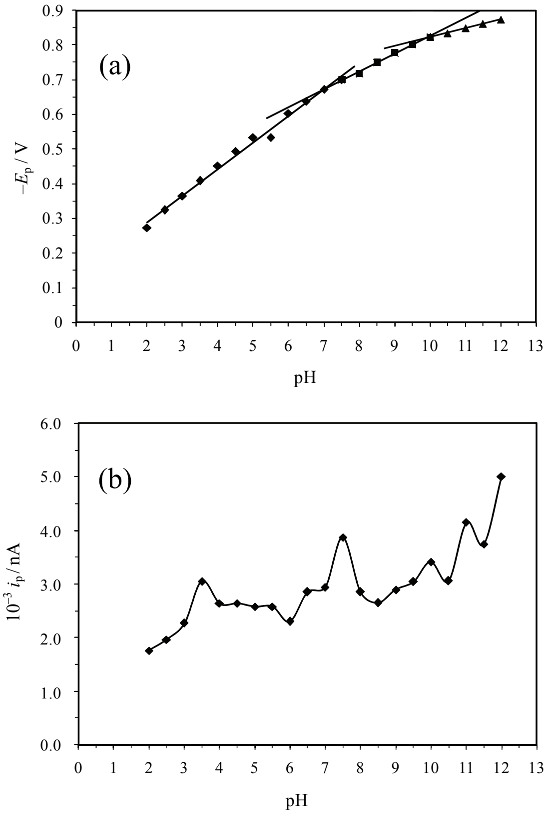


Figure 2. E_p *vs.* pH (a) and i_p *vs.* pH (b) plots for cyclic voltamograms of 2.44×10^{-5} mol dm^{-3} AR 1 in Britton-Robinson buffer at pH = 2–12. Other conditions as described in Figure 1.

$$\mathrm{d}(E_{1/2})/\mathrm{d(pH)} = -(0.05915\,p)\,/\,\alpha n_\alpha \qquad (1)$$

where α is the electron transfer coefficient, n_α is the electron transferred in the rate-determining step and $E_{1/2}$ is the half-wave potential.

Table 1. The results of CV of 2.44 × 10^{-5} mol dm^{-3} AR 1

pH	Scan rate range v / mV s^{-1}	Relation E_p vs. log v [(a)]	r[(b)]	αn	Relation log i_p *vs.* log v [(a)]	r[(b)]
4	50 – 1000	$E'_p = -0.0799 \log v' - 0.2458$	0.9995	0.74	$\log i'_p = 0.7542 \log v' + 1.3332$	0.9933
7	50 – 1000	$E'_p = -0.0666 \log v' - 0.4806$	0.9991	0.89	$\log i'_p = 0.8093 \log v' + 1.2756$	0.9959
10	50 – 1000	$E'_p = -0.0689 \log v' - 0.6358$	0.9978	0.86	$\log i'_p = 0.8296 \log v' + 1.2106$	0.9972

[(a)] Note that ′ denotes numerical values expressed in corresponding units: $E'_p = E_p/\mathrm{V}$; $v' = v/\mathrm{mV\ s^{-1}}$; $i'_p = i_p/\mathrm{nA}$

[(b)] Correlation coefficient

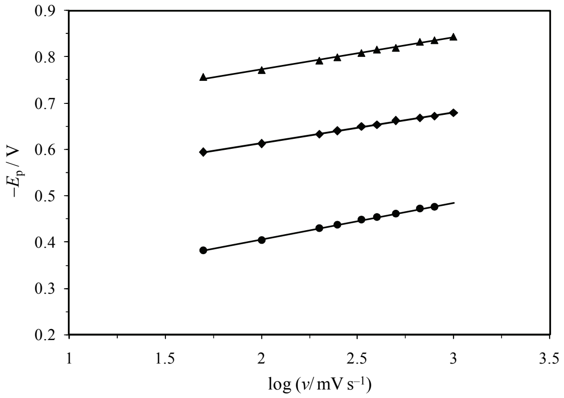


Figure 3. Dependence of the peak potential E_p on the logarithm of potential scan rate (log v). 2.44 × 10^{-5} mol dm^{-3} AR 1 with pH = 4.0 (●), pH = 7.0 (♦) and pH = 10 (▲) B-R buffer.

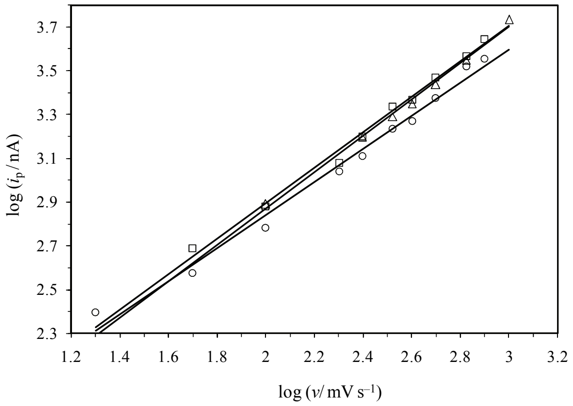


Figure 4. The dependence of the logarithm of the peak current (log i_p) on the logarithm of potential scan rate (log v). 2.44 × 10^{-5} mol dm^{-3} AR 1 with pH = 4.0 (○), pH = 7.0 (□) and pH = 10 (Δ) B-R buffer.

Many electrochemical reductions or oxidations are several step procedures. Often the first of these is the rate determining step and hence the potential-determining step. Subsequent steps are much more rapid and do not effect the potential, but merely the height of the wave. The shift of the half-wave potential with pH is determined by the number of hydrogen ions involved in and before the potential-determining step.[29]

According to Laviron,[30] the relationship between the peak potential and the scan rate for adsorbed species in the completely irreversible process can be expressed as

$$E_p = E^\circ + (2.3RT/\alpha n_\alpha F)\log(RTk_f^\circ/\alpha n_\alpha F v) \qquad (2)$$

in which α is the charge transfer coefficient and is normally between 0.3 and 1, n_α is the electron transferred in the rate-determining step, and k_f° is the standard heterogeneous rate constant, the other terms having their usual meaning.

According to the Eq. (2), $d(E_p)/d(\log v) = -0.059/\alpha n_\alpha$, αn_α values have been calculated from the slope of the linear relationship between the reduction peak potential and the logarithm of scan rate (Table 1). With using of the αn_α values obtained and applying E_p instead of $E_{1/2}$ at the Eq. (1), the values of p for two linear segments have been found to be *ca.* 1 (1.06 for segment 1 and 0.75 for segment 2) indicating that one proton has been consumed; therefore the rate of protonation is the rate determing step. This result is expected because of the fact that the azo bond is generally to be reduced in the protonated form.[31]

At different pH values, the linear relationships between the logarithm of peak current and the logarithm of scan rate have been seen in Figure 4. The slopes of the straight lines in the logarithm plots of peak currents *vs.* logarithm of scan rate at pH = 4.0, 7.0 and 10.0 (Table 1) are less than the theoretical value of 1.0, which is expressed for the adsorption controlled electrode process while they are more than the theoretical value of 0.5, which is expressed for the diffusion controlled electrode process. This case indicates both diffusion and adsorption controlled electrode process. As a result, it can be said that the peak current arises from the reduction process not only of AR 1 molecules which were already adsorbed on the mercury electrode surface prior to the potential scan stage, but also of those which reach to the electrode by means of diffusion.

Square-wave Voltammetry (SWV)

At pH = 3.5, the square-wave voltamogram of 2.44 × 10^{-5} mol dm^{-3} AR 1 is presented in Figure 5. As can be seen in Figure 5, three peaks are observed at –0.098, –0.302 and –0.614 V, respectively. The first and last peaks have not been seen in its cyclic voltamograms. The peak

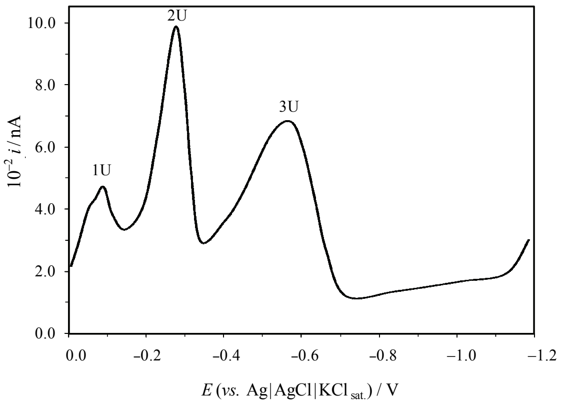


Figure 5. Square-wave voltamogram of 2.44×10^{-5} mol dm^{-3} AR 1 in B-R buffer (pH = 3.5). Experimental conditions: pulse height, $E_{\mathrm{sw}} = 20$ mV; scan increment, $\mathrm{d}E = 2$ mV; frequency, $f = 100$ Hz; scan rate, $v = 200$ mV s^{-1}. 1U, first adsorption peak; 2U, the main reduction peak of AR 1; 3U, second adsorption peak.

potential of the last peak has not practically dependent on the pH. The first peak was observed at the pH range between 3.0 and 11.5 while last peak was seen in the pH range 2.0–6.5. We have suggested that the first and last peaks can be sourced only from generic adsorbed species. However, the second peak is the main reduction peak. Thus, we have focused on this main reduction peak (2U at Figure 5) for the reduction mechanism study of AR 1. The potential of the main peak shifted to more negative values with the increase of pH up to 10. Plot of the potential of main peak *vs.* pH has showed three segments (Figure 6a) similar to that observed for cyclic voltamograms of AR 1 (Figure 2a). Over the linear segments (pH ≤ 10), the peak potential shifted to more negative values according to the following equations:

$$E_{\mathrm{p}}/\mathrm{V} = -0.0877\,\mathrm{pH} - 0.0009 \qquad r = 0.9985$$

(segment 1 in the pH range 2.0−7.5)

$$E_{\mathrm{p}}/\mathrm{V} = -0.0493\,\mathrm{pH} - 0.282 \qquad r = 0.9959$$

(segment 2 in the pH range 7.5−10.0)

while the effect of pH on the main peak potential in the pH region of 10−12 (segment 3) is practically negligible. In the pH range 2.0−10.0, the pH-dependence of the potential of main peak clearly shows that hydrogen ions act as a reactant in the reduction process of AR 1. Since the potential of the main peak at pH > 10 is practically independent of pH, the nonprotonized form is reduced and water, the proton donor, takes part in the reduction process.[32]

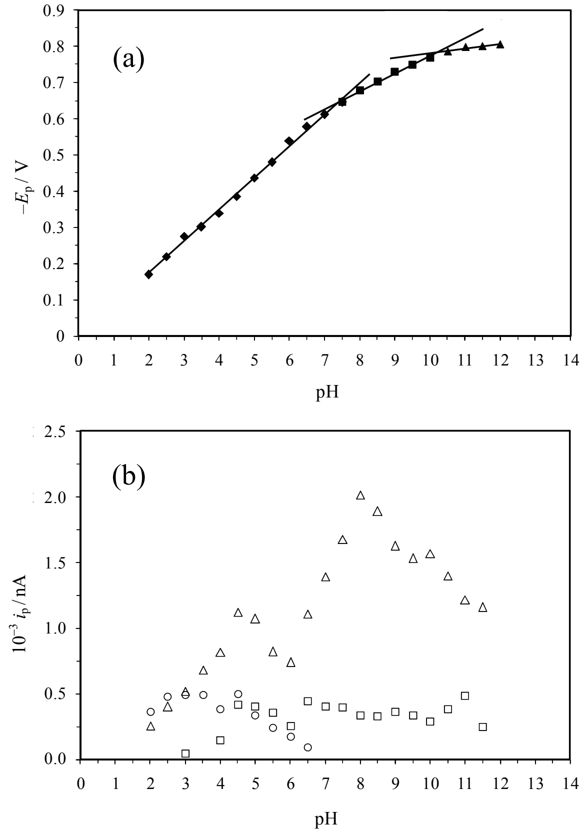


Figure 6. E_{p} *vs.* pH (a) and i_{p} *vs.* pH (b) plots for main peak on the square-wave voltamograms of 2.44×10^{-5} mol dm^{-3} AR 1 in Britton-Robinson buffer at pH = 2−12. Other conditions as described in Figure 5. First adsorption peak (□), second adsorption peak (○), main peak (Δ).

The influence of pH on the current of main peak has been also analyzed for 2.44×10^{-5} mol dm^{-3} AR 1 (Figure 6b). From the plot of i_{p} *vs.* pH, it is seen that the peak current reaches maximum values in the pH ranges 2.0 − 4.5 and 5.0 − 8.0, respectively (Figure 6b). These results are almost similar to those of cyclic voltamograms (Figure 2b).

Table 2. The results of SWV of 2.44×10^{-5} mol dm^{-3} AR 1

pH	f/Hz [(a)]	Relation E_{p}*vs.* log f [(b)]	r[(c)]	αn	Relation i_{p} *vs.* f	r[(c)]
4	20−120	$E'_{\mathrm{p}} = -0.0888 \log f' - 0.2254$	0.9968	0.67	$i'_{\mathrm{p}} = 8.4701 f' + 87.892$	0.9954
7	20−120	$E'_{\mathrm{p}} = -0.0688 \log f' - 0.4888$	0.9983	0.86	$i'_{\mathrm{p}} = 20.361 f' + 45.464$	0.9978
10	20−120	$E'_{\mathrm{p}} = -0.0679 \log f' - 0.6764$	0.9953	0.87	$i'_{\mathrm{p}} = 10.611 f' + 287.73$	0.9953

[(a)] Frequency range

[(b)] Note that ′ denotes numerical values expressed in corresponding units: $E'_{\mathrm{p}} = E_{\mathrm{p}}/\mathrm{V}$; $f' = f/\mathrm{Hz}$; $i'_{\mathrm{p}} = i_{\mathrm{p}}/\mathrm{nA}$

[(c)] Correlation coeficient

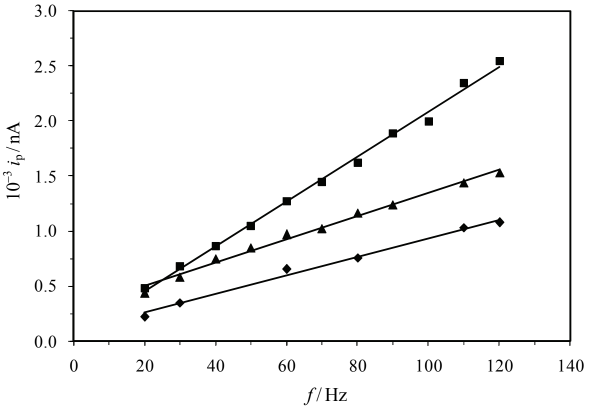


Figure 7. Dependence of the current of main peak (i_p) on the square-wave frequency (f). 2.44 × 10^{-5} mol dm^{-3} AR 1 with pH = 4.0 (♦), pH = 7.0 (▲) and pH = 10 (■) B-R buffer solutions.

Dependence of the current of main peak (i_p) on the square-wave frequency (f) has been studied at three different pHs. The linear relationships between the peak current and frequency have been found (Figure 7). Also, the regression equations are given in Table 2. According to the accepted theories for SWV,[33] this behaviour corresponds to a totally irreversible process controlled by adsorption of AR 1 molecules on the mercury electrode.

Moreover, the potential of main peak shifted to more negative values with increasing of the frequency. Figure 8 shows the dependence of E_p with log f. The peak potential is a linear function of the logarithm of square-wave frequency for the whole range studied (20–120 Hz). The regression analysis of the obtained straight lines has been given in Table 2. For a totally irreversible system, the relationship between the peak potential and the logarithm of the frequency is given by following equation:[21]

$$\Delta E_p / \Delta \log f = -2.3RT / \alpha nF \tag{3}$$

where α is the transfer coefficient and n is the number of electrons involved in the reaction. At the plots of E_p *vs.* log f (Figure 8), the slopes of these straight lines have been used to calculate αn values for the electrochemical reaction by means of Eq. (3). The calculated αn values are presented in Table 2. It is seen that these are very close the values obtained by cyclic voltammetry. Considering the molecular structure of AR 1, the obtained main reduction peak may be attributed to the reduction of –N=N– group. Assuming that the rate determining step involves the transfer of two electrons, the values of the charge transfer coefficients for the pH range 2–10 are found to be *ca.* 0.4 and suggest that the reduction process is irreversible.

In order to investigate the possibility of applying the square-wave voltammetry technique to the determination of AR 1, the peak current-concentration curves for different pH values (4.0; 7.0 and 10.0) have been constructed (Figure 9). A good linear relationship has been obtained between the peak current and AR 1 concentration monitored in B-R buffer pH = 10.0 (Figure 9). It has been found that the main reduction peak of AR 1 has been proportional to increase in concentration in the range of 9.9×10^{-7} to 6.5×10^{-6} mol dm^{-3} according to the regression equation:

$$i_p/\text{nA} = 8 \times 10^7\ [\text{AR 1}]/\text{mol dm}^{-3} + 101.3 \quad (r = 0.998).$$

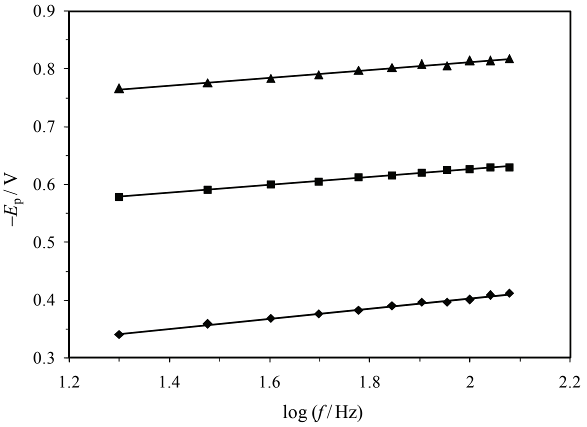


Figure 8. The dependence of the peak potential E_p on the logarithm of the frequency (log$f$). 2.44 × 10^{-5} mol dm^{-3} AR 1 with pH = 4.0 (♦), pH = 7.0 (■) and pH = 10 (▲) B-R buffer solutions.

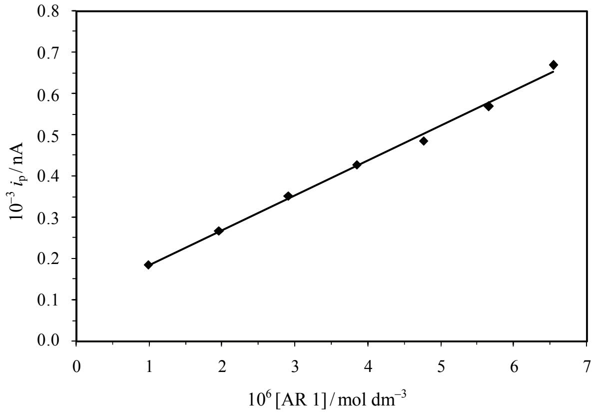


Figure 9. The main peak current–concentration plot of AR 1 at pH = 10 with the square-wave voltammetry technique being used.

Square-wave Adsorptive Stripping Voltammetry (SW-AdSV)

Effect of Deposition Time, pH and AR 1 Concentration

The square-wave adsorptive stripping voltamograms with increasing deposition times (15–120 s) have been recorded for AR 1 solutions at various concentration levels (3.85×10^{-6}; 4.76×10^{-6}; 5.66×10^{-6}; 6.54×10^{-6};

7.41×10^{-6} and 8.26×10^{-6} mol dm^{-3}) at different pH values (4, 7 and 10). It has been observed that the first peak of AR 1 has been strongly dependent on the deposition times according to the other peaks of AR 1 (Figure 10). So, the first peak of AR 1 has been used in this paper to study the AR 1 adsorption on the mercury electrode surface.

It is well known that the extent of preconcentration is a function of the deposition time. Figure 11 shows the dependence of deposition time (from 15 to 120 s) on the adsorptive stripping voltammetric response (first peak) of AR 1. As shown in Figure 11a, the peak current increases linearly with increasing deposition time in B-R buffer of pH = 4.0 and the fixed bulk solution concentrations of AR 1. Also, the growth of adsorption layer is faster as the bulk solution concentration of AR 1 increases. The slopes of these linear lines are proportional to the bulk solution concentration. At pH = 4.0 and the deposition time of 120 s, the height of the first peak of AR 1 has been also found to go up with increasing its bulk concentration (from 3.85×10^{-6} mol dm^{-3} to 8.26×10^{-6} mol dm^{-3}), but to approach a limiting maximum peak current value of $i_{\mathrm{p,max}} = 6800$ nA (Figure 11a). Figure 11a shows that the surface of mercury electrode is not fully saturated by adsorbed AR 1 molecules under the selected experimental conditions. At pH = 7.0 (Figure 11b), the proportional relationship between peak current and deposition time has been nearly observed up to 60 s and then it becomes virtually curved and leveled off owing to the saturation of the electrode surface at high AR1 concentration (8.26×10^{-6} mol dm^{-3}). For adsorption process at pH = 7.0, it has been also observed that when the deposition time and concentration of the bulk solution are increased, the saturation is reached. At pH = 10.0 (Figure 11c), the peak current has increased with increasing deposition time and has reached its maximum value at the deposition time about 70 s. At high deposition times ($70 < t_{\mathrm{d}} \leq 120$ s), the peak current started to decrease (Figure 11c). This decrease in the peak current could be explained by release of an amount of the adsorbed molecules due to possible repulsive interaction between the adsorbed species.[34]

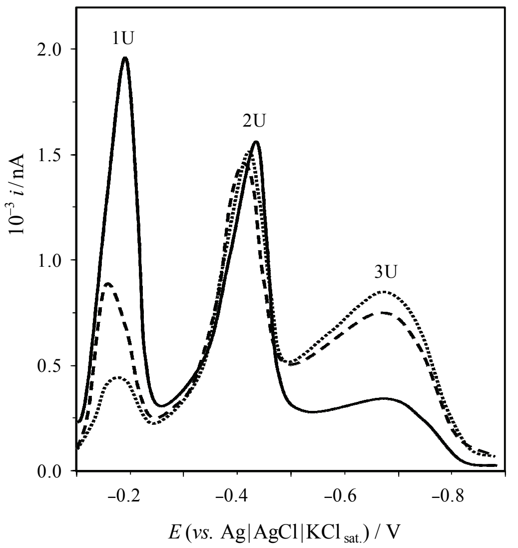


Figure 10. The square-wave adsorptive stripping voltamograms of 4.76×10^{-6} mol dm^{-3} AR 1 for different deposition times (t_{d}) at pH = 4. t_{d} = 15 s, (····); t_{d} = 30 s, (---); t_{d} = 60 s, (—).

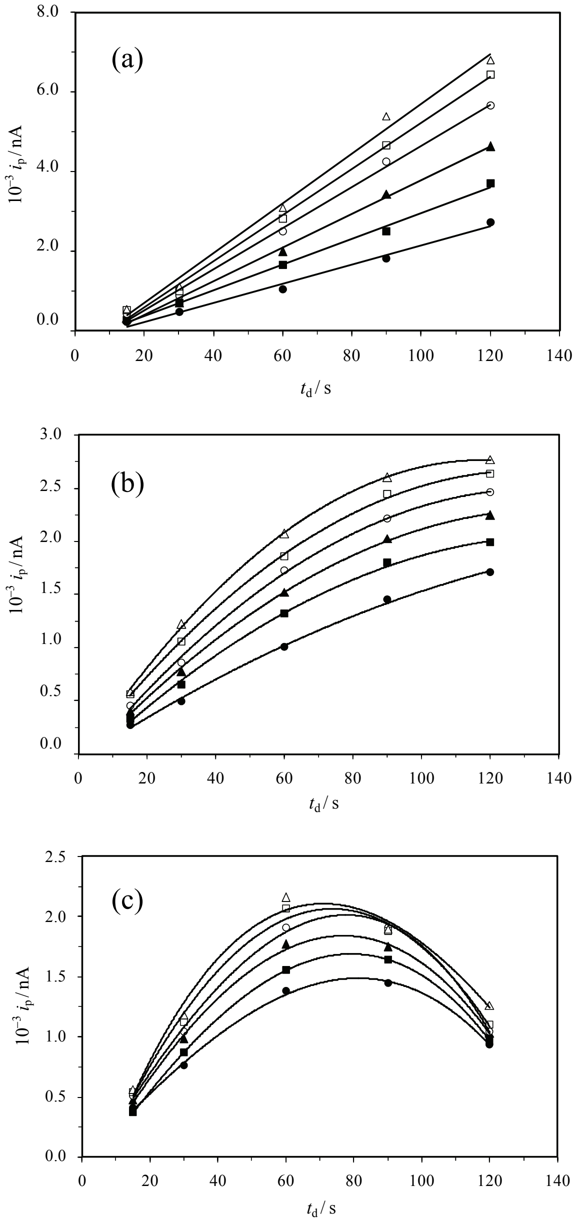


Figure 11. Plots of i_{p} *vs.* t_{d} for: 3.85×10^{-6} (●); 4.76×10^{-6} (■); 5.66×10^{-6} (▲); 6.54×10^{-6} (○); 7.41×10^{-6} (□); 8.26×10^{-6} (Δ) mol dm^{-3} AR 1 in B-R buffers of pH = 4 (a), pH = 7 (b), and pH = 10 (c) following deposition at pulse height = 20 mV, scan increment dE = 2 mV and frequency f = 100 Hz.

At pH = 4.0 and the deposition time of 120 s, a linear relation between the fractional coverage of the HMDE surface ($\Theta = i/i_{\mathrm{max}}$) and bulk concentration of AR 1 (c) has been shown (Figure 12). At this pH value, the mercury electrode surface has been partially covered. These observations for the adsorption process of AR 1 in acidic medium have been interpreted by fitting the experimental data to Henry's adsorption isotherm:

$$\Theta = i/i_{\mathrm{max}} = \beta c \qquad (4)$$

in which i is the peak current for a given bulk concentration, i_{max} is the peak current that is corresponding to maximum coverage at a fixed deposition time, and β (expressed in $\mathrm{mol^{-1}\,dm^3}$) is the adsorption coefficient which depends on the temperature and reflects the affinity of the adsorbate molecules toward adsorption sites. At Henry's adsorption isotherm, β is determined from the slope in the plot of Θ *vs.* c.

However, at high pHs (7.0 and 10.0), the results can be successfully described by Langmuir's model (Figures 13a, b). The linearized form of Langmuir isotherm can be expressed as:[35]

$$c/i_{\mathrm{sat}} = (1/\beta\, i_{\mathrm{max}}) + c/i_{\mathrm{max}} \qquad (5)$$

The saturation peak curent, i_{sat}, varies depending on AR 1 concentration (c) and i_{max} corresponds with the maximum peak current when the electrode is fully covered.

Although Langmuir isotherm does not take into account the attractive or repulsive interactions between adsorbate molecules,[36] it is still in agreement with the experimental data at pH = 10 (Figure 13b). If Langmuir isotherm is valid for a system, a plot of c/i_{sat} *vs.* c should yield a straight line with parameters i_{max} and β derived from the slope and intercept, respectively. β parameter could be represented as:[35]

$$\beta = (1/[\mathrm{S}])\exp(-\Delta G_{\mathrm{ads}}/RT) \qquad (6)$$

where R (= 8.314 $\mathrm{J\,mol^{-1}\,K^{-1}}$) is the gas constant, T is the thermodynamic temperature expressed in K, ΔG_{ads} (expressed in $\mathrm{J\,mol^{-1}}$) is the Gibbs free energy of adsorption, and [S] is the solvent concentration (= 55.5 $\mathrm{mol\,dm^{-3}}$). The parameters calculated for different pH values are given in Table 3. As can be seen in Table 3, the high values of the adsorption free energies indicate that AR 1 molecules are strongly adsorbed on the mercury electrode surface by chemisorption.

In order to obtain a significant analytical utility, the adsorptive stripping procedure has been also used. For this aim, the first peak of AR 1 which is responsible from the adsorption phenomena has been selected. As optimum deposition time, a value of 120 s and optimum pH value of 4 have been found because these values have provided the largest peak current in the linearity range (Figure 11a). The current response is linear in concentration range $9.9\times10^{-7} - 9.1\times10^{-6}$ $\mathrm{mol\,dm^{-3}}$ following the equation: $i_{\mathrm{p}}/\mathrm{nA} = 9.2\times10^{8}\,[\mathrm{AR\ 1}]/\mathrm{mol\,dm^{-3}} - 638.9$ with correlation coefficient of 0.996 (Figure 14). As a result, for the analytical determination of AR 1 in much the same concentration range, the SW-AdSV technique is more adequate at acidic medium while SWV technique can be used at basic medium.

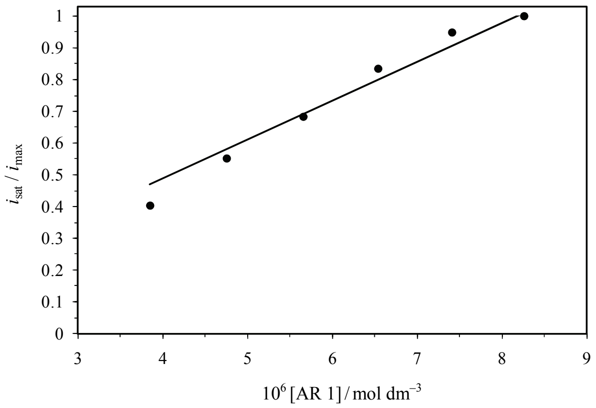


Figure 12. Plot of Θ (= $i_{\mathrm{sat}}/i_{\mathrm{max}}$) *vs.* bulk concentration of AR 1 ($c/\mathrm{mol\,dm^{-3}}$) at pH = 4 and t_{d} = 120 s.

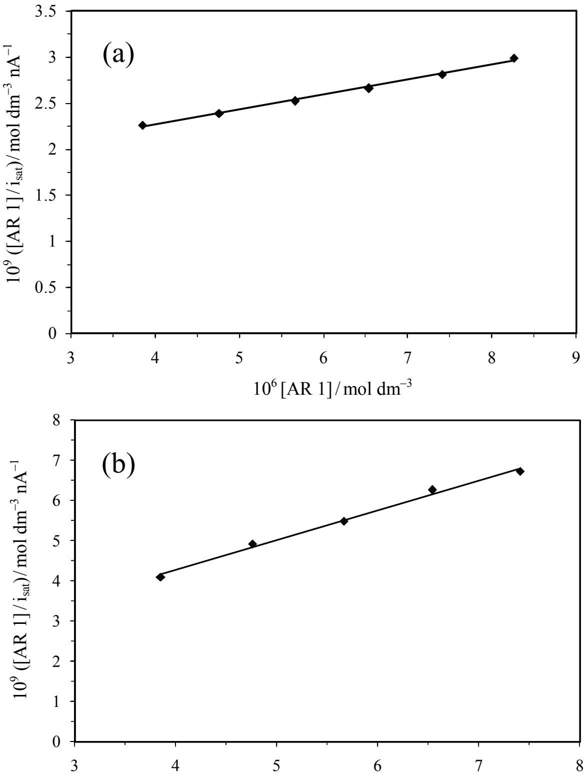


Figure 13. Plots of [AR 1]/i_{sat} vs. bulk concentration of AR 1, [AR 1]/$\mathrm{mol\,dm^{-3}}$, at pH = 7 (a) and pH = 10 (b). t_{d} = 120 s.

Table 3. The adsorption parameters of AR 1 calculated from the SW-AdSV results at different pH values

pH	Isotherm	$10^{-5}\,\beta$ / mol^{-1} dm^3	$-\Delta G_{ads}$ / kJ mol^{-1}	$r^{(a)}$
4	Henry	1.22	38.33	0.9841
7	Langmuir	1.00	37.85	0.9974
10	Langmuir	7.00	42.59	0.9967

$^{(a)}$ Correlation coeficient

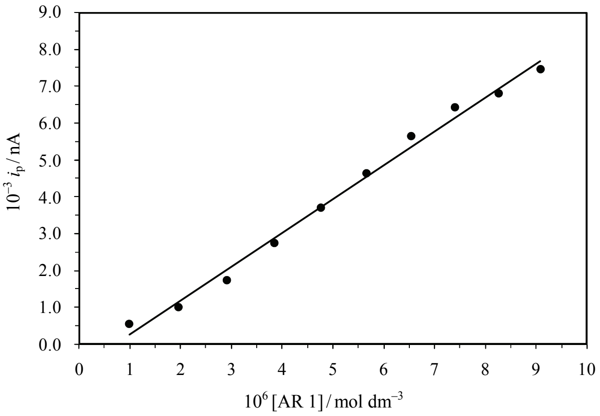


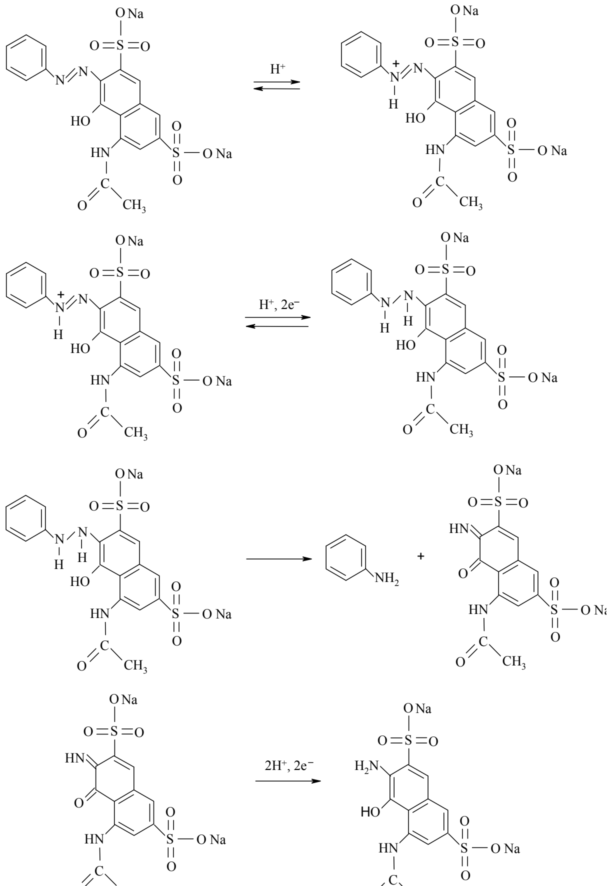
Figure 14. Plot of the first adsorption peak current, i_p, *vs.* bulk concentration of AR 1, [AR 1] / mol dm^{-3}, at pH = 4 and t_d = 120 s with the square-wave adsorptive stripping voltammetry technique being used.

Mechanism

Naphthalenazo compounds having a hydroxy or an amino group *ortho* to the azo linkage invariably produce single four-electron waves. In all these cases, reduction proceeds during the lifetime of the drop completely to the amines at all pH values.[1, 37–40] The electron-donating substituents in the *para* or *ortho* position, such as –OH or –NH_2, increase the electron density on the azo group, thus impeding reduction, but increasing at the same time the basicity of the nitrogen atoms, facilitating their protonization and cleavage of the N–N bond.[1, 41]

Azobenzenes with hydroxy and amino substituents are also reduced to the corresponding anilines, since the initially formed hydrazobenzene decomposes to aniline and quinone-imine, which is very readily reduced.[42] The limiting current often indicates only two-electron reduction.[42]

From the results presented it is obvious that the electrochemical reduction of AR 1 is a process leading to the cleavage of azo bond. As four electrons can be required in the reduction of the azo group of AR 1, and one proton is involved in the rate-determining step, a mechanism (Scheme 2) which is similar to that proposed by other workers[31,43,44] can be proposed for the reduction of AR 1 in the pH range of 2.0–10.0:

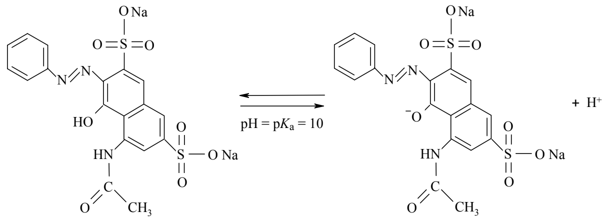


Scheme 2.

The proposed mechanism (Scheme 2) gets a support from the cathodic increase in E_p with pH, as the protons are consumed in the reduction process.

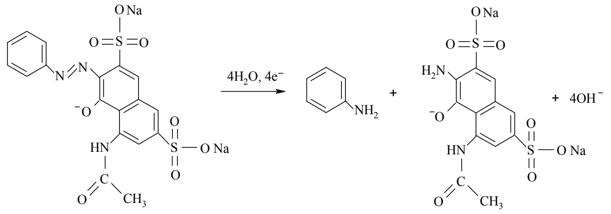
From the interceptions of the E_p *vs.* pH graph (Figures 2a and 6a), the pK_a values of AR 1 have been determined to be 7.5 (azonium group, pK_{a1}) and 10.0 (naphtholic group, pK_{a2}), respectively. It is well known that the pK_a value of naphtholic group has been very close to the value reported for 2-naphthol in the literature (9.51).[45]

The ionization equilibrium of naphtholic group has been presented in Scheme 3.



Scheme 3.

The overall reaction (Scheme 4) for the reduction of AR 1 in the pH range of 10.0–12.0 can be proposed as follows:



Scheme 4.

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SAŽETAK

Voltammetrijsko proučavanje elektrokemije spoja Acid Red 1 (Azofloksin) u vodenim otopinama

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Elektrokemija spoja Acid Red 1 (AR 1) u vodenim otopinama proučavana je metodama cikličke voltammetrije i pravokutnovalne voltammetrije u Britton-Robinson puferima (pH = 2–12). Snimljeni ciklički voltamogrami AR 1 pokazuju jednostruki ireverzibilni vrh u čitavom rasponu pH koji se pripisuje redukciji azo-grupe. Međutim, osim redukcijskog vrha azo-grupe, primjećena su još dva adsorpcijska vrha na pravokutnovalnom voltamogramu. U rasponu pH od 3,0 do 11,5, prvi adsorpcijski vrh primjećen je na pozitivnijem potencijalu od onoga azo-grupe i potencijalno je ovisan o pH. Nasuprot prvom adsorpcijskom vrhu, drugi, s negativnijim potencijalom, primjećen je u rasponu pH između 2,0 i 6,5, a taj je potencijal neovisan o pH. U skladu s prikupljenim voltametrijskim podacima, predložen je mogući mehanizam za redukciju AR 1. Također, proučavana je i adsorpcija AR 1 na međupovršini između žive i elektrolita pri različitim pH vrijednostima. Varijacije vršnih vrijednosti struje s vremenom taloženja i koncentracijom AR 1 također su prisutne. Henryjeva izoterma korištena je za podešavanje eksperimentalnih vrijednosti pri pH = 4,0 dok je Langmuirova izoterma korištena za podatke pri pH = 7,0 i 10,0. Izračunate su vrijednosti Gibbsove slobodne energije adsorpcije. Pored toga, adsorpcijska izoterma pri pH = 10,0 pokazala je prisutnost slabih odbojnih sila između molekula AR 1 adsorbiranih na živinu elektrodu uz duža vremena taloženja. pH elektrolita važan je čimbenik u adsorpcijskom ponašanju AR 1.