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Dichlorophenoxyacetic Acid Anchored on Silica-Gel Modified Carbon Paste for the Determination of Pesticide 2,4-D

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2,4-dichlorophexoyacetic acid was attached onto silica gel. For this immobilization, in the first step, 3-aminopropyltrimethoxysilane was attached onto silica gel surface in order to produce the precursor silica. The 2,4-dichlorophexoyacetic acid was incorporated onto precursor silica by reaction between chloride of 2,4-dichlorophexoyacetic acid and amine group precursor silica, forming a covalent bond ~~of~~ between 2,4-dichlorophexoyacetic acid ~~to~~ and the inorganic surface, resulting in the production of SiD material. Then, 1.02 mmol of 2,4-dichlorophexoyacetic acid per gram of silica exhibited a surface area of 250 m^2/g. Infrared and ^{29}Si NMR spectra were in agreement with the proposed structure of the modified silica. This modified silica was applied to develop a chemical carbon paste electrode to determine pesticide 2,4-D in water. Voltammetric studies showed that the 2,4-D electrochemical reduction involved 4 electrons for each 2,4-D molecule reduction. Detection and quantification limits of 2,4-D in water were 0.45 μmol/L.

Keywords: Dichlorophenoxyacetic Acid , Pesticide 2,4-D,carbon paste electrode , Cyclic voltammetry, Chronoamperometry

1. INTRODUCTION

Food shortage is caused not only by malnutrition and starvation, but also by economical, social and political instability. The main alternative to surpass the production crisis in agriculture is to increase the crop yield per acre [1]. In order to increase the production, many agrochemicals have been applied in agricultural fields [2]. However, indiscriminate application of these agrochemicals can cause serious, perhaps grave, environmental problems [3,4]. The excess of agrochemicals can quickly reach natural waters by leaching and runoff processes [5,6].

The continuous application of agrochemicals in crops results leads to food and drinking water contamination [7].

Among the several pesticides used in agriculture, 2,4-D (dichlorophenoxyacetic acid) is a common herbicide used in Brazilian agriculture [8,9]. 2,4-D is normally applied in weed control for crops such as palm oil, rubber crops, cocoa, as well as for weeds along highways, and mainly, in sugar cane plantations [10,11].

The amounts of various agrochemicals present in the surface and underground waters have increased in the last years [12]. The adverse effects on environment and mankind are leading to efforts for the development of efficient technologies to determine these agrochemicals in water.

The development of specific and sensitive assays for pesticides detection is one of the aims of modern chemistry [13]. Nowadays, most of the methods used to environmental monitoring of pesticide require an expensive instrumentation, as chromatography technique [14-17].

For this reason, the alternative electrochemical method can be more convenient [17-19]. In this context, nowadays, it is well established that one of the more promising areas of analytical applications of chemically modified electrodes is that in which immobilized redox mediators are used to make possible the charge-transfer between the electrode and analyte in solution at much lower potentials than otherwise be possible [20]. The chemically modified carbon paste electrodes have been widely applied in electroanalysis because of their versatility and simplicity of construction [21].

The development of a modified carbon paste, which is a sensitive electrochemical matrix, can be obtained by silica gel surface organofunctionalization [22]. The active hydrogen atom of the silanol groups dispersed on silica gel surface has the ability of reacting with organosilyl groups to give some organic nature of the inorganic carrier. The immobilization of this desired reactive atom group gives versatility to this surface; consequently, developing various functions.

In this report, 2,4-D was immobilized on silica gel surface and this matrix was used to develop a modified carbon paste electrode (SiD). This new electrode was applied in electroanalysis studies ~~to~~ for the determination of 2,4-D pesticide.

2. EXPERIMENTAL

2.1. Reagents

2,4-diclorophenoxiacetic acid (2,4-D) (Sigma), 3-(trimethoxysilyl)- propylamine (APTS) (Sigma) were used without purification. Silica gel (Merck) with a particle size of 70-230 mesh and with mean diameter pore size of 60 Å was activated by heating at 150°C for 10 h in a stream of dry nitrogen. After this activation, the silica was immediately used. A specific area of 410 m^2 g^{-1} was determined by BET method.

2.2. Organofunctionalization of silica with 2,4-D

Activated silica gel (45.0 g) suspended in 100.0 cm^3 of dry xylene was refluxed and mechanically stirred for 1 h under dry nitrogen. Then, 15.0 mL of APTS was added dropwise to this suspension. The mixture was kept in reflux for 72 h. The solid was filtered and washed with water and ethanol. This immobilized surface, named $SiNH_2$, was dried in vacuum at room temperature.

A sample of 5.0 of organofunctionalized silica, $SiNH_2$, was suspended in 100.0 mL of dry xylene was refluxed and mechanically stirred with 2.0 g of 2,4-D for 72 h under dry nitrogen. The surface containing the immobilized pesticide, named SiD, was filtered and the excess of 2,4-D was eliminated by washing it with water and ethanol. This final anchored surface was dried in vacuum at room temperature.

2.3. Characterization of modified silica

The content of 2,4-dichlorophenoxyacetic acid on silica gel surface was determined by elemental analysis.

The surface area of SiD material was determined by using a Qantachrome 2200 surface analyzer. Infrared spectra of SiD sample (as KBr pellets) were measured in a Jasco XXX FTIR spectrophotometer at a wavenumber range of 4000–400 cm^{-1}, with a resolution of 4 cm^{-1}, by accumulating 64 scans. ^{29}Si NMR spectra of the solid samples were determined at 59.61 Hz using a Varian Mercury Plus 300 spectrometer at room temperature. For each determination, approximately 1 g of modified silica ~~which~~ was compacted into a 7 mm silicon nitrite rotor and a magic angle spinning speed of 3 kHz was employed.

The CP/MAS technique was used in order to increase the signal-to-noise ratio of the solid-state spectrum and ^{29}Si CP/MAS spectrum was obtained with pulse repetition of 1 s and contact times of 1 ms, respectively.

2.4. Electrodes, electrochemical cell and Cyclic voltammetry

The work electrode was a modified carbon paste that was prepared by homogenizing graphite powder with an appropriate amount of SiD in a proportion of 1:1 weight/weight, with an appropriate amount of nujol oil.

Reference and counter electrodes for experiments were ~~a~~ Ag/AgCl and platinum wire electrodes, respectively, attached to a micro-Autolab potentiostat/galvanostat running. To certificate if carbon paste, silica gel or $SiNH_2$ did not show any signal, a modified carbon paste electrode were made with these compounds. The potential range studied was from -1.0 to +1.0 V in 0.2 mol L^{-1} aqueous solution of KCl at a scan rate of 5 mV s^{-1} under N_2 saturated.

2.5. Effect of pH in electrochemical signal

The electrochemical behavior of 9.05 10^{-5} mol L^{-1} 2,4-D was followed over a pH range varying between 1,0 and 7,0, using differential pulse voltammetry and scanning from –1.0 to +1.0 V in 0.2 mol L^{-1} aqueous solution of KCl at a scan rate of 10 mV s^{-1} under N_2 saturated.

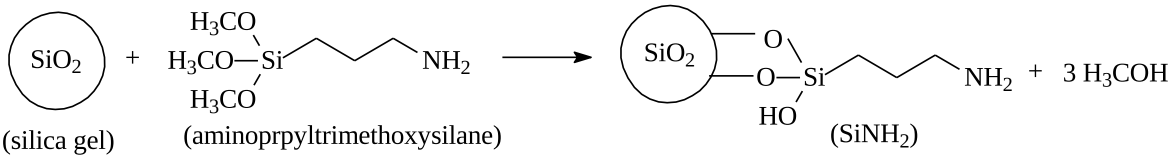
2.6. Chronoamperometry assays and a 2,4-D determination

All experiments were performed in 0.2 KCl, pH 6, at 25°C, under optimum experimental conditions. The determination of 2,4-D was performed after an incubation period, and a constant potential of +220 mV was applied to the 2,4-D solution. The evaluation of the inhibition power of 2,4-D was measured by using different concentrations of this pesticide in solution. The 2,4-D samples were prepared by diluting a 0.45 mmol L^{-1} stock solution in electrolyte solution.

3. RESULTS AND DISCUSSION

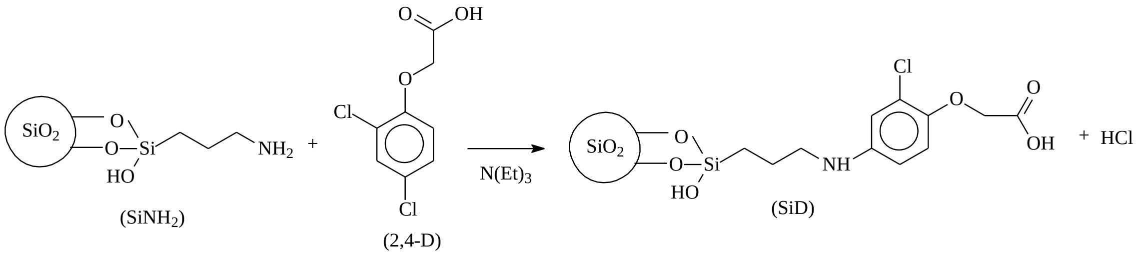
3.1. Synthesis and Characterization of modified silica

The synthetic procedure to produce the sensor SiD was based on the modification of silica gel with 3-aminopropyltrimethoxysilane to obtain the precursor surface ($SiNH_2$), as according to Eq. 1



(1)

The precursor ($SiNH_2$) reacted with 2,4-dichlorophenoxyacetic acid (2,4-D) to form the product SiD, as according to Eq. 2:



(2)

The amount of 2,4-D anchored onto silica gel surface was determined by elemental analyses using a PE-2400 elemental analyzer (Perkin-Elmer, USA), and the obtained value was 1.02 mmol of 2,4-D per gram of silica.

SiG nitrogen adsorption–desorption isotherms are shown in Fig. 1. These isotherms show that the adsorption–desorption process is not reversible. This is a consequence of the hysteresis loops caused by capillary condensation. The isotherm is reversible up to a relative pressure of about 0.50. Irreversibility is observed between 0.5 and 0.9, whereas the condensation in primary mesopores takes place slightly above the latter pressure limit, but the adsorption and desorption branches are not parallel to each other, resulting in the hysteresis loop. Specific area of 258 m^2/g was determined by a BET method.

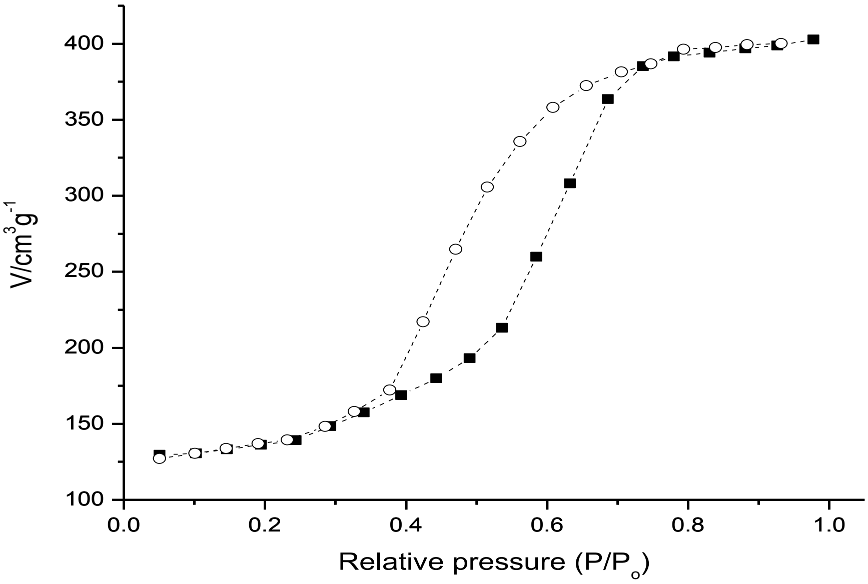


Figure 1. Nitrogen adsorption-desorption isotherms for SiD.

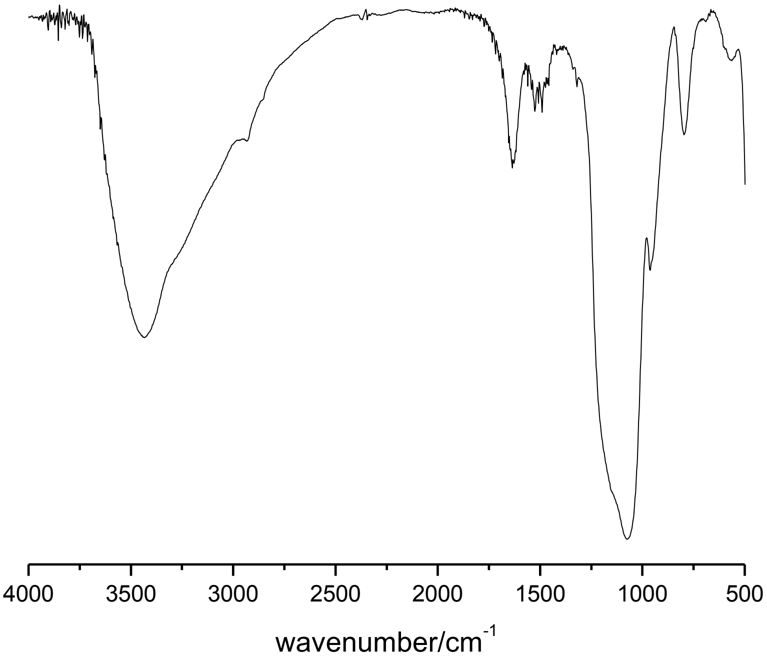


Figure 2. FTIR spectrum of SiD.

SiD sensor was characterized by the FTIR spectrum (Fig. 2), as follows: (i) a large broad band between 3600 and 3200 cm^{-1} related to the presence of the O–H stretching frequency of silanol groups, carboxylic acid groups and also to the remaining adsorbed water, (ii) a band at 2950 cm^{-1} assigned to carbon sp^3 of the organic pendant group attached to the surface, (iii) a band around 1650 cm^{-1}, assigned to the angular vibration of water molecules, (iv) a band at 1470 cm^{-1} assigned to the C–N stretching related reaction between N of $SiNH_2$ and carbon which lost chloride of 2,4-D. The appearance of these bands is in agreement with the formation of 2,4-D attached to the silica (v), an intense band at 1100 cm^{-1} related to the n(Si–O–Si) siloxane stretching and (vi) a band at 900 cm^{-1} assigned to the Si–OH stretching frequency of silanol groups [23].

Solid-state NMR of the Si-29 spectrum of SiD presented four typical peaks as shown in Fig.3. The first one at -51 ppm was assigned to the silicon atom of the silylating agent, which was bounded to one hydroxyl group [RSi(OSi)2(OH)], denominated T^3 signal. The second peak at -59 ppm was related to RSi(OSi)3 (T^4 signal). T^3 and T^4 signals confirm that the organic groups were covalently bonded to the silica matrix. Other two peaks, at -95 and -105 ppm, were related to pure surface signals Si(OSi)3OH, named Q^3 signal, and Si(OSi)4, corresponding to the Q^4 signal, respectively [24,25].

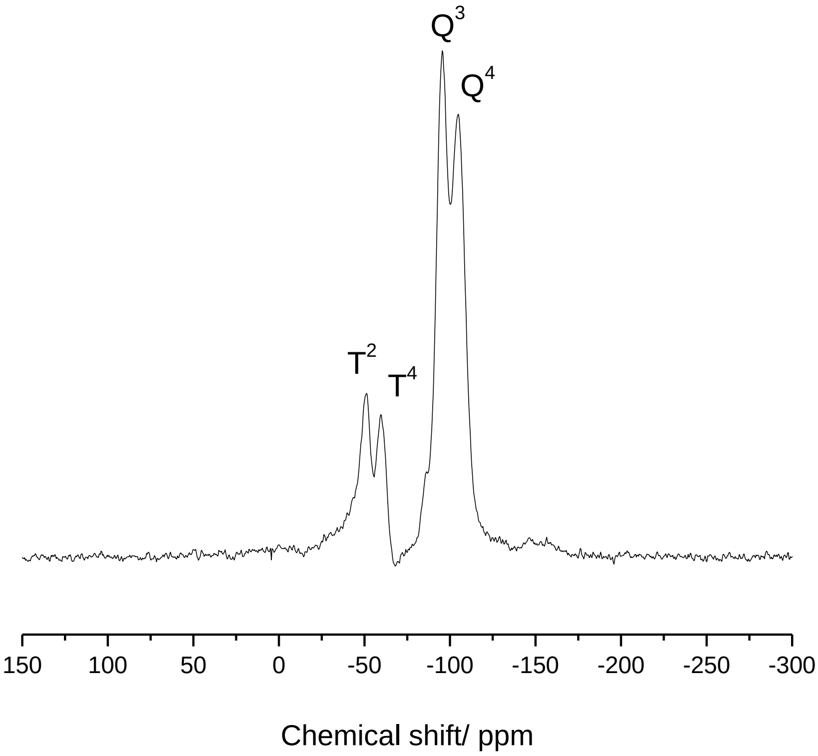


Figure 3. Solid-state ^{29}Si NMR spectrum of SiD.

3.2. Electrochemistry studies

The electrochemical treatment of the electrode surface was carried out after scan potential between +1.0 and –1.0 V.

The oxidation and reduction was first studied by cyclic voltammetry in order to probe the oxidation mechanism. The electrochemical oxidation of 2,4-D occurred at +266 mV and reduction at +192 mV vs Ag/AgCl in KCl 0.1 mol L^{-1} at pH 3, as presented in Figure 4.

The voltammetric behavior presented by 2,4-D on SiD electrode ~~have~~ showed a good reproducibility. However, the electrochemical adsorption was quite low resulting in a low sensibility.

To revert this problem, the electrochemical studies of 2,4-D was followed by differential pulse voltammetry in order to obtain more sensibility.

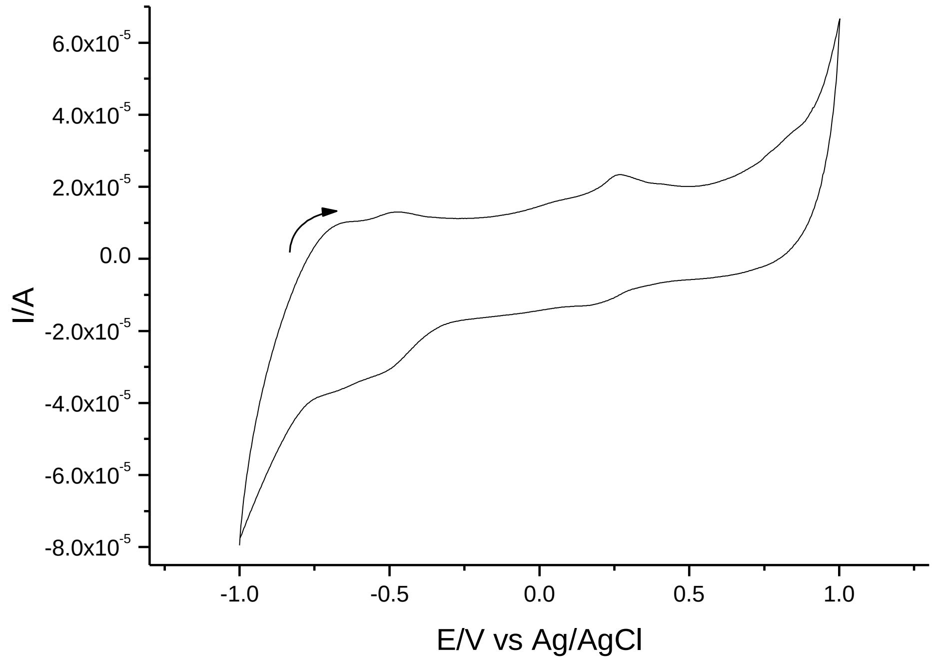


Figure 4. Cyclic voltammogram of 2,4-D in SiD electrode in 0.2 mol L^{-1} aqueous solution of KCl at a scan rate of 5 mV s^{-1} under N_2 saturated.

3.2.1.The effect of pH

The electrochemical behavior of 2,4-D was followed over a pH range between 1,0 and 7,0 using differential pulse voltammetry (Fig. 5) and scanning from –1.0 to +1.0 V. Voltammetric responses in Fig. 5 represent the oxidation half wave potential for 9.05 x 10^{-5} mol L^{-1} solutions in distinct pH values. These results show that the anodic process is dependent on pH. At pH 1 value, the peak current (Ip,a) is minimum. Besides, above this pH value the Ip,a increases up to pH 3, decreasing smoothly above this value, as presented in Table 1 and Fig.6. Moreover, it is also evident that maximum value of peak current is obtained at pH 3 values, which is close to the value of 2,4-D pKa [26], corroborating ~~of~~ with the protonation equilibrium preceding the electrons transfer reaction [27,28].

This figure also shows the peak potential (Ep,a) of 2,4-D decreases as the pH increases. The effect of pH changes in electrical potential can be represented by the equation 3:

$$E = 0.298 - 0.0152 pH \qquad (3)$$

This equation was obtained from straight line of the Fig. 6. This equation is predicted by Nernst equation for a reduction process involving 4 electrons.

Based on electrochemical data obtained from Fig. 6, the proposed mechanism of reduction of 2,4-D pesticide involving the reduction of the carboxylic acid group to alcohol function by protonation and four electron transfer reaction is presented in Fig. 7. This mechanism is supported by literature [29,30].

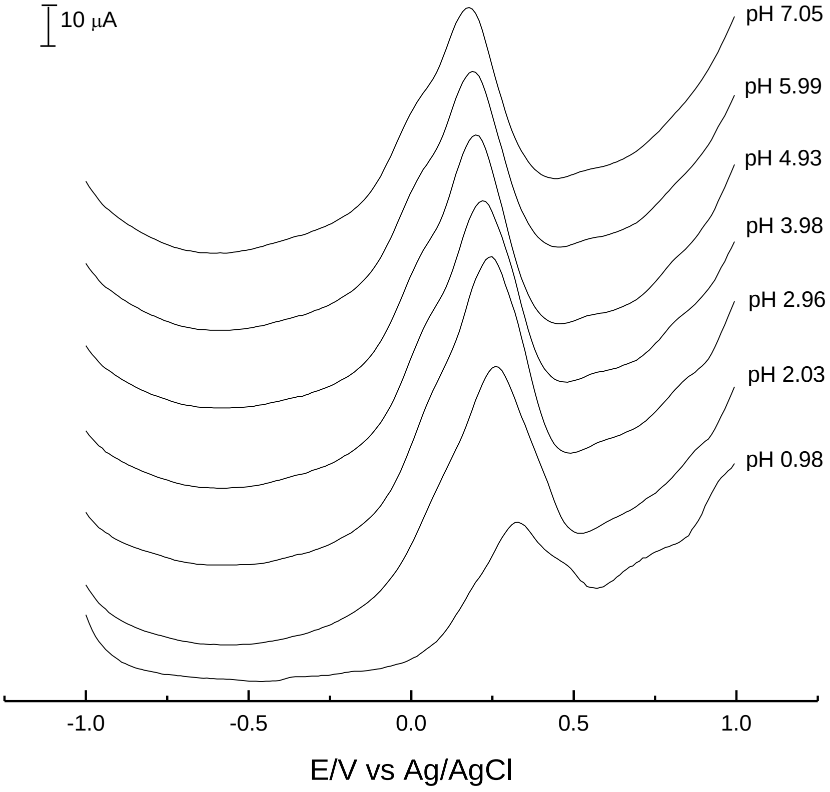


Figure 5. Pulse differential voltammograms of 9.05 x 10^{-5} mol $L^{-1}$of pesticide 2,4-D in different pH values in 0.2 mol L^{-1} aqueous solution of KCl at a scan rate of 10 mV s^{-1} under N_2 saturated.

Table 1. Effect of pH values on peak potentials and current values for pesticide 2,4-D determination using the SiD electrode in 0.2 mol L^{-1} aqueous solution of KCl at a scan rate of 10 mV s^{-1} under N_2 saturated.

pH	E/V	I/10^{-5}A
0.98	0.285	6.215
2.03	0.269	7.215
2.96	0.256	7.683
3.98	0.237	6.820
4.93	0.228	6.444
5.99	0.210	6.349
7.05	0.193	6.343

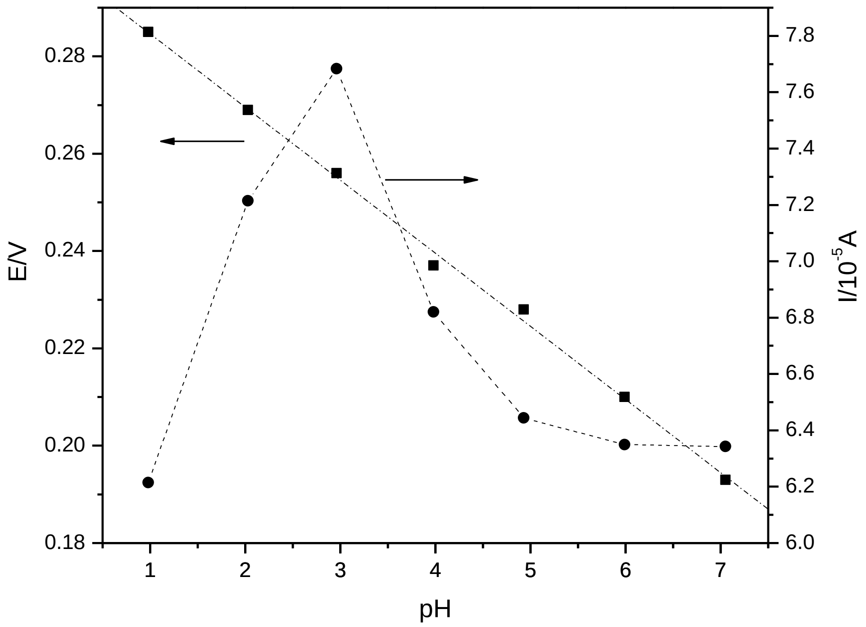


Figure 6. Effect of pH values on peak potentials (●) and current values (■) for pesticide 2,4-D determination using the SiD electrode in 0.2 mol L^{-1} aqueous solution of KCl at a scan rate of 10 mV s^{-1} under N_2 saturated.

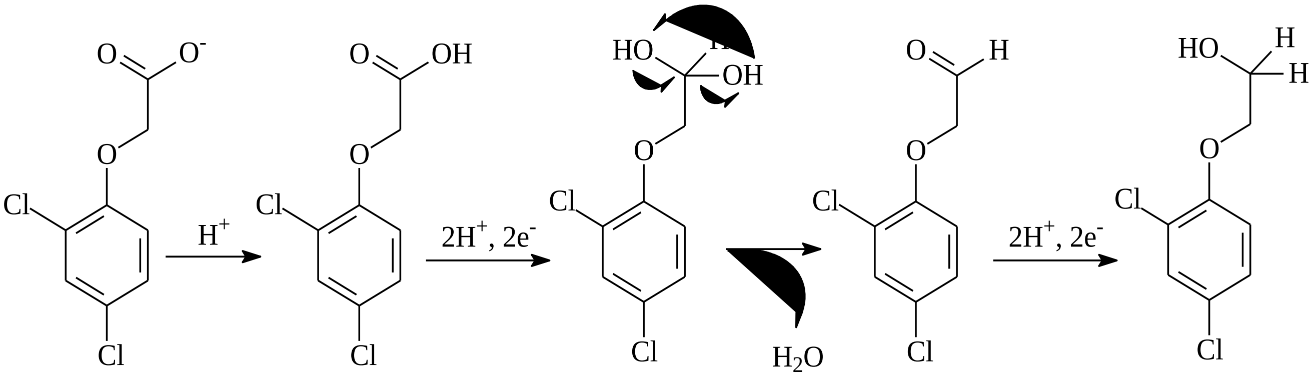
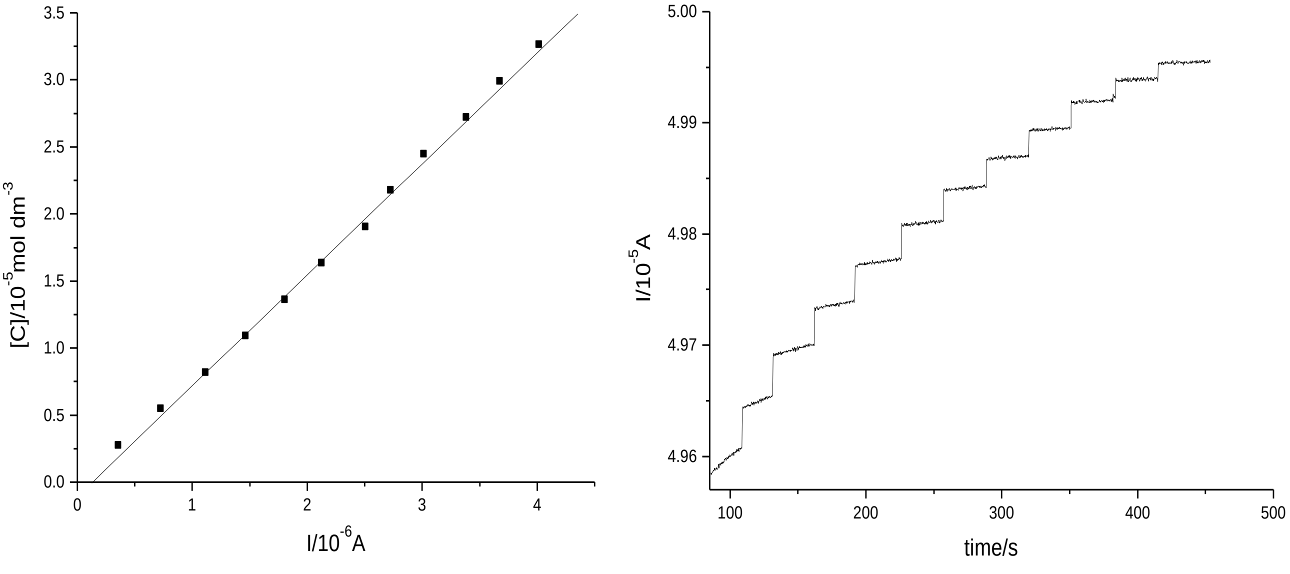


Figure 7. Proposed mechanism of 2,4-D electrochemical reduction process.

3.2.2. Chronoamperometry

This modified silica gel was applied to determine the pesticide 2,4-D concentration in water samples. Amperometric curve was obtained for 2,4-D concentration varying from zero to 10 μmol/L at pH = 5 (Fig.8). Linear correlation was obtained as shown in Figure 8A. The quantification limit was calculated from the calibration curve equation obtained by Fig. 8A and the detection limit value (0.4 mmol/L of 2,4-D), which was determined by signal 3 times higher than the noise.

This obtained result showed the viability of the SiD electrode application for pesticide 2,4-D quantification.



A B

Figure 8. 2,4-D concentration against current density values between: 5.0 X 10^{-6} and 2.0 X 10^{-3} mol/L in 0.2 mol/L KCl, obtained by chronoamperometry at a carbon paste electrode modified with SiD (A). Details of the electrode response in the chronoamperogram (B). The potential applied in these assays was 0.22 V.

4. CONCLUSION

2,4-dichlorophenoxyacetic acid was attached on silica gel surface, and NMR 29-Si, FTIR and Elemental Analysis confirmed the success of this immobilization. This modified silica showed promissory properties as eletrochemical sensor in order to quantify the pesticide 2,4-D in water, with a quantification limit of 0.45 µmol/L (99.47 ppb). This new electrode is an important new tool for the determination of herbicides, avoiding the use of conventional electrodes.

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