ELECTROCHEMICAL DETERMINATION OF SIMAZINE USING CLAY MODIFIED CARBON PASTE ELECTRODE

By

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DECLARATION

I, the undersigned, declare that this thesis is my original work and has not been presented for a degree in any university and that all the sources of materials used for this thesis has been duly acknowledged.

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Abstract

The electrochemical behavior of simazine (triazinic herbicide) was investigated by cyclic voltammetry at clay modified carbon paste electrode. The appearance of two fold peak current obtained at clay modified carbon paste electrode was used as an analytical signal for developing differential pulse adsorptive stripping voltammetric method for the determination of simazine using clay modified carbon paste electrode. Systematic and detailed studies of various experimental conditions were conducted to establish the optimal clay amount, pH of solution and instrumental parameters. A linear dependence between peak current and concentration of simazine was observed for concentrations between 1.0 x 10^{-6} M to 20 x 10^{-6} M. At higher concentrations (20 x 10^{-6} M to 80 x 10^{-6} M), another linear dependence was observed. The relative standard deviation for six successive determinations were 3.3 and 2.58% for 2.0 x 10^{-6} M and 20 x 10^{-6} M simazine, respectively. The detection limit (concentration equal to three times the standard deviation of peak current) was 0.25 x 10^{-6} M. The developed method was applied to the direct determination of simazine in spiked potable water sample with satisfactory result.

***Keywords**:* Voltammetry, Herbicides, Simazine, Clay, Carbon paste electrode.

health and well being of the ever growing human population. Unfortunately, these chemicals are potential pollutants having deleterious effects on human health and environment [3, 4] when their concentrations are higher than certain limits. In this connection, Pio and Hall [5] put the following general statement: " Pollution exists when the concentration of the substance are large enough to interfere with the normal use of the environment and the well being of biota, especially man".

Not only herbicides, but also the solvents in which they are being dissolved and chemical substances with which they are sometimes mixed have their own toxicity [6]. There are many pathways for exposure: in drinking water from contaminated wells and from residues on plants as they are picked, from herbicide drift as it is being sprayed, from spills during transport and from dermal exposure during mixing and application [7]. Farm workers within agricultural sectors, mixers, applicators and others who directly handle agricultural chemicals are, therefore, at the highest risk for herbicide related illness [8].

Most of the herbicides released to the environment are known and reported to be toxic and the toxicity aspects have received considerable attention. Considering the water quality, for example, the legislation authorities have in the recent years, issued stringent regulations [9]. The current European Union (EU) directive dictates that the concentration of individual herbicides should not exceed a maximum admissible concentration of 0.1 μg/L in drinking water for a single herbicides and 0.5 μg/L for a total herbicides concentration. Similar regulations have been set in the United States, by USEPA; for example, 3 μg/L for atrazine and 4 μg/L for simazine [9, 10].

Therefore, the determination of herbicides in food, soil, rivers and lakes, as well as in human and animal tissues is necessary to insure our overall health and to assess the environment's impacts of these chemicals.

1.1. Background History of Herbicides

Herbicides, (from Latin herba-means herb, plant and -cida means killer, murderer), is a chemical product which can be used to destroy or inhibit the growth of weeds, or unwanted plants at a given time and space. Weeds, besides drastically reducing the crop yields and quality, serve as alternative hosts for crop infecting fungi [11].

Herbicides have been in use since the mid-nineteenth century. Up to World War II, a variety of inorganic acids and salts, e.g., iron sulphate, sulphuric acid, sodium chlorate, arsenicals and copper sulphate, were applied to control weeds. In 1930s the first organic chemical herbicide, 4,6-dinitro-o-cresol (DNOC) was introduced for control of weeds. DNOC was used as an insecticide before its herbicidal effect was discovered [12]. In the 1940s chlorinated phenoxyacetic acids were developed for use as herbicides, followed by phenoxypropionic acids and phenoxybutyric acids. These acids are still among the most commonly used herbicides today, with an estimated production of 34×10^6 kg/year in USA in the mid 1980s. Since the introduction of the phenoxyalkanoic acids, many other classes of compounds have been introduced for use as herbicides. In the mid 1980s amides were the largest group of herbicides produced in USA (estimated production 90×10^6 kg/year). The triazines, which were introduced in the 1950s, had at the same time a production estimate of about 50×10^6 kg/year and the second largest group produced [13].

1.2. Symmetrical Triazine Herbicides

Symmetrical triazines (s-triazines) belong to a class of six membered heterocyclic containing three azomethine nitrogen centers and three carbons alternatively located in the ring. The designation 1,3,5-triazine is also common where the number refers to the position of the ring nitrogen atoms. Figure 1 shows the structure of s-triazine.

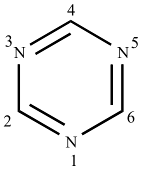


Figure 1. Structure of s-triazine.

Symmetrical triazines are one of largest classes of agrochemicals produced and the most commonly used herbicides for pre-and post-emerged weed control for a variety of crops including green vegetables [14, 15]. A recent report on world pesticide market indicates that about 30% of all herbicides produced are triazines [16]. They are synthesized by substituting 1,3,5,-triazine (s-triazine) in the 2-, 4-, and 6-positions. Their properties are determined mainly by the substituents at 2-position, generally chlorine (the general name ending with-azine), methoxy-(ending-tone) and methyl (alkyl) thio -(ending-tryn). The 4- and 6-positions are usually substituted with various amino alkyl groups [15, 17]. The widespread use of s-triazine compounds is always accompanied by the introduction of the contaminants and residue in plants, soils, water bodies and the general human environment owing to their relative persistence and easy transport [18].

1.3. Simazine

Simazine (6-chloro-N,N’-diethyl-1,3,5-triazine-2,4-diamine) is a selective triazine herbicide (Figure 2). It is used to control broad leaf weeds and annual grasses in several food crop fields [19-21].

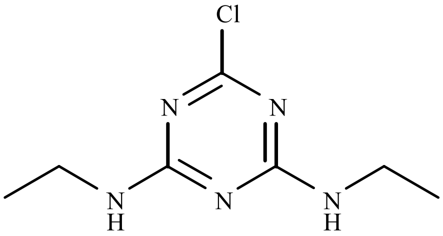


Figure 2. Chemical structure of simazine.

Simazine is a white crystalline solid. It is stable to natural light and extremes of temperature. It is stable in neutral to slightly basic or acidic media, but is hydrolyzed by stronger acids and bases. Simazine presents a slight fire hazard if exposed to heat and flame. It may burn, but does not readily ignite. Thermal decomposition of simazine may release toxic oxides of nitrogen and carbon, and toxic and corrosive fumes of chlorides [22].

The Swiss company J. R. Geigy [23] first introduced simazine in 1956 and it is part of the triazine family of chemical compounds. Simazine (Figure 3 D) can be produced in > 90% yield by the reaction of cyanuric chloride (Figure 3 A) with ethylamine (Figure 3 B) and sodium hydroxide (Figure 3 C) in aqueous medium [24].

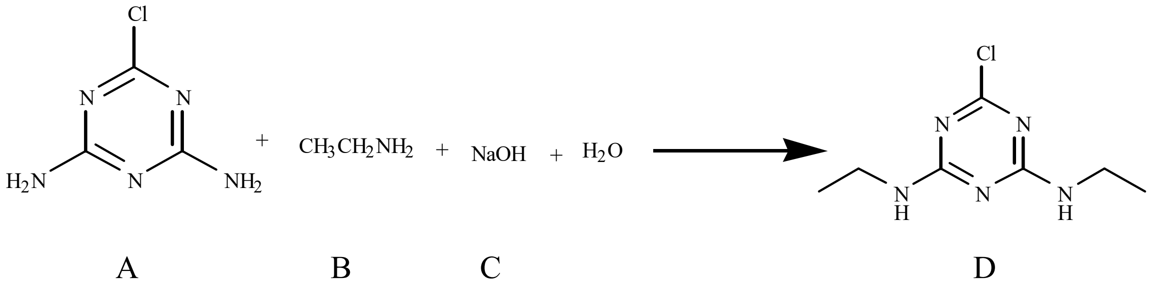


Figure 3. The production of simazine (D) from cyanuric chloride (A), ethylamine (B), and sodium hydroxide (C) in aqueous medium.

1.3.1. Breakdown of the Simazine in Vegetation

According to Cremlyn [23], simazine uptake is via the roots of emerging seedlings. Subsequently, it is translocated upward to the stems, leaves and growing shoots of the plant and inhibits the photosynthetic electron transport process in the plant leaves and causes them to turn yellow and die. Many varieties of maize and sugar cane plants are resistant to the herbicidal properties of simazine as these plants contain an enzyme that detoxifies the compounds by hydrolysis (Figure 4) in the plant tissues. Plants that are sensitive to simazine accumulate it unchanged. It is possible that livestock or wildlife grazing on these plants could be poisoned.

1.3.2. Environmental Fate of Simazine

Simazine is continuously in contact with the environment due to its persistence in soils caused by the low solubility in water [25, 26]. In combination with a lengthy soil half-life, this factor suggests that simazine is likely to contaminate groundwater. Simazine is subject to decomposition by ultraviolet radiation, but this effect is small under normal field conditions. Simazine can be dechlorinated when the compound is heated with caustic alkalies under laboratory conditions. In environmental systems, the same dechlorination process and subsequent hydrolysis may take place under high pH conditions (Figure 4). The resulting compound is 2-hydroxy-4,6-bis (ethlyamino)-s-triazine (Figure 4 B). Interestingly, this compound does not have herbicidal properties [24].

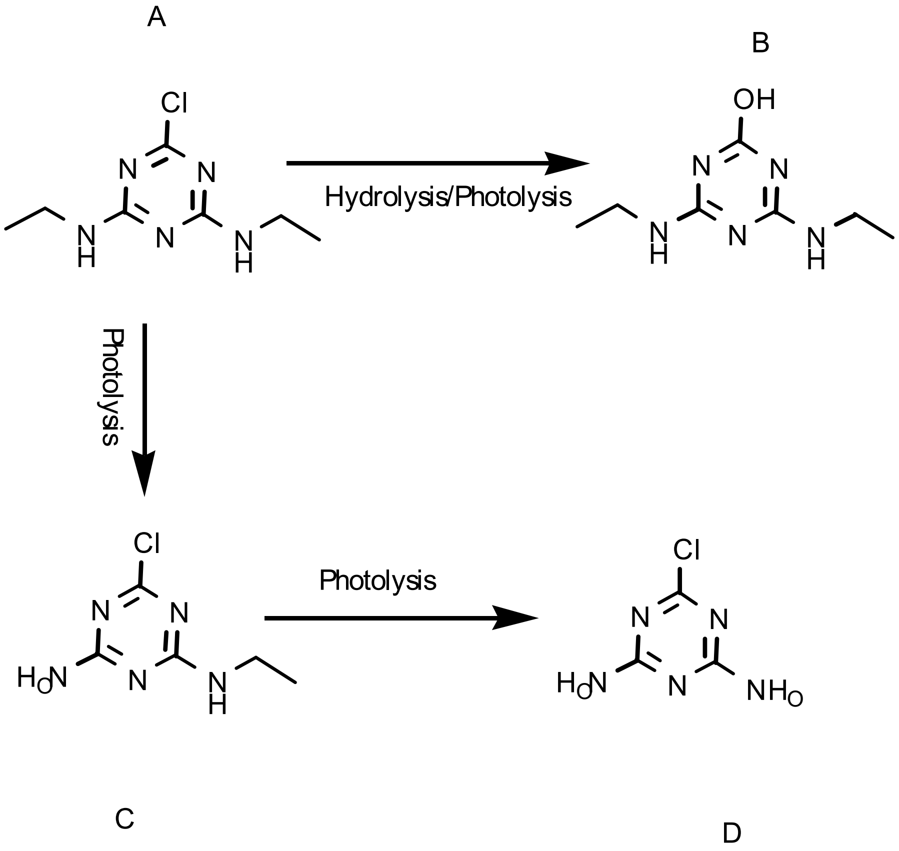


Figure 4. The general degradation pathways of simazine (A) where 2-hydroxy-4,6-bis (ethlyamino)-s-triazine (B) is produced by hydrolysis. Photolytic loss of alkyl groups produce deisopropyl atrazine (C) and diamino chlorotriazine (D).

1.3.3. Toxicological Effects

Simazine is highly toxic if inhaled, moderately toxic if ingested, and slightly toxic via dermal exposure. The triazine herbicides disturb energy metabolism (thiamin and riboflavin functions). Toxicity symptoms include difficulty in walking, tremor, convulsions, paralysis, cyanosis, slowed respiration, miosis (pin point pupils), gut pain, diarrhea and impaired adrenal function. Simazine is also a possible human carcinogen [27].

1.4. Method of Analysis

There have been many studies focused on the ecological and health hazards of simazine and its toxic effects are very well known [19, 28]. It is included in both European Communities and US Environmental Protection Agency (USEPA) list of priority pollutants, which are mainly organic compounds, herbicides, insecticides, solvents and chlorinated base compounds liable to be found in rivers and effluents [29]. Consequently, the routine monitoring of simazine level is necessary.

Several methods have been published for the determination of simazine. These include chromatographic techniques, such as thin layer chromatography (TLC) [30], liquid chromatographic (LC) separation with spectrophotometric [31] and electrochemical detection [21], and gas chromatography (GC) [32]. However, in these methods, the separation is often complex, time consuming and involves expensive apparatus [33]. For this reason, there is a need to develop a method, which is faster, simple and accurate for the determination of simazine in environmental samples.

Electroanalytical techniques such as voltammetry and polarography are very suitable for analysis and quantitation of organic compounds due to their speed, high analytical sensitivity, low detection limit, relatively compactness, low-cost instrumentation with low maintenance costs, and the possibility of employing inexpensive electrodes. These attracting features have resulted in rapid developments and wide spread application of voltammetry and polarography [15].

M. J. Higuera and co-workers studied the electroreduction of simazine on a mercury electrode [34]. The work of M. J. Higuera and his co-workers indicates the possibility of determination of simazine by electroanalytical techniques especially by adsorptive stripping voltammetry at a hanging mercury drop electrode (HMDE). However, the toxicity of mercury [35] and the growing interest for on-site environmental monitoring have prompted the search for new "mercury free" electrodes.

At present clay modified electrodes have attracted a great deal of attention for organic and inorganic pollutant analysis [36] because clays share many of the desirable properties of ionic polymers [37]. The beauties of clay modified electrodes are eliminating mercury and its soluble salts from the analytical procedure and, their ability to enhance the sensitivity and selectivity of electrochemical techniques. In addition, they are cheap, easy to modify and use, and exhibit good stability and reproducibility.

Despite the suitability of clay mineral as electrode modifier for voltammetric determinations, no studies on the electrochemical determination of simazine with the use of clay modified carbon paste electrode has been reported so far. In this work, the possibility of adsorptive preconcentration of simazine onto clay modified carbon paste electrode is investigated and differential pulse adsorptive stripping voltammetric method for the determination of simazine has been developed using clay modified carbon paste electrode. The proposed method was applied to the determination of simazine in a synthetic sample of potable water.

1.5. Clay Mineral [38-41]

1.5.1. Definition of Clay Mineral

Clay minerals are the most important chemical weathering product of the soil. Clay has many uses today including, pottery, ceramics, computer chips, cosmetics, pharmaceuticals and modifying electrodes in electroanalytical chemistry.

In spite of recent developments in clay mineralogy, there is still no generally accepted definition of the term clay mineral.

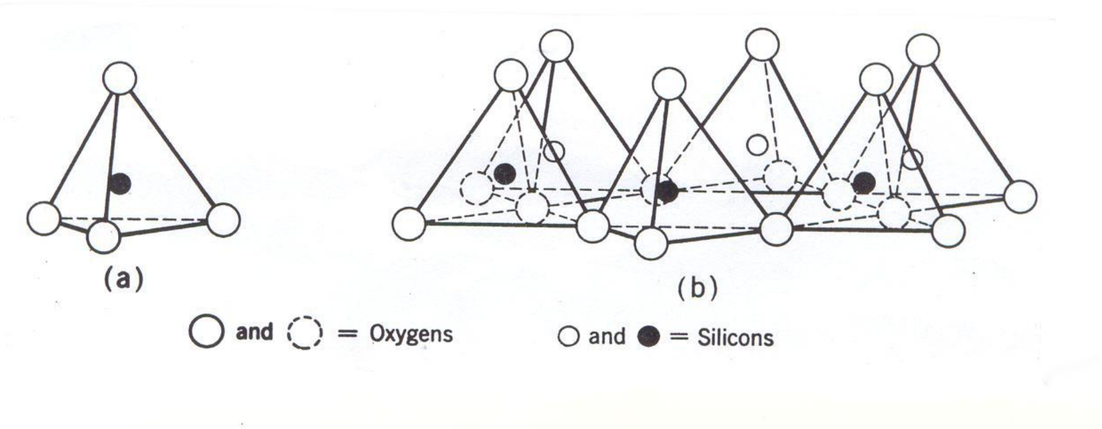
To a clay mineralogist, a clay mineral is a layer silicate mineral (phyllosilicate) or natural, earthy, fine grained material that develops plasticity when mixed with a limited amount of water and hardens upon drying or firing. The word "clay" is also used to refer to a particle size in a soil or sediment. The term is used in the United States (US) and by the International Society of Soil Science for a rock or mineral particle in the soil having a diameter less than 2 μm, whereas sedimentologists classify particles smaller than 4 μm as clay.

1.5.2. Basic Clay Mineral Structure

Recently clay minerals have been widely investigated for their applications in modifying electrodes in electroanalytical chemistry because of the negative charge they contribute for cation exchange (cation exchange capacity), swelling, porosity and sorption [42]. In order to understand the above mentioned advantages of clay mineral, it is important to look at the basic structure of clay and why this contributes to their properties.

Clay minerals are part of the larger class of silicate minerals: the phyllosilicates. The principal building elements of the clay minerals are two-dimensional arrays of silicon-oxygen tetrahedral and two-dimensional arrays of aluminum-or magnesium-oxygen-hydroxyl octahedral polymeric sheets.

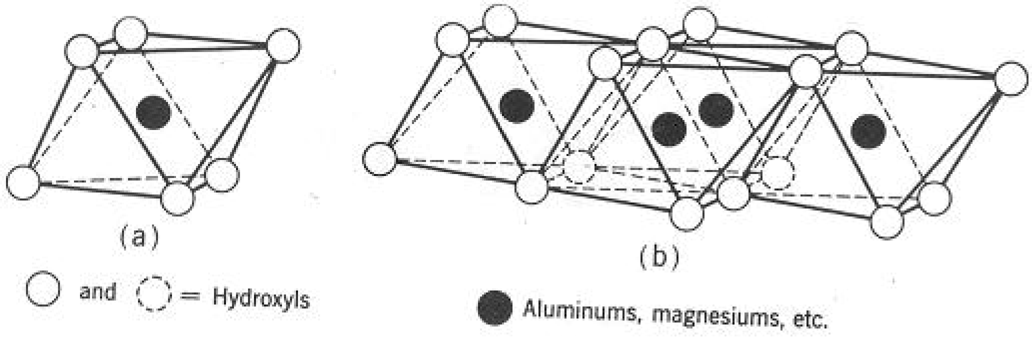
In the silicon-oxygen sheets, the silicon atoms are coordinated with four oxygen atoms. The oxygen atoms are located on the four corners of a regular tetrahedron with the silicon atom in the center (Fig. 5a). In the sheet, three of the four oxygen atoms of each tetrahedron are shared by three neighboring tetrahedral. This sharing of three neighboring tetrahedral groups results in a sheet such as that shown in Figure 5b, which is repeated indefinitely to form a sheet of composition $Si_4O_6(OH)_4$. The tetrahedrons are arranged so that the tips of all of them point in the same directions, and the bases of all tetrahedrons are in the same plane (Fig. 5b).



(a) (b)

Figure 5. Diagrammatic sketch showing (a) a single silica tetrahedron unit and (b) the sheet structure of silica tetrahedrons units.

In the Al-, Mg-O-OH sheets, the Al or Mg atoms are coordinated with six oxygen atoms or OH groups, which are located around the Al or Mg atom with their centers on the six corners of a regular octahedron (Fig. 6a). The sharing of oxygen atoms by neighboring octahedrons results in a sheet such as that shown in perspective in Figure 6b.



(a) (b)

Figure 6. Diagrammatic sketch showing (a) a single alumina octahedral unit and (b) the sheet structure of alumina octahedral units.

The analogous symmetry and the almost identical dimensions in the tetrahedral and the octahedral sheets allow the sharing of oxygen atoms between these sheets. The octahedral sheet shares the fourth oxygen atom protruding from the tetrahedral sheet. This sharing of oxygen atoms may occur between:

1. one silica and one alumina sheet, as in the case of 1:1 layer mineral (Fig. 7) and
2. two silica and one alumina sheet, as in the case of 2:1 layer mineral (Fig. 8).

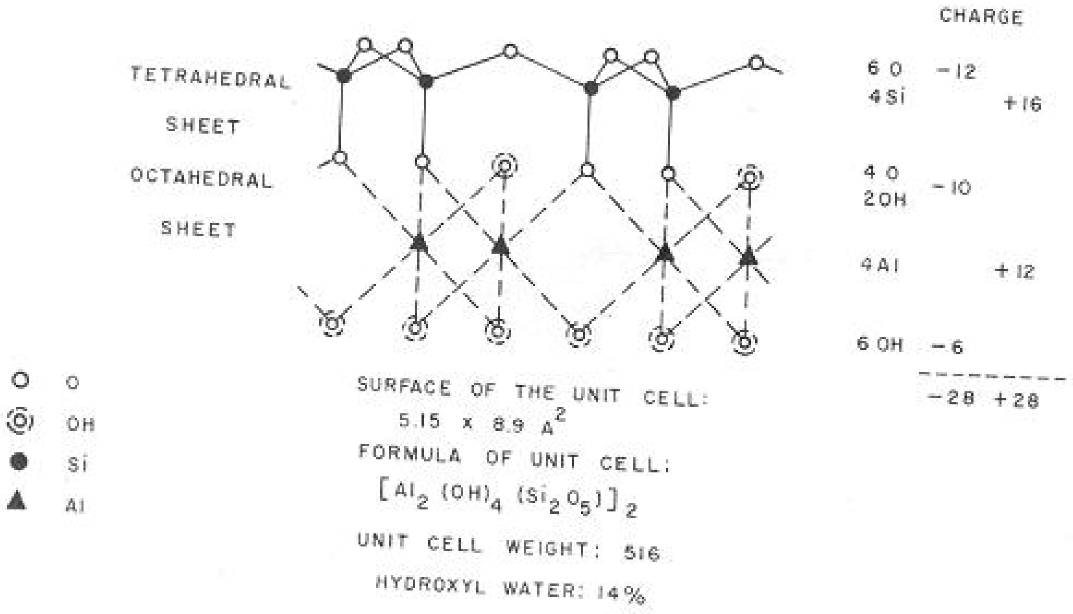


Figure 7. Atomic arrangement in the unit cell of a 1:1 layer mineral.

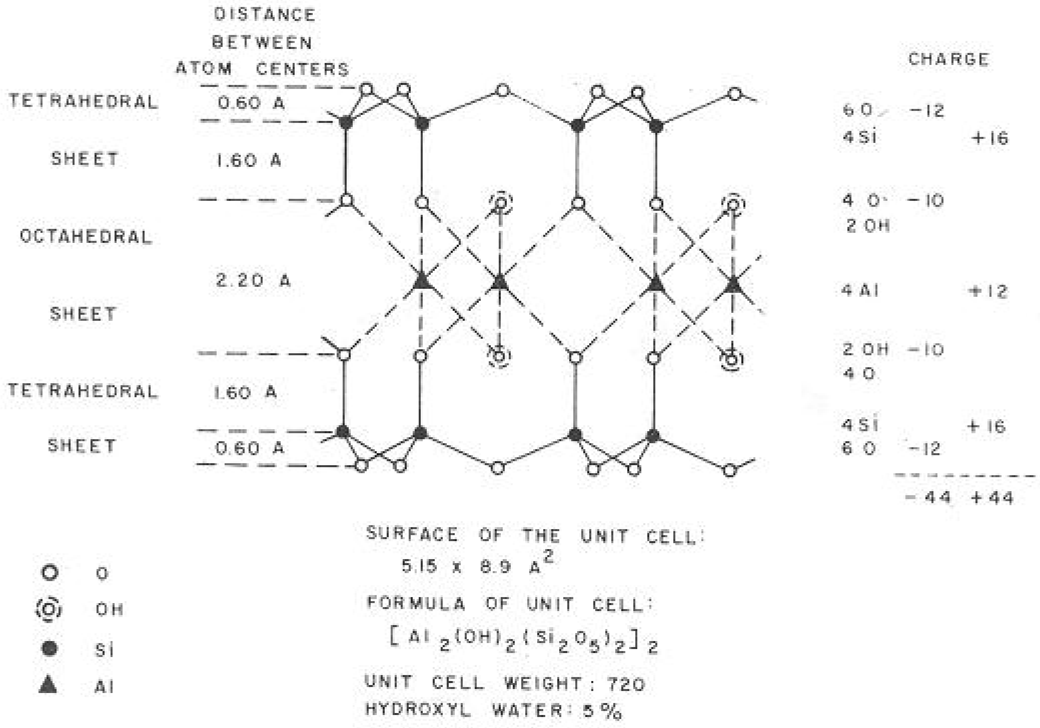


Figure 8. Atomic arrangement in the unit cell of a 2:1 layer mineral.

The combination of an octahedral sheet and one or two tetrahedral sheet is called a layer. Within each layer a certain unit repeats itself in a lateral direction and is called a unit cell. In the columns on the right of Figures 7 and 8, the positive and negative atom valences are tabulated. From the equality of the sums of positive and negative valences, it follows that in the depicted unit cells all valences are saturated.

1.5.3. Source of Clay Mineral Negative Charge

In the tetrahedral sheet tetravalent Si is sometimes partly replaced by trivalent Al. In the octahedral sheet, there may be replacement of trivalent Al by divalent Mg without complete filling of the third vacant octahedral position. Fe, Cr, Zn, Li and other atoms may also replace Al atoms. Replacement of atom of higher positive valence by lower positive valence atom results in a deficit of positive charge, or, in other words, an excess of negative charge. This excess of negative layer charge is compensated by adsorption of cations (Na^+, K^+, NH_4^+, Cs^{+2}, Ca^{+2} etc) on the layer surfaces.

In the presence of water, the compensating cations on the layer surface may be easily exchanged by other cations when available in solutions; hence they are called exchangeable cations. The total amount of these cations expressed in milliequivalent per 100 g of dry clay is called the cation exchange capacity. These cation exchange capacities predetermine clay minerals for preparation of clay modified electrodes.

1.5.4. Classification of the Clay Mineral

On the basis of currently available data on their structure and compositions, the crystalline clay minerals are broadly classified into the following main groups:

Montmorillonite

Montmorillonite is a clay mineral composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. When these units are stacked one above the other a 2:1 layering is formed.

The chemical formula for montmorillonite is $(Si_{7.8}\ Al_{0.2})^{IV}(Al_{3.4}\ Mg_{0.6})^{VI}O_{20}(OH)_4$. The formula indicates that there is a substitution of Si^{4+} by Al^{3+} in the tetrahedral layer and of Al^{3+} by Mg^{2+} in the octahedral layer. In order to calculate the net charge of montmorillonite, one has to remember that the charge of Si is +4, Al is +3, Mg is +2, oxygen is -2 and OH is -1. Thus net layer charge of montmorillonite per unit cell is:

$$= [7.8(+4)] + [0.2(+3)] + [3.4(+3)]+[0.6(+2)] + [[20(-2)] + [4(-1)]$$
$$= 43.2 - 44.0$$
$$= -0.8 \text{ charge/unit cell}$$

Kaolinite

The unit cell of kaolinite contains the octahedral and tetrahedral layers in a ratio 1:1. The two units are stacked one above the other and results in 1:1 layering. The chemical formula of kaolinite is $(Si_4)^{IV}(Al_4)^{VI}O_{10}(OH)_8$, which indicates that there is no substitution of Si^{4+} with Al^{3+} in the tetrahedral layer and no substitution of Al^{3+} with Mg^{2+}, Zn^{2+}, Fe^{2+}, Ca^{2+}, Na^{+}, or K^{+} in the octahedral layer.

The net layer charge of kaolinite is:

$$
\begin{aligned}
&= [4(+4)] + [4(+3)] + [10(-2)] + [8(-1)] \\
&= 28 - 28 \\
&= 0
\end{aligned}
$$

In nature, kaolinite has a small net negative charge because the clay crystals have broken edges.

Illite

The unit cell of illite contains two silicon tetrahedral layers and one aluminum octahedral layer. The formula for illite is $(Si_{6.4}\ Al_{1.6})^{IV}(Al_4)^{VI}O_{20}(OH)_4K_{1.4}M_{0.2}{}^{+}$. There is no substitution for Al in the octahedral layer but there is significant substitution in the tetrahedral layer. The potassium (K) and metal (M) ions are present to satisfy the negative charge and will not be used in the calculation of negative charge. Thus net layer charge of illite per unit cell is:

$$
\begin{aligned}
&= [6.4(+4)] + [1.6(+3)] + [4(+3)] + [[20(-2)] + [4(-1)] \\
&= 42.4 - 44.0 \\
&= -1.6 \text{ charge/cell}
\end{aligned}
$$

1.6. Chemically Modified Carbon Paste Electrodes

Carbon paste electrode (CPE), an electrode made from a mixture of electrically conducting graphite powder and various water-immiscible, non-conducing, low volatile organic liquid, was introduced by Adams in 1958 [43]. Carbon paste electrode has been employed over the past 45 years in electroanalytical chemistry as a substitute for noble metals because it decreased residual currents while providing a very wide range of anodic and cathodic potentials. Moreover, carbon paste electrode offer many advantages: it is inexpensive, easy to prepare, easy to handle, easy to modify, and easily renewable. [44, 45].

In a carbon paste electrode, the low volatile organic pasting liquid serves the useful purpose of filling up the crevices between the graphite particles and maintaining a firm electrode shape. A wide choice of pasting liquid is possible, but practical considerations of low volatility, purity, and economy narrow the choice to a few liquids. These include Nujol, paraffin oil, silicone grease, and bromo naphthalene [46]. The paste composition strongly affects the electrode reactivity; with the increase in the pasting liquid content decreasing the electron transfer rates [47].

The modification of carbon paste electrode began in 1964 with the fundamental studies of Kuwana and co-workers who dissolved electroactive organic compounds in the liquid component of the paste to investigate their electrochemical behaviors [48, 49]. The studies of Kuwana and co-workers could be considered to be the first pioneering contribution to the forthcoming development of chemically modified carbon paste electrodes (CM-CPEs) in the 1970s.

After a decade of the work of Kuwana and co-workers, in 1975 Murray and co-workers [50] introduced the expression ʿChemically Modified Electrode' into the field of electrochemistry to designate an electrode with a chemically active species deliberately immobilized onto its surface. Chemically modified electrodes diverge sharply from the traditional field of adsorption on electrode surfaces. The most essential difference is that one deliberately seeks [51, 52] in some hopefully rational fashion to immobilize a chemical on an electrode surface so that the electrode thereafter displays the chemical, electrochemical, optical, and other properties of the immobilized molecule(s) [53].

The actual breakthrough for widespread application of modified carbon paste electrode was triggered by the work of Ravichanrdan and Baldwin in 1981, who proposed a simple approach to the modification of carbon paste electrode [54].

Recently, chemically modified carbon paste electrodes represent a modern approach to electrode system [46]. They are characterized by deliberately altered surface with material, which reacts selectively and reversibly with the target analyte [55]. Specific reactions at the modified surface represent an efficient way for accumulation of the target analyte, from dilute solution, onto the electrode surface prior to quantitation of the analyte by the usual voltammetric measurements. The rich chemistry that can be used for preconcentration at these molecularly tailored electrodes offers exciting prospects for trace analysis of organic and inorganic compounds [56]. Hence, chemically modified carbon paste electrodes have attracted considerable attention for their application in electroanalytcal chemistry in recent years.

1.6.1. Reasons for Modification

Electrochemical methods based on direct reduction or oxidation of the analyte at bare electrodes are not always suitable for analytical applications, due to the high overvoltage required for the electrode charge transfer to occur or poisoning adsorption (unwanted reaction) on the electrode surface, leading to unreliable, poorly reproducible responses. The modification of the electrode surface is acknowledged as a suitable method of possibly overcoming both obstacles, and improving its analytical performance [57].

Because of the above advantages, chemically modified electrodes have been widely applied in voltammetric procedures involving an analyte preconcentration step prior to electrochemical measurements. The preconcentration step preceding the measurement can be performed with or without the application of potential (closed or open-circuit condition, respectively) depending on the nature of the preconcentration. The accumulated analyte in this way is subsequently measured by its electrochemical response to a potential step or sweep. This approach is an interesting analytical tool because it allows the construction of sensitive voltammetric sensors and developments of novel analytical procedures that are specific, or at least selective, for a particular analyte once a judicious choice of modifier and experimental conditions have been made [58].

1.6.2. Advantages of Chemically Modified Carbon Paste Electrodes

Besides their non-toxicity, chemically modified carbon paste electrodes are endowed with many interesting qualities including ease of fabrication, convenient renewability providing a fresh surface unaffected by the electrode story, low background current allowing the determination of low analyte concentrations, low cost, and wider useful electrochemical windows [44, 59]. There are broad range of materials and methodologies of electrode modification that can be employed for such purpose.

1.6.3. Methods of Modification

One of the merits of chemically modified carbon paste electrodes is their ability to be easily fabricated. Some of principal routes to modify carbon paste electrodes include:

Direct Mixing

This method is most commonly used for preparing chemically modified carbon paste electrodes. The unique advantage of this approach is pronounced ease of modification, most simply done by admixing of a reagent (modifier) to the paste [60]. In order to obtain reproducible and comparable results, the concentration of the modifier on the electrode surface must be similar in analogous experiments. For this reason thorough mixing of the two solid phases is essential to ensure that the same amount of modifier is always exposed to the analyte solution.

Electrode Coating

The basal plane of the carbon electrode is cleaned and polished. Then, the electrode coating modifier dissolved in a suitable solvent is transferred on the exposed area of the electrode and allowed to dry [61]. While this method is simple, it is difficult to control the amount of material that ends up on the electrode surface. Hence, spin coating is mostly used to yield uniform film thickness [62].

1.6.4. Requirements for a Modifier

In general, the modifiers used with direct mixing method should meet the following criteria. First of all, they should be insoluble in the analyte solution, or they should at least strongly adsorb to the paste components in order to avoid dissolution of the molecules from the electrode surface during the measurement. Otherwise, its leaching causes modifier concentration gradients in the surroundings of the electrode surface as well as variable amounts in the interface itself. This, in turn, results in poor reproducibility of the analytical signal. The other important requirement is that the modifier itself should not undergo electrochemical transformations around the redox potential of the analyzed species. Otherwise, the high background current would reduce or even impair the desired analytical properties of the electrode [63].

One selects modifier for a particular analysis on the basis of known and desired properties such as the modifier’s affinity and specifity for the species to be extracted. The kinetics of the reaction should also be moderately fast both to shorten the time of analysis and to avoid diffusion from the surface into the paste where it is not accessible for the measurement.

1.7. Objectives of the Present Study

The desire of electrochemist to reach the perfect electrode surface of required properties and of excellent quality together with their effort to understand and to control adsorption processes on the electrode surface have led to the development of chemically modified electrodes [64].

Among several modifier molecules, it is well documented that, the use of polymer modified electrode in preconcentration and detection of electroactive species and in supporting redox mediators for electrocatalysis has rapidly diffused more and more widely since the beginning of the 80's. In the last decade, attention has been also devoted to the possibility of modifying an electrode surface with inorganic structured materials such as zeolites, clays or microporous solids. When compared with organic polymers, these materials exhibit interesting peculiarities, such as good or even excellent stability, chemical inertia, tolerance to high temperatures and to extremely oxidative conditions [65].

From electrodes modified by inorganic structured materials, clay modified electrodes have attracted the attention of many electrochemists during the last decade [37]. In 1983 Ghosh and Bard [66] described the first electrode modified with clay film and further studies of electrochemical behavior of redox couples on clay modified electrodes were started since that moment by a number of researches.

Very recently, clay minerals are employed for the modification of the electrode surface. These clay minerals have many attractive properties to be utilized for the modification of the electrode surface. Clays are aluminosilicates that presents a number of interesting properties such as cation exchange capacity, intercalation, porosity, catalytic activity and sorption [67]. Clay modified electrodes have recently been widely investigated for their application in chemical and biochemical analysis [36].

In this work, it is planned to combining the interesting concepts mentioned above for the electrochemical determination of simazine (triazine herbicide) by using clay modified carbon paste electrode. The clay to be used to modify the electrode in this work is montmorillonite, which is efficient for electrode modification.

The specific objectives of the present study are directed to:

(i) study the electrochemical behavior of simazine at clay modified electrode.

(ii) establish the optimal experimental parameters for the determination of simazine at the clay modified electrode (i.e., to study the basic electroanalytical parameters of the modified electrode, such as effect of clay amount, pH of solution, accumulation time, accumulation potential, liner range, sensitivity, detection limit, etc).

(iii) study the analytical application of the developed method for determination of simazine in synthetic potable water sample.

2. Theoretical Backgrounds

2.1. Cyclic Voltammetry

Cyclic voltammetry (CV) is one of the first electroanalytical techniques reported in 1938 and described theoretically in 1948 by Randles and Sevcik. It has grown enormously in popularity over the past few decades, so much so that obtaining CV is often the first experiment performed by the electrochemist, giving invaluable information as to the presence of electroactive species in solution or at the electrode surface. The effectiveness of cyclic valtammmetry results from its ability for rapidly observing redox behavior over the entire potential range available [46].

Cyclic voltammetry is an essential technique for initial electrochemical studies of new systems and has proven very useful in obtaining mechanistic information about fairly complicated electrode reactions. Although CV is particularly useful in qualitative studies of electrode processes, it is less well suited for quantitative determinations. Its merits are, thus, largely in qualitative experiments. Quantitative measurements are best obtained by employing other (step or pulse) techniques [68, 69].

Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode, using a triangular potential waveform (Fig. 9). Depending on the information sought, single or multiple cycles can be used. During the potential sweep, the triangular potential excitation signal causes the potential of the working electrode to sweep between two designated values, called the switching potentials. During the potential sweep, the potentiostat measures the current resulting from the applied potential. The resulting plot of current vs. potential is termed a cyclic voltammogram (Fig. 10).

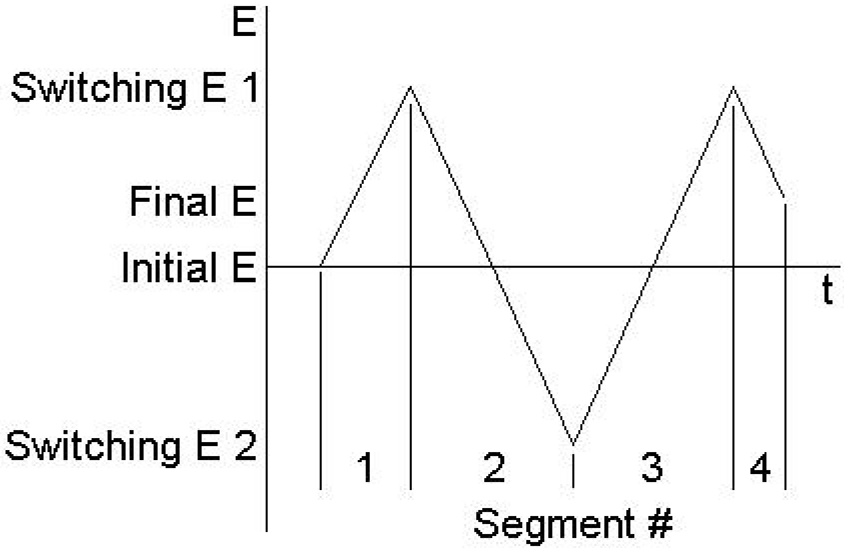


Figure 9. Potential waveform for cyclic voltammetry.

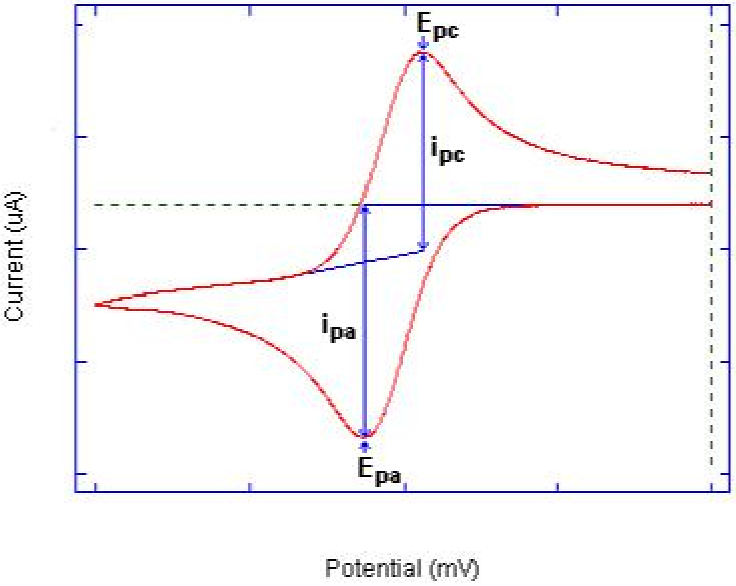


Figure 10. A typical cyclic voltammogram showing the important peak parameters.

Reversible systems

A redox couple in which both species rapidly exchange electrons with the working electrode is termed a reversible system.

The important parameters of a cyclic voltammogram are the magnitude of the anodic peak potential (E_{pa}), cathodic peak potential (E_{pc}), anodic peak current (i_{pa}), and cathodic peak current (i_{pc}).

The expression of the peak current for a reversible couple (at 25°C), is given by the Randles-Sevcik equation:

$$i_p = (2.69 \text{ x } 10^5)\, n^{3/2} AC^*D^{1/2}\upsilon^{1/2} \qquad (1)$$

where i_p = peak current, n = is the number of electron equivalent exchanged during the redox process, A= the active area of the working electrode, D and C* are the diffusion coefficient and the bulk concentration of the electroactive species respectively, υ is the voltage scan rate.

Accordingly, the peak current is directly proportional to the concentration and increases with square root of scan rate. The relation of i_p to bulk concentrations is particularly important in analytical applications and in studies of electrode mechanisms. The values of i_{pa} and i_{pc} are similar in magnitude for a simple reversible electron transfer reaction, i.e., $i_{pa}/i_{pc} \approx 1$. However, the ratio of the peak current can be significantly influenced by the chemical reactions coupled to the electrode process. For example, if there is a chemical reaction following the electron transfer reaction, the peak current on the reverse scan is decreased.

The position of the peaks on the potential axis (E_p) is related to the formal potential of the redox process. The formal potential for a reversible couple is centered between E_{pa} and E_{pc}:

$$E^\circ = (E_{pa} + E_{pc})/2 \qquad (2)$$

The separation between the peak potentials (for a reversible couple) is given by:

$$\Delta E_p = E_{pa} - E_{pc} = 59/n \text{ mV} \qquad (3)$$

Thus, the peak separation can be used to determine the number of electrons transferred, and as a criterion for a Nernstian behavior. Accordingly, a fast one electron process exhibits a ΔE_p of about 59 mV.

Irreversible Systems

For irreversible processes (those with sluggish electron exchange), the individual peaks are reduced in size and widely separated, i.e., the separation of peak potentials is greater than 59/n mV.

The peak current, given by:

$$i_p = (2.99 \times 10^5) n (\alpha n_a)^{1/2} A\, C^* D^{1/2} \upsilon^{1/2} \qquad (4)$$

where α is the transfer coefficient and n_a is the number of electrons involved in the charge transfer step, is still proportional to the bulk concentration, but will be lower in height (depending upon the value of α) [46, 68, 69]. For totally irreversible systems, the reverse scan may not reveal any peak.

2.2. Differential Pulse Voltammetry

The basis of all pulse techniques is the difference in the rate of the decay of the charging and the faradaic currents following a potential step (or "pulse"). The charging current decays exponentially, whereas the faradaic current (for a diffusion controlled current) decays as a function of $1/(\text{time})^{1/2}$; that is, the rate of decay of the charging current is considerably faster than the decay of the faradaic current. The charging current is negligible at a time of $5R_uC_{dl}$ after the potential step (R_uC_{dl} is the time constant for the electrochemical cell, and ranges from µs to ms). Therefore, after this time, the measured current consists solely of the faradaic current; that is, measuring the current at the end of a potential pulse allows discrimination between the faradaic and charging currents.

When the background current is large and/or coverage of the attached redox species is low, greater sensitivity is needed to detect electroactivity of surface redox species. Differential pulse voltammetry (DPV) was introduced for such situations. Differential pulse voltammetry is one of the most important and versatile achievements for electrochemical measuring of trace levels of organic and inorganic species. It is now incorporated in every voltammetric device as the most significant function for analytical practice. Recording of the response from differential pulse mode applied in voltammetry is performed according to the principle introduced by Parry and Osteryoung [70, 71].

The potential waveform for differential pulse voltammetry is shown in Figure 11. The potential waveform consists of small pulses (of constant amplitude) superimposed upon a staircase waveform. These fixed magnitude pulses are applied to the working electrode. Current is measured at two points for each pulse, the first point (1) just before the application of the pulse and the second (2) at the end of the pulse. These sampling points are selected to allow for the decay of the non-faradic (charging) current. The first current is instrumentally subtracted from the second, and this current difference is plotted against the applied potential. The resulting differential pulse voltammogram (Fig. 12) consists of a current peak, the height of which is directly proportional to the concentration of the corresponding analyte:

$$i_p = nFA\, C^*(D/\pi t_p)^{1/2}\, (1-\sigma)/(1+\sigma) \qquad (5)$$

where $\sigma = \exp(nF\Delta E/(2RT))$

ΔE = pulse amplitude

$t_p = t - t'$, t' and t are the first and second current sampling time respectively.

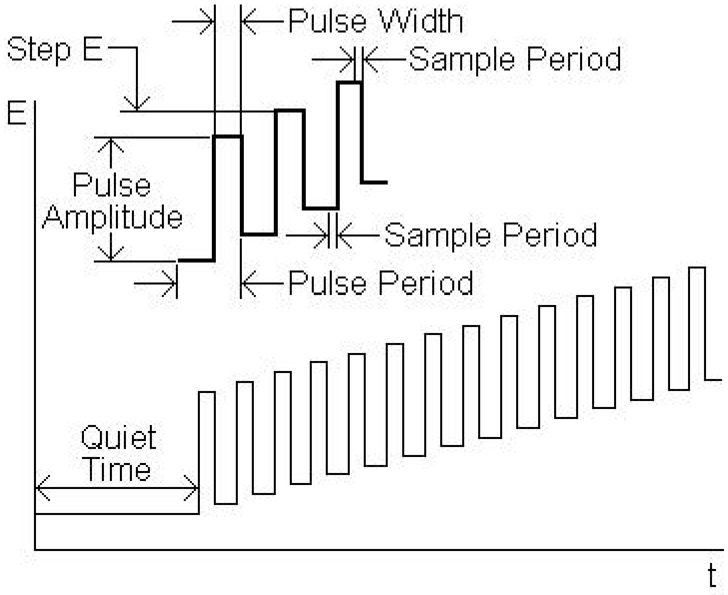


Figure 11. Potential waveform for differential pulse voltammetry.

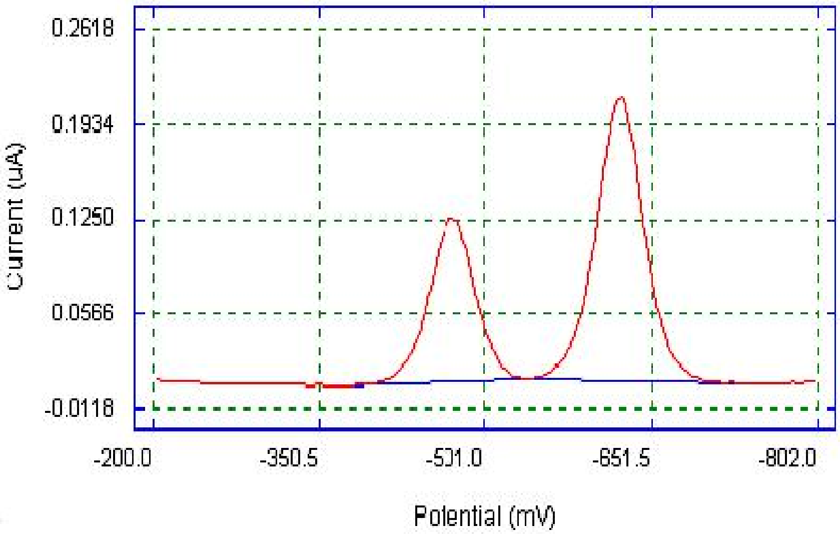


Figure 12. A typical differential pulse voltammogram.

The differential pulse operation results in a very effective correction of the charging background current. Such background contribution is smaller by more than an order of magnitude than the charging current of normal pulse voltammery. Accordingly, differential pulse voltammetry allows measurements at concentrations as low as 10^{-8} M.

2.3. Stripping Voltammetry

Modern life makes very diverse demands on analytical electrochemistry. Present problems in technology, biology, environmental protection and medicine and other fields require determination of ever decreasing amounts of substances in progressively more complex systems and so place increasing demands on the method of trace analysis. Among these methods votammetric stripping analysis occupies a relatively important place. It combines extraordinary determination sensitivity (especially when combined with DPV) with inherently high accuracy and good precision. Its analytical power originates from the unique coupling of an effective preconcentration step with an advanced measurements scheme of the accumulated substance. The instrumentation is very compact and can, therefore, be easily used in field studies. The costs invested for instrumentation are also significantly lower than any of the other alternatives in trace organic and inorganic analysis [72].

Conventionally, voltammetric stripping method employs a two-step approach: First, the analyte species in the sample solution is concentrated onto or into a working electrode. It is this crucial preconcentration step that results in the exceptional sensitivity that can be achieved. During the second step, the preconcentrated analyte is stripped from the electrode by the application of a potential scan. Any number of potential waveforms can be used for the stripping step (i.e., differential pulse, square wave, linear sweep, or staircase). The most common are differential pulse and square wave due to the discrimination against charging current. Stripping voltammetry is a very sensitive technique for trace analysis.

The voltammetric stripping method may be classified as anodic stripping voltammetery (ASV), cathodic stripping voltammetry (CSV), and adsorptive stripping voltammetry (AdSV).

2.3.1. Anodic Stripping Voltammetry

Anodic stripping voltammetry (ASV) is most widely used for trace metal determination and has a practical detection limit in the per-trillion range. This low detection limit is coupled with the ability to determine simultaneously four to six trace metals using relatively inexpensive instrumentation. It involves non-electrolytic preconcentration and the metal ions or their complexes concentrated on the electrode surface are reduced to the elemental forms by the application of a sufficiently negative potential for a preselected time period. These reduced metals are then stripped (oxidized) from the surface of the electrode by scanning the applied potential in the positive direction. The resulting peak currents (i_p) are proportional to the concentration of each metal in the sample solution, with the position of the peak potential (E_p) specific to each metal.

2.3.2. Cathodic Stripping Voltammetry

Cathodic stripping voltammetry (CSV) is the mirror “image" of ASV. Briefly, it involves anodic deposition of the analyte on the electrode; and subsequent stripping off during a negative going potential scans. It is best suited for the determination of inorganic anions such as halide, sulfide and oxyanions such as MoO_4^{2-} and VO_3^{5-}.

2.3.3. Adsorptive Stripping Voltammetry

Adsorptive stripping voltammetry (AdSV) is quite similar to anodic and cathodic stripping methods. The primary difference is that the preconcentration step of the analyte is accomplished by adsorption on the electrode surface or by specific reactions at chemically modified electrodes. The adsorbed species is quantified by using voltammetric techniques such as differential pulse voltammetry or square wave voltammetry either in the negative or positive direction to give a peak shaped voltammetric response with amplitude proportional to concentration. Many organic species (such as heme, chlorpromazine, codeine, and cocaine) have been determined at micromolar and nonmolar concentration levels using AdSV.

2.4. Choice of Operating Parameters in Differential Pulse Adsorptive Stripping Voltammetry

2.4.1. Type of Working Electrode

A working electrode acts as a source or sinks of electrons for exchange with molecules in the interfacial region (the solution adjacent to the electrode surface), and must be an electronic conductor. It should provide a favorable signal to noise characteristics, as well as reproducible response. It would be better if the electrode has wider potential range of utility, low resistance, and low background current. The suitability of an electrode for analytical application can also be dictated by electrons transfer rate, mechanical properties, and type of reaction used for accumulation. The cost, availability, and stability during storage must be taken in account as well [72, 73].

2.4.2. Stirring the Electrolyte Solution

Because electrolysis and open circuit accumulations are heterogeneous reactions, mass transport of materials toward and away from the electrode is an important consideration. Though the transport in unstirred solutions (via diffusion) is very reproducible, it is much slower than that of convection. Therefore, in most cases it will be desirable to agitate the solution in order to speed up mass transport during accumulation and cleaning. However, the stirring must be uniform, gentle and at a controlled rate. The position of electrodes within the cell and hence the solution should also be reproducible [74].

2.4.3. Choice of Waveform

It is important to choose a waveform that can suitably be used for measuring the surface bound analyte. For instance, the peak shaped response of differential pulse voltammograms has increased sensitivity due to the discrimination against charging current. This favorable feature has made differential pulse a waveform of chose for the voltammetric determination of trace organic species. Once the waveform chosen, the various waveform parameters such as accumulation potential, accumulation time, scan rate, etc., should be optimized.

2.4.4. Accumulation Potential

The efficiency of accumulation of trace amount of organic compounds as a preconcentration technique for analysis is significantly influenced by the applied potential for accumulation. Accumulation potential used in the preconcentration step is the most important variable, since it essentially controls the adsorption rate. Therefore, the accumulation potential that result in higher current response should be selected.

2.4.5. Accumulation Time

Generally speaking, the concentration of the analyte around the surface of the electrode is directly related to the accumulation time provided the concentration of the analyte being determined scarcely decreases during the measuring process. If direct proportionality between the final signal and the accumulation time is to be maintained, the accumulation time must not be too long. It is advisable to use relatively short accumulation time for higher analyte concentration in order to avoid saturation and the subsequent non linearity between concentration and voltammetric signal. On the other hand, it is possible to enhance the sensitivity of the stripping determination by employing prolonged accumulation periods for lower concentration.

2.4.6. Pulse Amplitude

It can be seen from equation 5 that peak current (i_p) increase as pulse amplitude, ΔE increases because $[(1-\sigma)/(1+\sigma)]$ approaches unity as pulse amplitude increases. However, the peak width also increases with increasing pulse amplitude. It can also increase residual current ending up in peaks deformation. Therefore, the optimum pulse amplitude must be found to maximize both sensitivity (i_p) and resolution (small peak width).

2.4.7. Scan Rate

The choice of scan rate is one of the most important instrumental variable that requires due consideration. Just like pulse amplitude, fast scan rate increases the height of the peak accompanied by the undesirable peak broadening. On the other hand, very slow scan rates give low but narrow signals and, increase the total analysis time. Hence, the selection of scan rate usually requires a compromise among sensitivity, resolution, and speed.

3. Experimental

3.1. Reagents and Chemicals

Montmorillonite clay (Aldrich), graphite powder (Fluka-Switzerland), paraffin oil (Fluka-Switzerland), simazine (Dr. Ehrenstorfer - Schafers Bgm. - Schlosser - Str. 6A. D - 86199 Ausburg. Germany), methanol, KOH, KCl, NaCl, $AgNO_3$, and H_2SO_4 were used as received. A stock solution (1×10^{-2} M) of simazine was prepared in methanol by weighing and kept in a refrigerator. Working standard solutions of lower concentrations were prepared freshly by dilution of stock solution in 30% (v/v) methanol aqueous solution to ensure the solubility of simazine. The pH of the medium was varied between 0.4 and 3.2. A solution, made of 0.1 M KOH, 0.1 M KCl and 0.1 M H_2SO_4 in 30 % (v/v) aqueous methanol was used as the medium for the analysis. For measurements at pH < 1.2, 2.25 M H_2SO_4 was used. After addition of simazine the pH of cell solutions was measured and adjusted to the required pH value using 0.1 M KOH or 0.1 M H_2SO_4 solutions. All solutions were prepared from distilled water.

The Na^+ form of clay was prepared by adding 2.5 g of montmorillonite clay, surface area 20 - 40 m^2/g, to 100 mL of a 1.0 M NaCl solution and stirring with a magnetic stirrer for 72 hr. Colloids were prepared by centrifuging the above suspensions at 1200 rpm for 30 min. The clear supernatant was discarded and 100 mL of distilled water was added and the mixture was stirred for 30 min. This procedure was repeated until a negative chloride test was obtained. Then supernatant was decanted and clay colloid was dried at room temperature.

3.2. Apparatus

The electrochemical behavior of simazine at clay modified carbon paste electrode was studied by voltammetric method using a BAS-100W electrochemical analyzer (Bio-analytical systems) connected to a personal computer. A one compartment electrochemical cell with a three electrode system (clay modified or unmodified carbon paste electrode as working electrode, Ag/AgCl saturated with KCl as reference electrode, and a platinum wire as the auxiliary electrode) was used for the measurement. The measurements were repeated with each solution until a good reproducibility of the result was obtained. A pH 300 series bench top pH meter (Hanna instruments) was used for the measurement of pH. A magnetic stirrer (Cole-Parmer instruments Company) with a Teflon coating stirring bar and centrifuge (EBA 20 Zentrifugen) were used during preparation of clay colloid. A magnetic stirrer with a Teflon coating stirring bar was also used in the preconcentration and cleaning steps to provide convective transport. Standard solutions were added to the electrochemical cell with a micropipette with disposable tips. A stop clock (Harris Digitmer) was employed for time measurement. Figure 13 shows the experimental set up schematically.

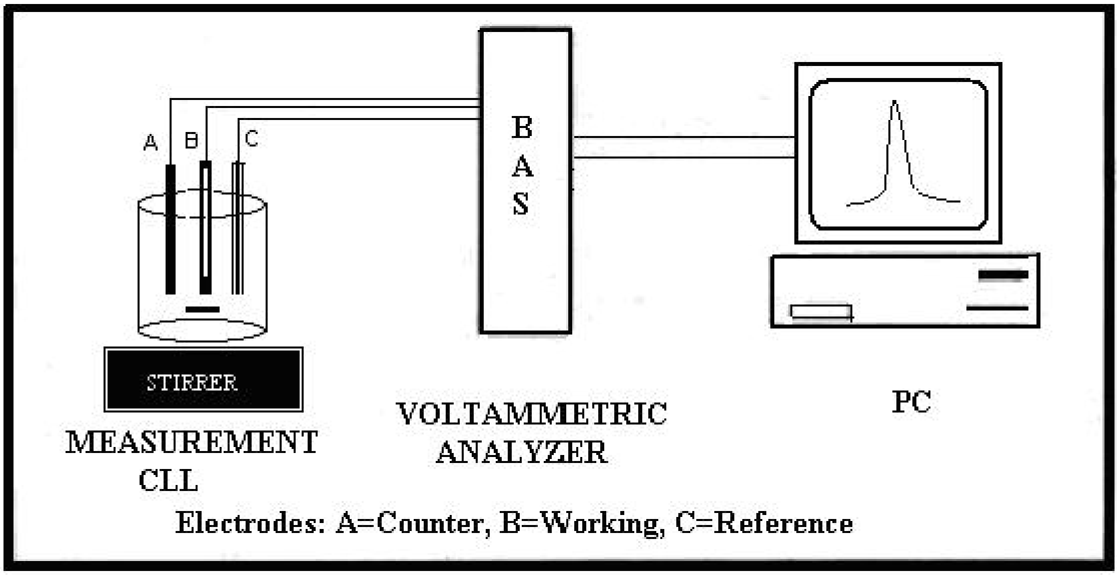


Figure 13. Experimental set up for the study of voltammetric behavior of simazine at clay modified carbon paste electrode.

3.3. Preparation of a Working Electrode

In general, carbon paste electrodes (CPEs) modified with clay mineral are prepared by the same way as other modified carbon paste electrodes.

Unmodified carbon paste was prepared by adding 0.36 mL paraffin oil to 1 g of carbon powder. Modified carbon paste was prepared by substituting corresponding amount of the carbon powder (5%, 10%, 15%, 20% and 25% weight – to – weight ratio) by clay and then adding the paraffin oil and thoroughly hand-mixing in a mortar and pestle for 40 min. Thorough homogenization during mixing clay with carbon powder is very important to obtain reproducible measurement on the modified electrode. The CPE body was fabricated from 1 mL plastic syringes (B/BRAUN) of 3 mm outer diameter and the electric contact was made in the center of the rod with the carbon paste through a copper wire as shown in Figure 14.

Unmodified and modified carbon paste electrodes were prepared by pressing the unmodified and modified carbon paste respectively into the well (3 mm diameter) of a plastic syringe electrode body by a spatula. Then, their surfaces were smoothed against a plain white paper while a slight manual pressure was applied to the plastic syringes until a shiny surface emerged.

The freshly assembled and polished clay modified electrode was conditioned by subjecting it to few cyclic scan in the supporting electrolyte followed by accumulation of simazine from the preconcentration medium and the subsequent electrochemical stripping and regenerations schemes to improve its performance. The preconditioned electrode had good stability, sensitivity, and reproducibility. A single preconditioned electrode surface could be used for 5 to 7 measurements without a decrease in reproducibility. Thereafter the clay modified carbon paste electrode had to be renewed and conditioned again. The modified electrodes were stored at room temperature.

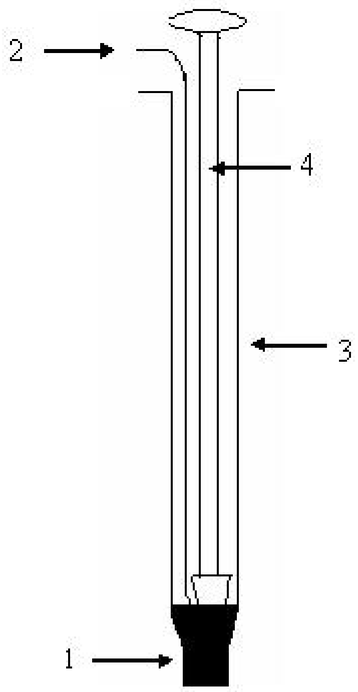


Figure 14. Clay modified carbon paste electrode: (1) paste, (2) copper wire, (3) syringe body and (4) piston.

3.4. Voltammetric Procedure

Cyclic Voltammograms (CVs) of the unmodified and modified electrodes were run after purging the solution containing simazine for at least 10 min with argon via a Teflon tube. During the measurement argon was passed over the solution. The CVs were recorded between 0 and –1.3 V.

To achieve the best condition for the trace analysis of simazine, differential pulse adsorptive stripping voltammetry were used. Adsorptive stripping analysis is a two-step technique. The first step involves the adsorption of a small portion of the analyte on the electrode surface for preconcentration. The second step involves stripping of the adsorbed analyte from the electrode surface by the application of potential. For the preconcentration step, appropriate amounts of simazine working solutions were placed in a voltammetric cell containing a supporting electrolyte solution at the selected pH and the magnetic stirrer was switched on.

Afterwards, a stream of argon was bubbled through the solution for 10 min to de-aerate it. The solution was stirred with magnetic stirrer at rate of 1000 rpm at a chosen accumulation potential throughout the selected accumulation period. The stirring was then stopped and after a 10 s rest (equilibration) period cathodic sweep was carried out towards more negative potentials, using the selected voltammetric technique. All experiments were carried out at room temperature.

3.5. Preparation of Sample Solution

Potable water was collected from a municipal water supply pipeline in the Electroanalytical Chemistry Laboratory. It was sampled after allowing the water to flow out in full stream for one minute before collection.

Supporting electrolyte solution of pH 2.0 was prepared in 100 mL pipe water. Then the water sample was spiked with simazine to a concentration of 4.0×10^{-6} M. A 25 mL aliquot of this solution was transferred into the preconcentration cell for simazine accumulation and subsequent voltammetric measurements. The amount of simazine in the water sample was quantified by standard addition method.

4. Results and Discussions

4.1. Cyclic Voltammetric Investigation

The cyclic voltammetric behavior of simazine at unmodified and clay modified carbon paste electrode was studied. Cyclic voltammograms (CVs) were obtained at unmodified and clay modified CPEs in 0.1 M H_2SO_4 + 0.1 KOH + 0.1 M KCl at pH 2.0. The CV of the unmodified and clay modified electrodes were run with and without accumulation of simazine. The CVs of clay modified and unmodified carbon paste electrodes with and without simazine preconcentration are shown in Figure 15. The clear cathodic peak and the absence of anodic peak on the reverse scan is a good indication of irreversible reaction of simazine at both modified and unmodified CPEs.

The CV of the unmodified electrode without simazine peconcentration (curve-4) shows very small signal but with preconcentration of simazine an enhanced signal (curve-3) was observed. The clay modified electrode without simazine preconcentration (curve-2) showed a voltammetric wave which was greater than that of an unmodified electrode with preconcentration whereas the CV of the modified electrode with simazine preconcentration (curve-1) shows a voltammetric signal which was almost two times the unmodified electrode. The appearance of two-fold increased cathodic peaks in the CV of modified electrode obtained after accumulation of simazine proved qualitatively the ability of the clay modified electrode to preconcentrate simazine from aqueous solutions.

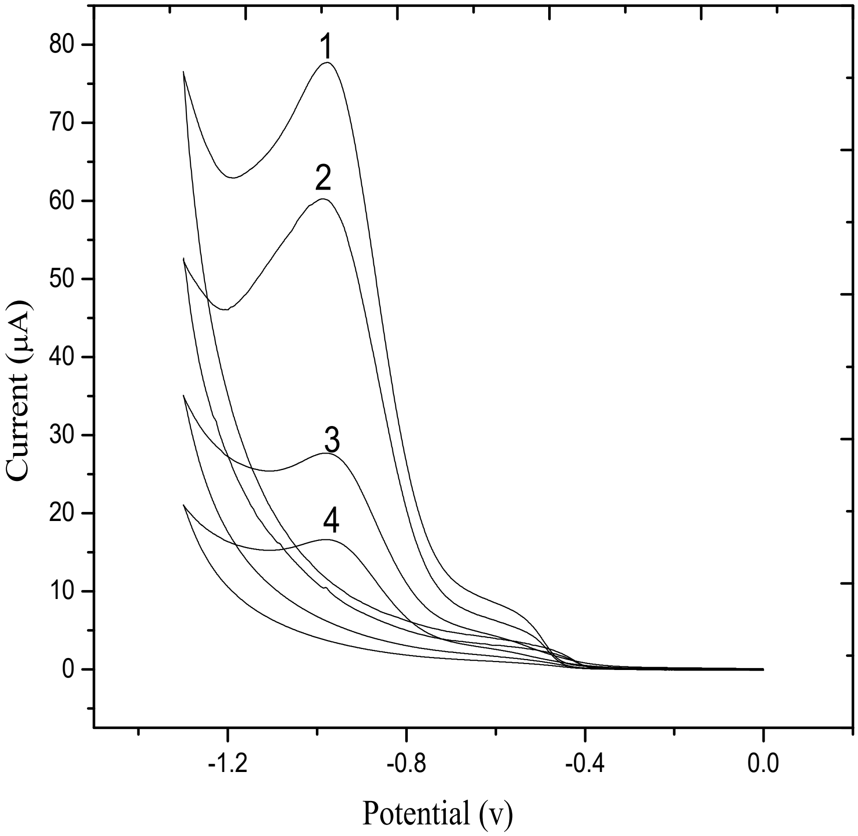
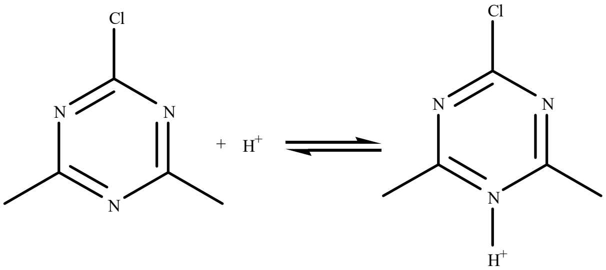


Figure 15. Cyclic voltammograms of 1.0 x 10^{-3} M simazine at scan rate of 100 mV/s: (1) Clay modified carbon paste electrode with simazine preconcentration at pH 2.0; preconcentration time: 1 min; (2) Clay modified carbon paste electrode without simzine preconcentration; (3) unmodified carbon paste electrode with simazine preconcentration at pH 2.0; preconcentration time: 1 min, and (4) unmodified carbon paste electrode without simazine preconcentration.

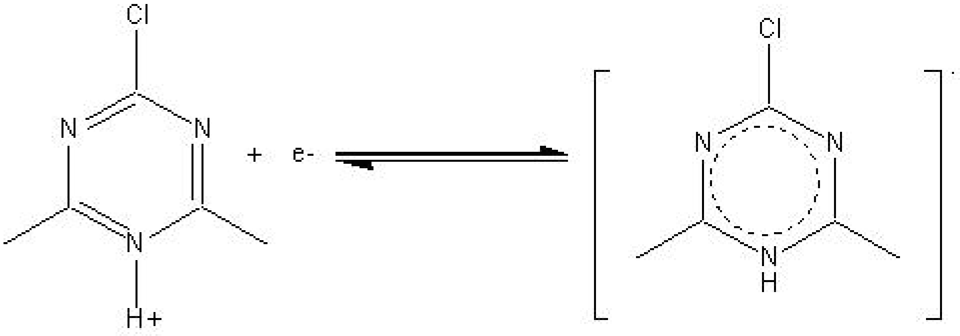
The mechanism of simazine reduction is attributed to the following steps [34]. In the reduction of simazine, it is the protonated form of simazine that undergoes reduction reaction. Therefore the first step is the protonation of simazine ring.



(1)

The above chemical step explain the increased peak current in CV which is because of higher concentration of simazine at the clay modified electrode as a result of electrostatic attraction between the positively charged simazine (protonated simazine) and negatively charged clay mineral.

The protonated form of simazine undergo a two electron ECE process, i.e., a two electron reduction having a chemical step placed between both electron transfers, which is the rate determining step (rds) of the process [34].



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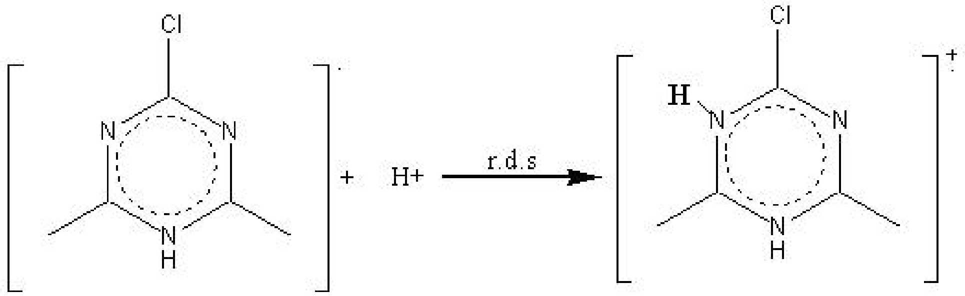
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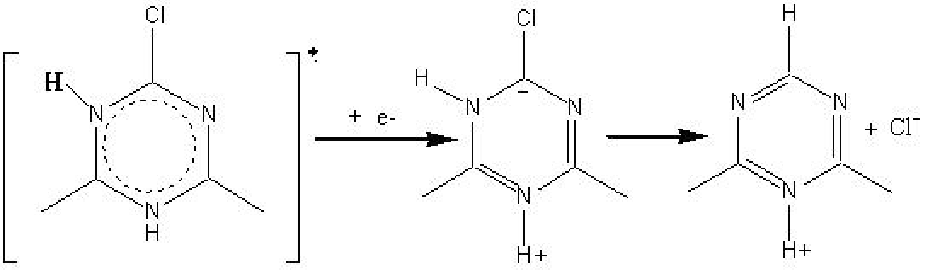
(4)

The reductive cleavage of Cl ion is confirmed by titration of electrolyzed solution with $AgNO_3$ that results in precipitation of AgCl.

4. 2. Differential Pulse Voltammetric Investigation

As can be seen in Figure 16, the reduction peak obtained for simazine with the clay modified electrode is larger than that obtained with the unmodified CPE in differential pulse adsorptive stripping voltammetry. Hence the clay modified electrode was systematically studied by differential pulse adsorptive stripping voltammetry to exploit it for the analysis of simazine.

Evaluation of the analytical performance of clay modified CPE for simazine analysis requires optimization of many aspects of the clay modified electrode, and the associated preconcentration and stripping procedures. These include modifier amount, solution condition during accumulation, preconcentration time, accumulation potential, scan rate, pulse amplitude, pulse period and so on. Accordingly, this study covered a series of experiments in which suitable experimental conditions for the determination of simazine were established. The effect of a particular variable was studied by the procedure described in section 3.4 under identical conditions keeping all the variables constant except the one under study.

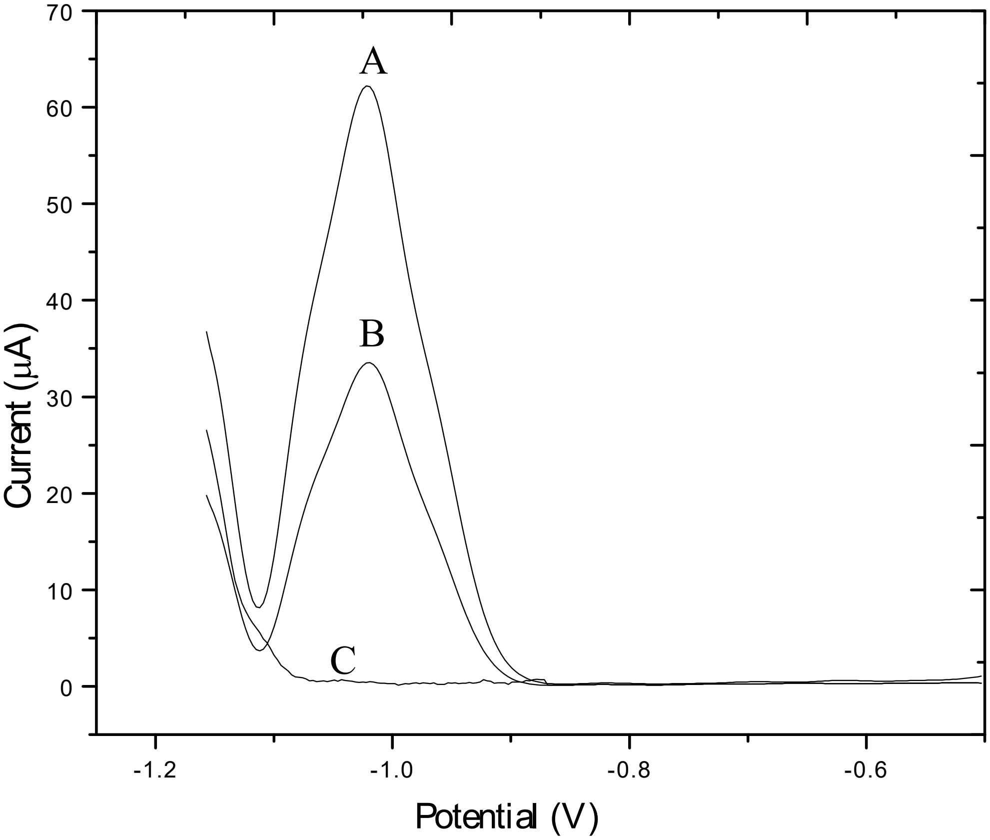

Figure 16. Typical differential pulse adsorptive stripping voltammograms of simazine at: Clay modified carbon paste electrode (A), unmodified carbon paste electrode (B), blank solution of pH 2.0 (C); preconcentration time: 30 sec, accumulation potential: -500 mV; rest time: 10 s; stirring rate: 1000 rpm; scan rate: 100 mV/s; concentration: 40 x 10^{-6} M; pulse amplitude: 100 mV; pulse period: 160 ms.

4.2.1. Effect of the Amount of Clay

The amount of simazine that gets adsorbed on the surface of electrode is expected to be directly affected by the amount of clay on the surface of the electrode. Thus the quantity of clay in the carbon paste is presumed to significantly affect the voltammetric response. There was a small voltammetric signal observed with unmodified electrode after preconcentration either at open circuit or under potential condition. The observed small voltammetric signal indicates very weak adsorption of simazine on the unmodified electrode surface. However, the clay modified electrode gave significantly increased cathodic peak for simazine (Figure 16). This obviously indicates that simazine adsorbed on the clay modified electrode surface during the preconcentration process are responsible for the enhanced voltammetric signal.

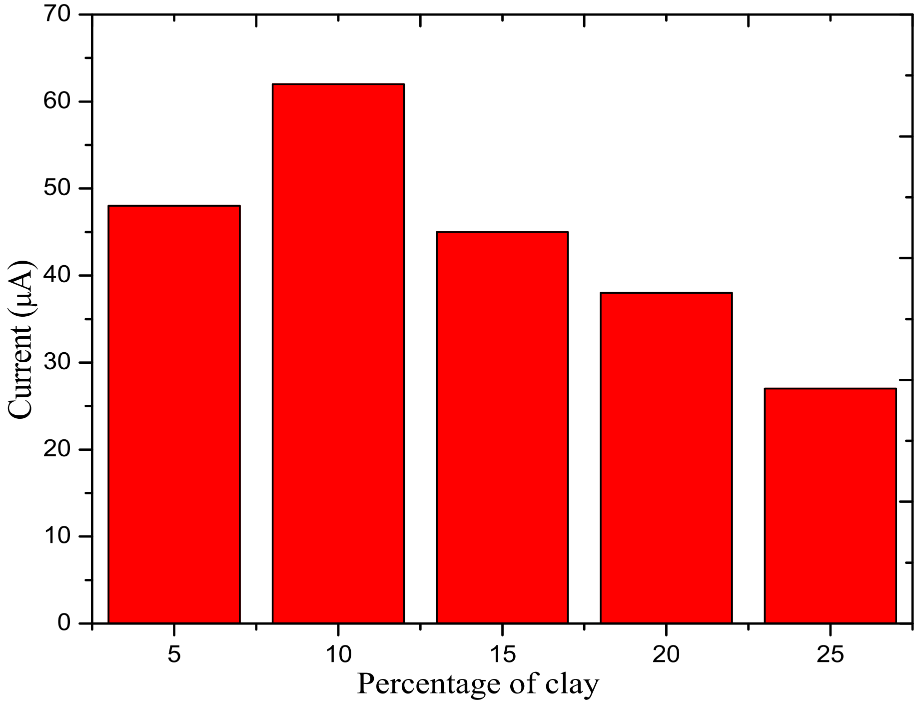

Figure 17. Effect of clay amount on the adsorptive stripping peak current.
Other conditions are as in Figure 16.

The effect of the amount of clay on the peak current was then studied using clay modified electrodes prepared from 5%, 10%, 15%, 20%, and 25% (w/w) of clay and carbon powder-contained pastes under identical conditions. The maximum peak current was obtained when the clay amount in the carbon paste was 10% (Figure 17). Generally, the response is almost constant in the range 8-12% of clay. Electrodes containing either lower or higher clay amount gave smaller voltammetric signal.

Use of electrodes with higher proportion (≥ 15%) led to a decrease in peak intensity owing to the increase in the residual current that distorts the reduction wave of simazine. This high residual current may be due to the increase in the electrode resistance, which resulted in a decreased peak current. The decrease in the peak current can also be attributed to a reduction of real active surface area at the modified electrode. While the decreases in the peak current at lower percentages of clay (≤ 5%) is due to lower extent of adsorption because of relatively lower coverage of the modifier on the electrode surface. Accordingly, an electrode containing 10% clay was employed for all voltammetric experiments.

4.2.2. Effect of pH

The pH of the media used for the purpose of accumulation has profound effect on the voltammetric response. It affects both the rate and equilibrium state of the accumulation process and the rate of the electrode reaction. Therefore, throughout the process of accumulation the pH of the solution plays crucial role. This important variable was studied for simazine at clay modified CPE by differential pulse adsorptive stripping voltammetry in the pH range 0.4 to 3.2. The reduction peak disappeared above pH 3.6, since the reducible species is the protonated form of simazine.

The simazine peak current as a function of pH is shown in Figure 18. Simazine shows different voltammetric behavior in the pH range studied. This different voltammetric behavior may be due to the electrostatic interaction between the simazine and clay modified electrode surface. Therefore, the pH of the solution should influence the accumulation process. Generally clay modified electrode showed negligible accumulations at pH higher than 3.2, whereas in acidic media the accumulation is more favorable. Nevertheless, the amount of accumulated simazine is larger only at pH 2.0. The above observed behavior can be explained on the basis of the protonated/unprotonated character of simazine and the fact that clay modified electrode exhibit negatively charged layer.

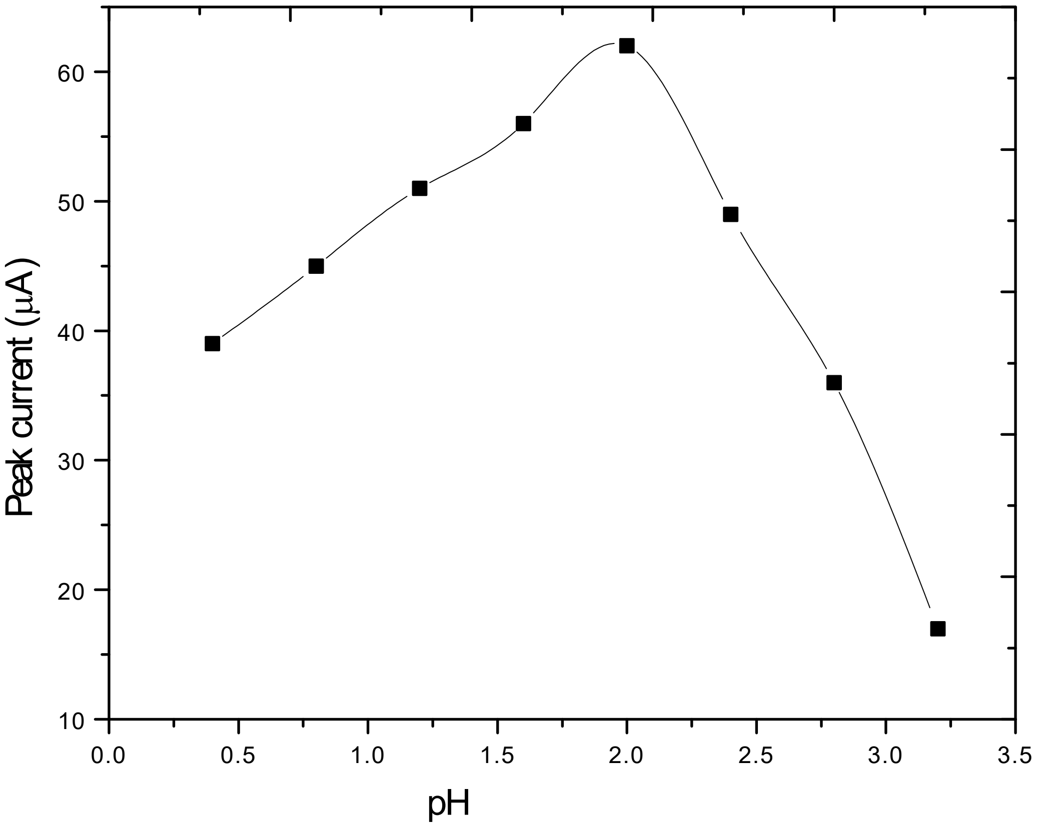

Figure 18. Dependence of the peak current on pH. Other conditions are as in Figure 16.

The favorable accumulation in acidic media is due to the electrostatic interaction between the protonated form of simazine and the negatively charged clay layer at the electrode surface. At pH < 2.0 or in more acidic media, the decreased accumulation observed could be the result of the competition between the protonated simazine and protons from the medium for the negatively charged active site in the clay layer. At pH greater than 2.0, the accumulation obtained is much lower than at pH 2.0 suggesting that the area covered by protonated simazine must be much lower. In fact, it can be assumed that at pH greater than 2.0 the protonated and unprotonated forms of simazine are co-adsorbed, the electrode being fully covered, though only a part of the molecules (those charged) contribute to the observed voltammetric behavior. According to the above result, clay modified electrode at pH 2.0 have been selected to improve simazine detection.

4.2.3. Effect of Accumulation Time

The accumulation time is a decisive factor in any technique dealing with a preconcentration step. The dependence of peak current on the preconcentration time was studied for 40 x 10^{-6} M concentration of simazine under carefully controlled convective conditions. As would be expected, rapid convectional transport during the accumulation process was essential for a sensitive determination.

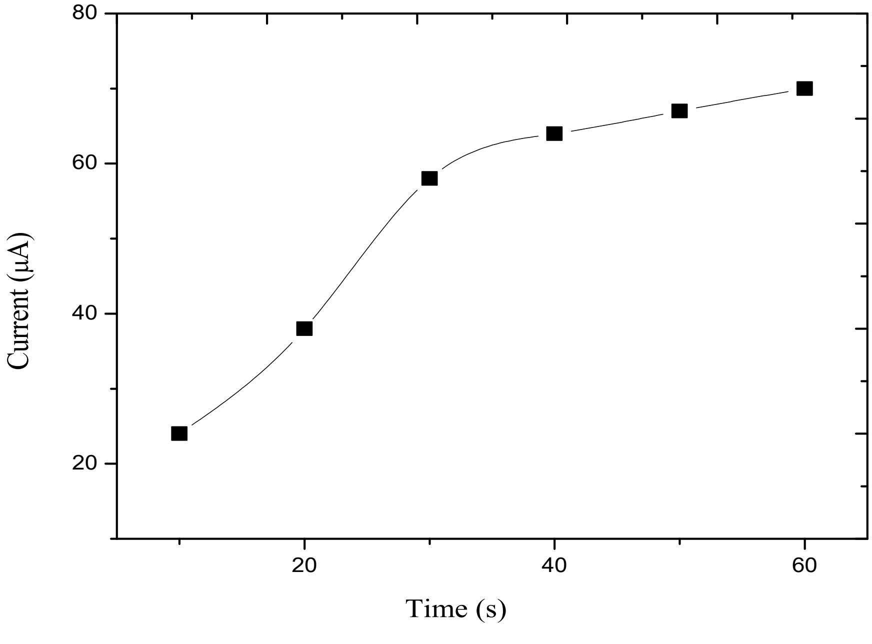

Figure 19. Effect of accumulation time on the differential pulse adsorptive stripping voltammetric peak current. Other conditions are as in Figure 16.

Figure 19 shows the dependence of the peak current on the accumulation time. The peak current increase with increasing accumulation time, indicating an enhancement of the simazine concentration at the surface of the clay modified carbon paste electrode. The dependence of the peak heights on the accumulation time is an evidence for the adsorption controlled current. Short preconcentration periods (up to 30 s) yield a linear and rapid increase in the peak current with an increase in time. Beyond 30 s accumulation periods, the increasing portion of the curves soon became leveled off approaching a limiting value. The manifestation of this limiting value for the current at longer accumulation periods could originate from attainment of adsorption equilibrium between simazine at the modified electrode surface and in the solution or saturation of the adsorption sites.

As it is evident from the above curves, the accumulation process was relatively rapid within the first 30 s of exposure. Hence 30 s of accumulation time was chosen as a compromise between peak current and the length of time required for analysis.

4.2.4. Effect of Accumulation Potential

The effects of accumulation potential (E_{acc}) on the peak current (i_p) in the differential pulse adsorptive stripping voltammogram were studied for accumulation potentials of: 0 to –800 mV. Figure 20 shows the effect of the accumulation potential on the stripping peak current. At both low and high accumulation potential values the peak current were independent of accumulation potential, whereas at intermediate accumulation potential values there was a strong variation of the peak current.

The curve i_p–E_{acc} in the intermediate accumulation potential values can be explained assuming the adsorption of the simazine on the electrode surface. The equilibrium constant of the adsorption process varies strongly with the accumulation potential, and reaches maximum in the vicinity of the potential of –500 mV. The adsorption process is maximum at accumulation potentials close to –500 mV, and decreases drastically when the potential increases or decreases from this value.

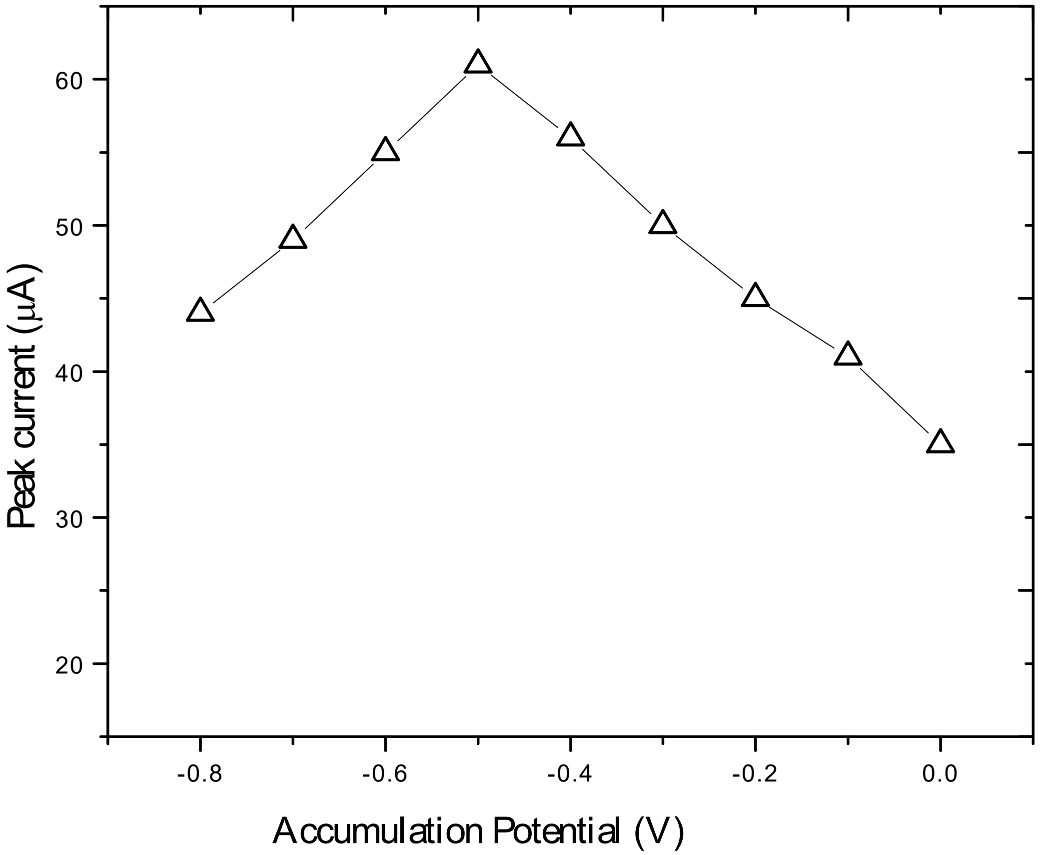

Figure 20. Effect of the accumulation potentials on the differential pulse adsorptive stripping voltammetric peak current. Other conditions are as in Figure 16.

The i_p–E_{acc} curve is a result of the reduction of simazine in solution as well as the reduction of adsorbed molecules. In consequence, the values of the current in the voltammograms are higher than those obtained in the absence of adsorption. When the accumulation potential is far enough from the maximum adsorption potential the only components of the electrode response is that due to the diffusion process. This hypothesis can be confirmed in a relatively simple manner as will be shown in the following section.

The dependence of the peak currents of the voltammograms on accumulation time at different accumulation potential values is shown in Figure 21. At low (curve-B) and high (curve-C) accumulation potential values the peak current is independent of accumulation time, whereas at intermediate accumulation potential values, the peak current increases with accumulation time until a limiting value is reached at high enough accumulation time. This confirms the above mentioned hypothesis: at a constant accumulation potential value near to the maximum adsorption potential the process is favored and the higher the accumulation time, the higher is the surface concentration of simazine (i.e., peak current is maximum).

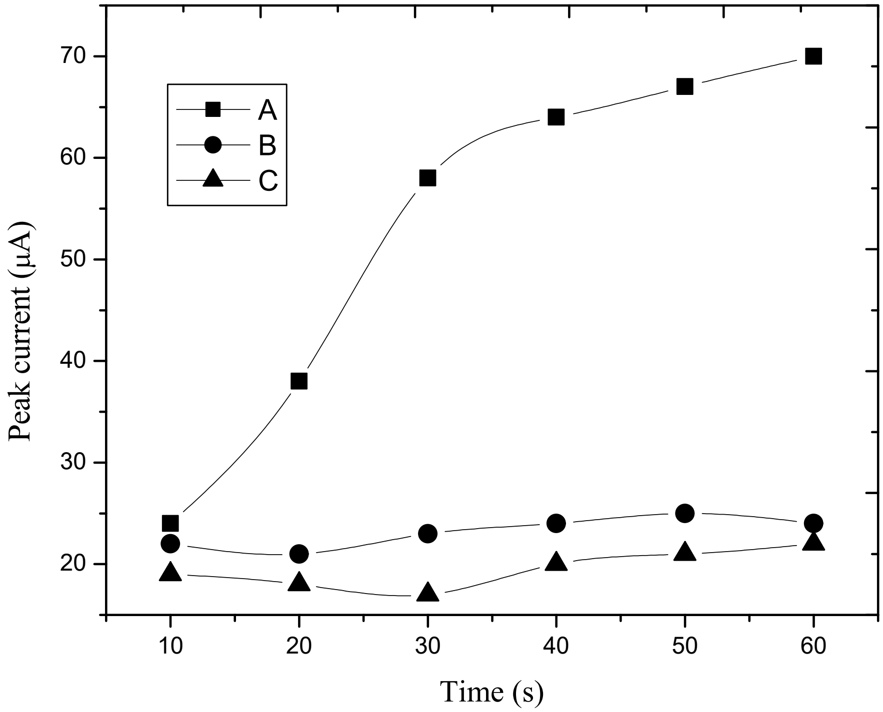

Figure 21. Dependence of the peak current on accumulation time (t_{acc}) and accumulation potential (E_{acc}): E_{acc} = -500 mV (A); E_{acc} = 0.0 mV (B); E_{acc} = -800 mV (C). Other conditions are as in Figure 16.

At a high enough accumulation time the electrode surface is fully covered by a layer of simazine molecules, and an increase in accumulation time does not increase the electrode coverage (curve-A). If accumulation potential is far from the maximum adsorption potential, there is no contribution of the adsorption (i.e., the electrode coverage is null or very low) and the peak current values are very close and independent of accumulation time. The maximum peak current that was observed at an accumulation potential of –500 mV is because of an increased accumulation rate, due to the more favorable alignment of the molecules by the electric field at the electrode solution interface. Because of the maximum peak current obtained at –500 mV, this potential was chosen as accumulation potential for further analytical studies at clay modified carbon paste electrode.

4.2.5. Effect of Scan Rate, Pulse Amplitude, and Pulse Period

The effect of scan rate, pulse amplitude and pulse period on the peak current were studied by varying one of them while keeping any two of the three parameters constant. The scan rate was varied from 20 to 200 mV/s. The effect of scan rate on the response obtained is shown in Figure 22. The peak current increased and a broader and broader with increasing scan rate. A scan rate of 100 mV/s was chosen for subsequent experiments taking the peak broadening and background distortion into account.

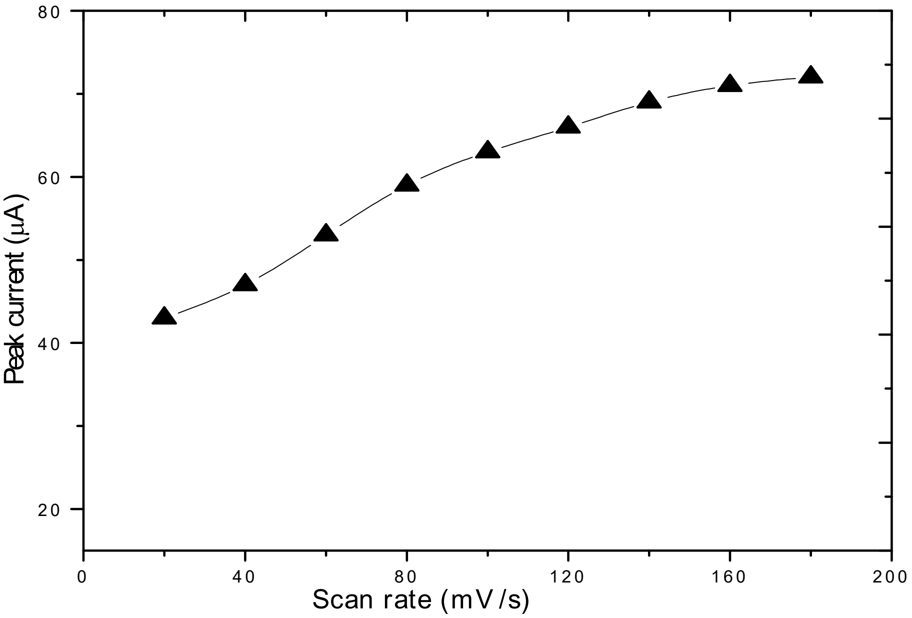

Figure 22. Effect of the scan rate on the differential pulse adsorptive stripping voltammetric peak current. Other conditions are as in Figure 16.

Similar pattern of peak current was observed upon increasing the pulse amplitude from 20 to 200 mV, in which the peak current increased linearly accompanied by peak broadening. Figure 23 shows the dependence of the differential pulse adsorptive stripping peak current on the pulse amplitude. Pulse amplitude of 100 mV was chosen for subsequent experiments as a compromise between peak broadening and signal enhancement.

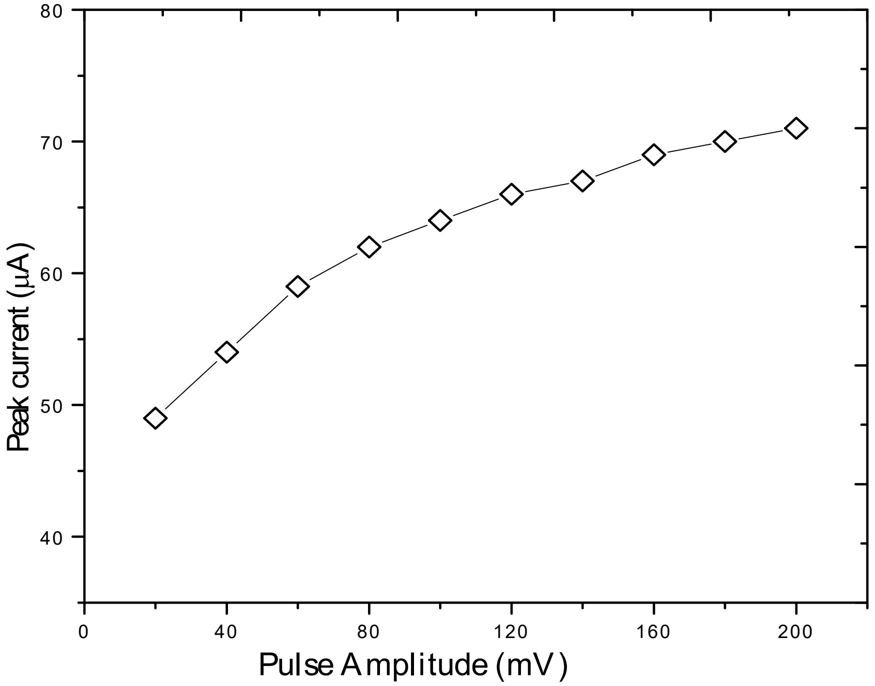

Figure 23. Effect of the pulse amplitude on the differential pulse adsorptive stripping voltammetric peak current. Other conditions are as in Figure 16.

The effect of pulse period on the voltammetric response obtained is shown in Figure 24. The pulse period was varied from 40 to 240 ms. Variation of the pulse period from 40 to 160 ms increased the peak current along with broadening of the peak. Hence, a pulse period of 160 ms was used in all subsequent experiments since it yielded sufficiently high and narrower peak.

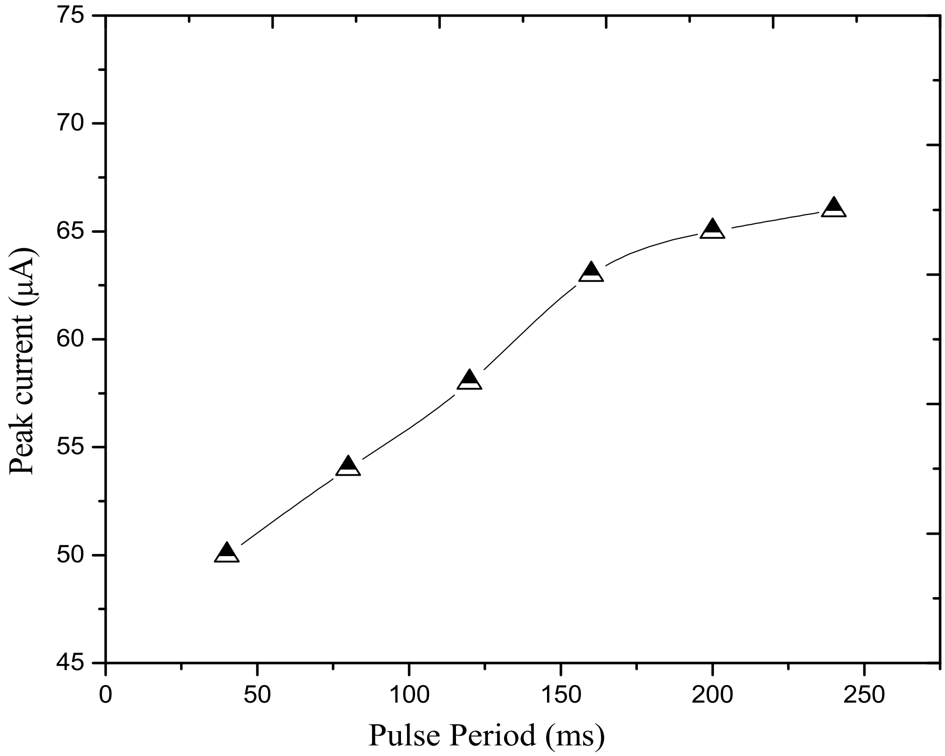

Figure 24. Effect of the pulse period on the differential pulse adsorptive stripping voltammetric peak current. Other conditions are as in Figure 16.

4.2.6. Optimum Experimental Conditions

The effects of several experimental parameters have been studied to obtain optimum experimental conditions for the differential pulse adsorptive stripping voltammetric (DP-AdSV) determination of simazine at clay modified carbon paste electrode. The selected optimum experimental conditions are summarized in Table 1.

Table 1. Optimum experimental conditions for the determination of simazine by DP-AdSV at clay modified carbon paste electrode.

Parameters studied	Optimum values obtained
Clay amount (%)	10
pH of the solution	2.0
Preconcentration time (s)	30
Accumulation potential (mV)	-500
Scan rate (mV/S)	100
Pulse amplitude (mV)	100
Pulse period (ms)	160
Stirring speed (rpm)	1000

4.2.7. Linear Range, Detection limit, and Precision

The analytical utility of a given procedure depends on achieving well defined concentration dependence. According to the optimum experimental conditions and the procedure described above the dependence of the voltammetric signal on concentration of simazine and inherent sensitivity of the method are illustrated by the differential pulse adsorptive stripping voltammetry at different concentration of simazine (Figure 25 and 26). The peak current was found to be directly proportional to the bulk concentration of simazine.

Under the optimum experimental conditions two linear ranges were found. The response found to be linear in the concentration range 1.0 x 10^{-6} M – 20 x 10^{-6} M simazine (r = 0.999) and 20 x 10^{-6} M – 80 x 10^{-6} M simazine (r = 0.998) with 30 s preconcentration time. Deviation from linearity was observed at higher concentrations (> 80 x 10^{-6} M), as expected from nature of the preconcentration process (i.e., saturation of binding sites on the modified electrode surface). In other word deviation from linearity suggested that simazine is adsorbed on the electrode surface at high concentration. This saturation effect is typical for modified electrodes where a limited number of active sites are available at the surface.

The detection limit (concentration equal to three times the standard deviation of peak current for six determination of 1.0 x 10^{-6} M simazine with 30 s preconcentration time) was found to be 0.25 x 10^{-6} M, which corresponds to 50.4 ppb of simazine. The effective cleaning and reproducible preconcentration were illustrated by the precision obtained during repetitive determinations with two representative concentrations. The relative standard deviations were found to be 3.3% and 2.58% for six successive determinations of 2.0 x 10^{-6} M and 20 x 10^{-6} M simazine, respectively. The low value of standard deviation indicates good reproducibility and feasibility of this method for the determination of simazine in environmental samples. Slight variations in the peak current (about 6%) were observed for different batches of the electrode containing the same amount of clay modified carbon paste. Thus, the preparation of new calibration curves is recommended each time when a new surface is used.

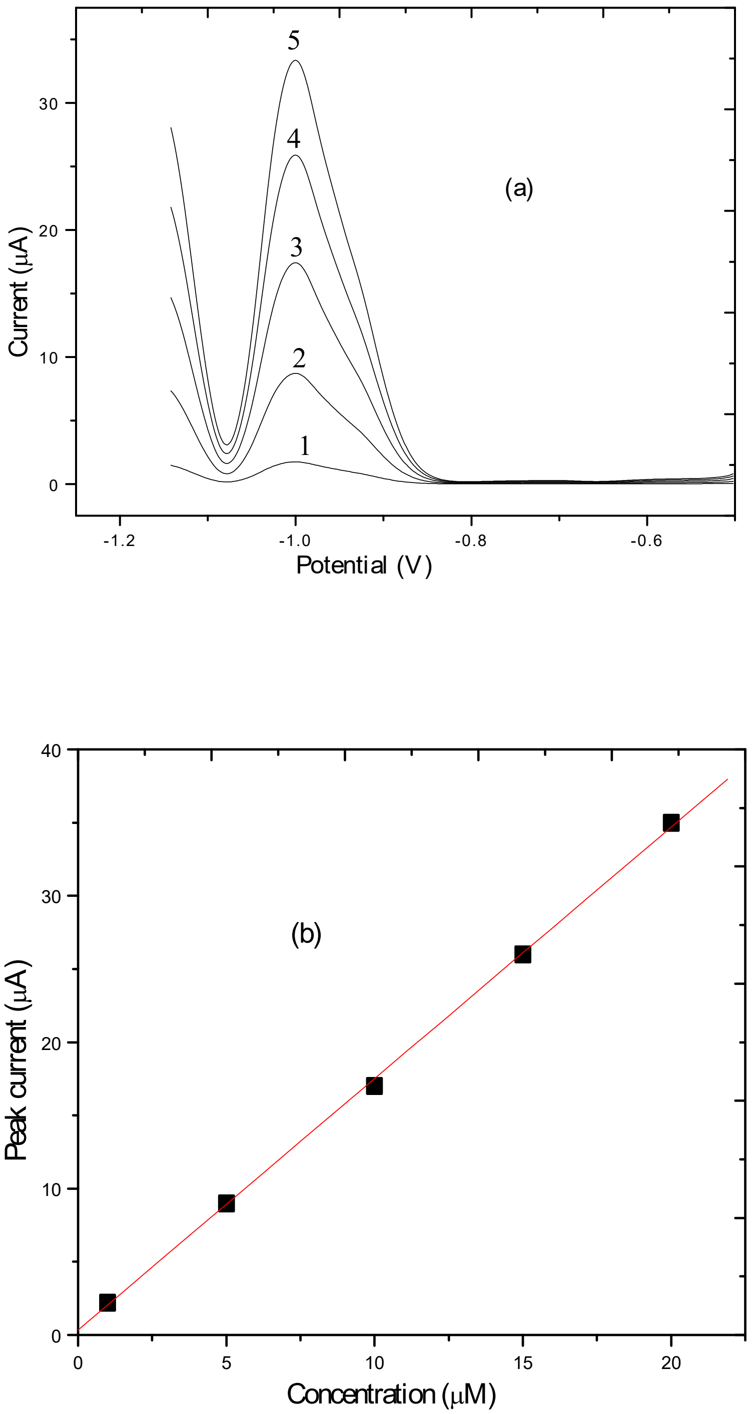

Figure 25. Differential pulse adsorptive stripping voltammograms (a) and calibration curve (b) for determination of simazine accumulated at clay modified carbon paste electrode. Simazine concentrations: (1) 1.0 x 10^{-6} M; (2) 5.0 x 10^{-6} M; (3) 10 x 10^{-6} M; (4) 15 x10^{-6} M; (5) 20 x 10^{-6} M. Other conditions are as in Figure 16.

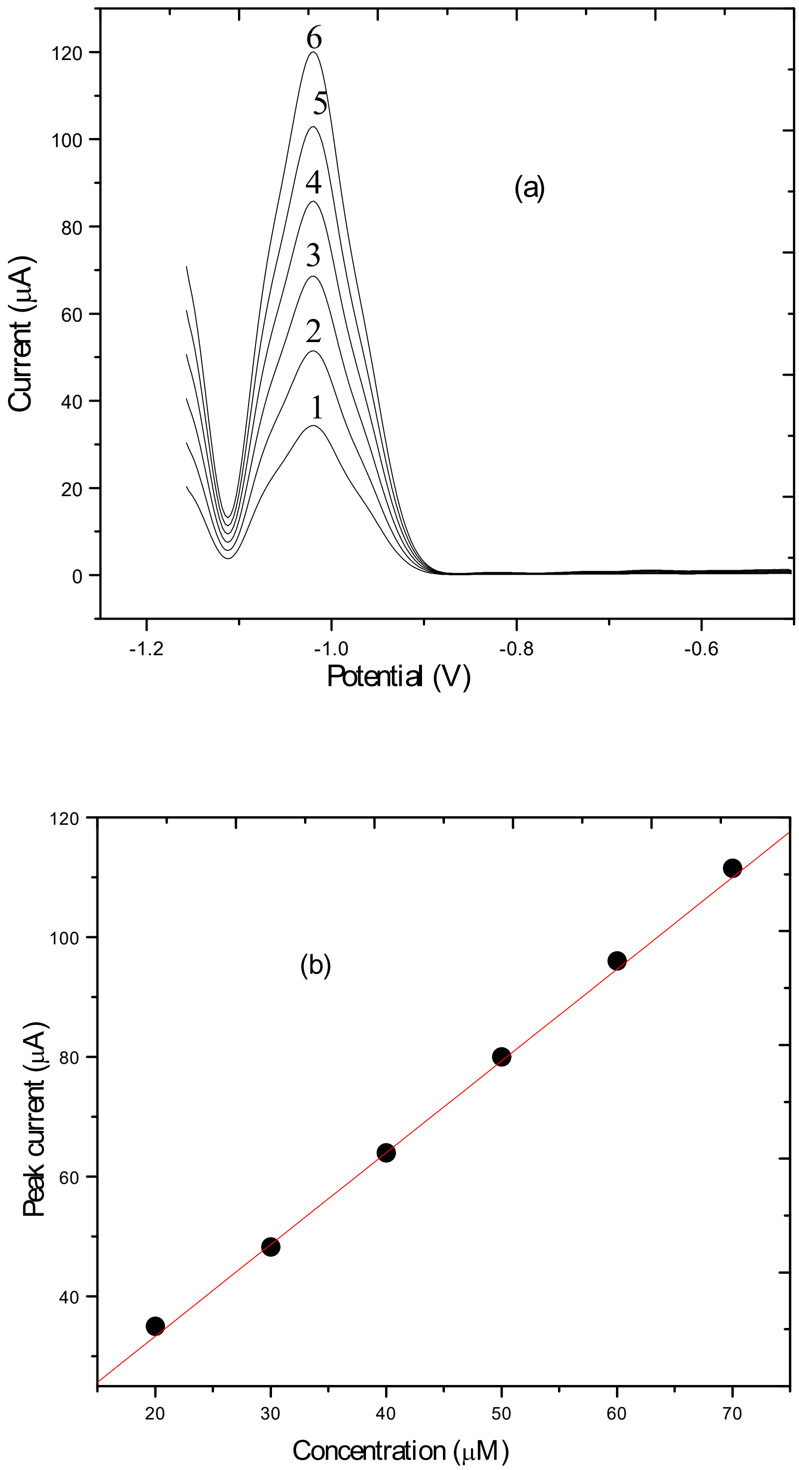

Figure 26. Differential pulse adsorptive stripping voltammograms (a) and calibration curve (b) for determination of simazine accumulated at clay modified carbon paste electrode. Simazine concentrations: (1) 20 x 10^{-6} M; (2) 30 x 10^{-6} M; (3) 40 x 10^{-6} M; (4) 50 x 10^{-6} M; (5) 60 x 10^{-6} M; (6) 70 x 10^{-6} M. Other conditions are as in Figure 16.

4.2.8. Quantitative Analysis

The utility of the proposed differential pulse adsorptive stripping voltammetric method described for the determination of trace amount of simazine was assessed by the determination of simazine in spiked municipal potable water from Addis Ababa. The sample was prepared for the analysis as described in the experimental section. The water sample did not show any peak of simazine. Known concentration (4.0 x 10^{-6} M) of simazine solution was added to the water sample and the concentration of simazine in the water samples was determined by standard addition method. The differential pulse adsorptive stripping voltammograms that were recorded after each addition are shown in Figure 27. The recovery is given in Table 2.

Table 2. Recovery of simazine in spiked tap water sample by DP-AdSV at clay modified carbon paste electrode.

Water sample	Amount added	Average amount found * ± SD	Average recovery, %
Municipal water	4.0 x 10^{-6} M	(3.5 ± 0.3) 10^{-6} M	87.5

∗Mean of three determinations

The average recovery that was obtained without any sample preparation or extraction of simazine confirms the validity of the proposed method for simazine analysis in water samples.

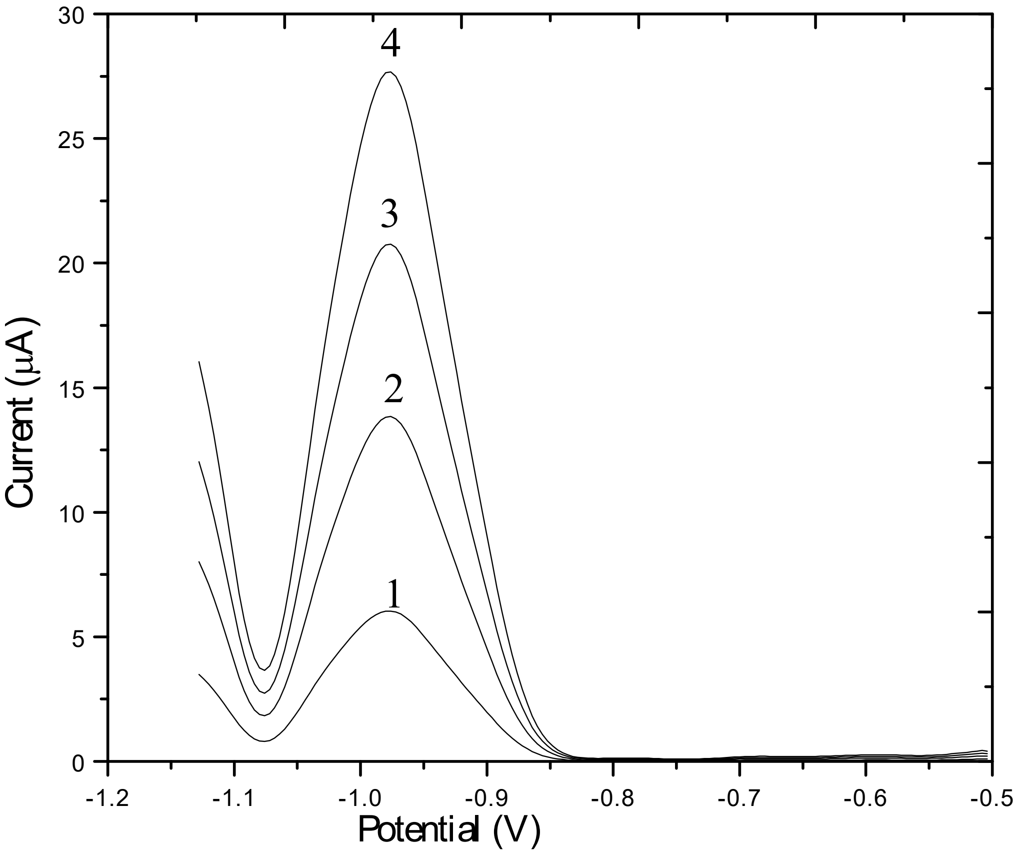

Figure 27. Differential pulse adsorptive stripping voltammograms for the determination of simazine in Addis Ababa municipal water. (1) Supporting electrolyte at pH 2.0 prepared in water sample spiked with known concentration of simazine to make its concentration 4 x 10^{-6} M; and after addition of: (2) 4 x 10^{-6} M; (3) 8 x 10^{-6} M; and (4) 12 x 10^{-6} M simazine to the simulated unknown described in (1). Other conditions are of the optimal conditions.

5. Conclusion

This work demonstrates that clay mineral is an appropriate carbon paste electrode modifier for use in conjunction with the preconcentartion/voltammetric measurement technique for the determination of simazine. The clay modified CPE showed good stability, sensitivity and ability to be easily generated. The proposed method was applied to the direct determination of simazine in potable water sample with satisfactory result.

The electrochemical reduction of simazine, under the conditions used in this work, is irreversible. Using the voltammetric procedure described, a detection limit of 50.4 ppb was found, which is slightly lower than that reported for chromatographic techniques [76]. However, this voltammetric procedure is simpler than chromatographic techniques and it is an inexpensive, less time consuming and does not involve complex sample preparation. Therefore, the method developed can be considered as a reasonable alternative to other methods to determine simazine at trace levels.

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