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THE EFFECT OF HOMOGENEOUS CATALYST FOR THE DEGRADATION OF SODIUM DODECYLBENZENE SULFONATE (SDBS) IN WATER BY MEANS OF ULTRASONIC IRRADIATION.

(KESAN PEMANGKIN HOMOGEN KE ATAS DEGRADASI *SODIUM ALKYLBENZENE SULFONATE* (SDBS) DI DALAM AIR DENGAN MENGGUNAKAN TEKNOLOGI ULTRABUNYI)

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THE EFFECT OF HOMOGENEOUS CATALYST FOR THE DEGRADATION OF SODIUM DODECYLBENZENE SULFONATE IN WATER BY MEANS OF ULTRASONIC IRRADIATION.

(Keywords: Linear Alkylbenzene Sulfonate, Sodium Dodecylbenzene Sulfonate, ultrasound irradiation, TOC)

Linear Alkylbenzene Sulfonate (LAS) is a major anionic surfactant used widely in industrial detergents and the production of household products throughout the world because of its effectiveness. Its presence in wastewaters may cause environmental concern. Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems. Additionally, it has successfully increased and enhanced the removal and destruction of volatile compounds in aqueous solution. The aim of this research is to study the treatment of synthetic aqueous solutions containing a commercial Linear Alkylbenzene Sulfonate (LAS), namely Sodium Dodecylbenzene Sulfonate (SDBS), by means of ultrasound irradiation. The possibility of coupling ultrasound with a suitable oxidation catalyst to improve treatment efficiency will also be investigated. HPLC, TOC, COD and pH analyses will be carried out to investigate the effect of degradation of SDBS. In this research, SDBS degradation with three different treatments (US alone, US with H_2O_2 and US with Fenton reagent) was investigated. All treatment presented in this research were performed in triplicate by using sonication bath at 30 °C, 40 kHz , 500 W and sonication time of 120 min. From the discussion, by using the US + Fenton treatment appears to be the highest in terms of % TOC removal which is 67% and followed by the others two treatment which is US + H_2O_2 and US alone treatment have been achieved at 55% and 12%. It was found that the main degradation of SDBS proceeds via a reaction with OH radicals and since SDBS is anionic surfactant of negligible volatility. The initial degradation rate (d[SDBS]/dt, within the first 30 min) increases by using the US + Fenton treatment which is 0.68 μM/min followed by US + H_2O_2 and US alone were achieved at 0.52 μM/min and 0.44 μM/min respectively.

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(Katakunci: Linear Alkylbenzene Sulfonate, Sodium Dodecylbenzene Sulfonate, ultrabunyi, TOC)

Linear alkylbenzene sulfonate (LAS) biasanya merupakan surfaktan aktif permukaan utama yang digunakan dalam industri bahan cuci.dan pengeluran barangan keperluan rumah di seluruh dunia kerana keberkesanannya. Kehadirannya di dalam air boleh menyebabkan pencemaran air. Ultrabunyi merupakan teknologi yang baik dalam meningkatkan tindak balas dalam pelbagai jenis system. Tambahan lagi, ia berjaya meningkatkan dan memperbaikkan

Tujuan penyelidikan ini adalah untuk menganalisis rawatan ke atas larutan sintetik yang mengandungi Linear Alkylbenzene Sulfonate (LAS), iaitu *Sodium Dodecylbenzene Sulfonate (SDBS)* dengan teknologi ultrabunyi. Keberkesanan ultrabunyi dengan kehadiran mangkin pengoksidaan akan dibuat. HPLC, TOC dan pH analisis digunakan untuk mengkaji kesan pengdegradasian SDBS di dalam kajian ini. Dalam kajian ini, pengdegrasian SDBS dengan tiga rawatan yang berlainan (US sahaja, US dengan Hidrogen peroksida dan US dengan reagen Fenton) telah di buat. Kesemua rawatan dijalankan sebanyak 3 kali dengan menggunakan *sonication bath* pada keadaan 30 C, 40 kHz, 500 W dan masa ujikaji selama 120 minit. Daripada perbincangan yang telah di buat, penggunaan US dengan reagen Fenton adalah yang tertinggi dalam pemindahan TOC iaitu sebanyak 67% dan diikuti oleh dua rawatan yang lain iaitu US dengan hydrogen peroksida dan US sahaja dengan peratus 55% dan 12% bagi setiap rawatan. Hasil daripada kajian ini juga mendapati bahawa OH radikal mendominasikan proses pengdegradasian SDBS dan SDBS adalah sebatian yang tidak meruap. Kadar degradasi awal (d[SDBS]/dt, pada 30 minit terawal), bertambah dengan penggunaan rawatan US dengan reagen Fenton iaitu 0.68 μM/minit dan diikuti dengan penggunaan rawatan US with hidrogen peroksida dan US sahaja dengan kadar degradasi 0.52 μM/ minit dan 0.44 μM/minit bagi setiap rawatan.

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4 RESULTS AND DISCUSSION

LIST OF FIGURES

NOMENCLATURE

AOPs	Advanced Oxidation Processes
[ ]	Concentration
CMC or cmc	Critical Micelle Concentration
EDTA	Ethyelenediaminetetraacetic acid
HPLC	High performance liquid chromatography
H_2O_2	Hydrogen peroxides
L	Liter
LAS	Linear alkylbenzene sulfonate
mol/ L	Molar
$^{\cdot}OH^{\bullet}$	Hydroxyl radical
pH	The acidity or basic nature of a solution
SDBS	Sodium dodecylbenzene sulfonate
°C	Temperature
TOC	Total organic carbon
US	Ultrasound
UV	Ultra-violet
W	Watts

CHAPTER 1

INTRODUCTION

1.1 Background

Linear and branched alkylbenzene sulfonates (LAS) is a major anionic surfactant used widely in industrial detergents and the production of household products throughout the world because of its effectiveness. Its presence in wastewaters may cause environmental concern (Mantzavinos et al. 2001). They are biodegradable to some extent; however, some of the products of biodegradable (alkylphenols) are much more problematic than the parent compound. LAS presence in sewage works is variable depending on their use in industrial processing in addition to domestic activities. An average LAS concentration of 1–10 mg/L can be found in municipal wastewater treatment dealing only domestic wastewater (Field *et al*., 1995) but this range is noticeably increased when industrial wastes from washing processes are also treated (Beltran *et al*., 2000).

In recent years, considerable interest has been shown on the application as a destructive process for the treatment of hazardous contaminants in water. Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems (Thompson et al. 1999). Additionally, it has successfully increased and enhanced the removal and destruction of volatile compounds in aqueous solution (Dewulf et al. 2001). The use of ultrasound may enable operation at milder operating conditions (e.g. lower temperatures and pressures and eliminate the need of extra costly solvents. For these reasons, use of ultrasound appears to be a promising alternative for chemical treatment of hazardous contaminants in water.

Ultrasonic irradiation of aqueous solutions induces acoustic cavitations, which can be defined as the cyclic formation, growth and subsequent collapse of microbubbles or cavities occurring in extremely small intervals of time and releasing large quantities of energy over a small location (Gogate, 2002). Extreme temperatures of several thousand degrees and pressure of several hundred atmosphere are developed locally within the bubbles during their collapse with these bubbles serving as hot spot microreactors in an otherwise cold liquid. Thus, the acoustic cavitations in an aqueous solution results in chemical will be effects by the ultrasound.

1.2 Problem statement

In this study, the effect of the sonochemical degradation of wastewater containing anionic surfactant (below CMC) will be discussed. Ultrasound irradiation is one of the processes that have been used widely for wastewater treatment. SDBS solution will be used as the wastewater sample. Furthermore, the effect of the additional of H_2O_2 and Fenton reagent will be discussed in this section.

1.3 Objective of study

The aim of this research is to study the treatment of synthetic aqueous solutions containing a commercial Linear Alkylbenzene Sulfonate (LAS), namely sodium dodecylbenzene sulfonate (SDBS), by means of ultrasound irradiation. The possibility of coupling ultrasound with a suitable oxidation catalyst to improve treatment efficiency will also be investigated

1.4 Scope of study

SDBS solutions with different initial concentrations below critical micelle concentration (CMC) will be subjected to sonication. Ultrasound irradiation will be carried out continuously with probe-type sonicator. During sonication, the liquid bulk temperature will be kept constant at 30degC and at ambient pressure. For catalytic ultrasound irradiation runs where iron will be used as a homogeneous catalyst, a lower metal concentration (<20 mg/l) will be used because of greater concentration will lead to greater pollutant removal.

CHAPTER 2

LITERATURE STUDY

2.1 Ultrasound

Instead of chemical treatment, the application of high power ultrasound (US) for the destruction of organic pollutants has recently drawn much attention. It is an Advanced Oxidation process wherein it can affect organic oxidation in three different mechanisms: nucleation, growth and cavitations (Huang *et al*., 1993). According to this theory, the effect of ultrasound arises from the longitudinal vibration in liquid molecules through a series of compression and rarefaction cycles resulting in the tearing of solvent layers during rarefaction.

Cavities are formed at the point where the pressure in the liquid drops well below its vapour pressure. These cavities turn into bubbles and filled with vapour of the solvent molecules. Bubbles start reverberating with the propagating ultrasound wave and grow in size after every rarefaction cycle until an optimum stage attained where the energy supplied by the wave is no longer capable of sustaining these bubbles. At this stage, the bubble implodes, thereby allowing solvent molecules from the bulk to rush into the void space of relatively low pressure in the form of micro jets. This process results in the rise of temperature as high as 5000 K and pressure of several thousand atmospheres (100 MPa) during the collapse of the micro bubbles generated by ultrasound, which now acts as a micro-reactor. These are the real sites of chemical reactivity. The typical ultrasound decomposition of toxic organics is 10,000 times faster than the natural aerobic oxidation. However, in a recent economic analysis of treatment of wastewater containing organics, the cost of sonochemical oxidation has found to be comparable to incineration (Chitra *et al*., 2004).

In general, ultrasound treatment is one of several technologies that promote hydrolysis – the rate-limiting stage during sludge treatment. The basic principal of ultrasound is based on the destruction of both bacterial cells and difficult-to-degrade organics. In sludge, various substances and agents collect in the form of aggregates and flakes, including bacteria, viruses, cellulose and starch.

The energy produced during ultrasound treatment causes these aggregates to be mechanically broken down, altering the constituent structure of the sludge and allowing the water to be separated more easily. Because ultrasound attacks the bacterial cell walls, the bacterial cells release ezo-enzymes that bio catalyses hydrolytic reactions. This results in acceleration in the breakdown of organic material into smaller readily biodegradable fractions.

The subsequent increase in biodegradable material improves bacterial kinetics resulting in lower sludge quantities and, in the case of anaerobic digestion, increased biogas production. Therefore, its use is most suited to streams containing large quantities of refractory material and/or cellular matter such as waste activated sludge streams.

2.1.1 Previous Treatment of Ultrasound

Sonochemistry is a new branch of chemistry in which sound is used to accelerate chemical reaction or to open a new route of chemical reaction (Ruo and Huamao, 1992). Sonochemistry is now advanced rapidly in many fields of chemistry and chemical technology.

In the previous studied, ultrasound irradiation have been investigated for acid, alcohol and aqueous solution. As an example the research of ultrasonic treatment of liquid waste containing EDTA by Chitra *et al.* (2004) investigated the decontamination wastes from the presence of EDTA can cause complexation of radioactive cations resulting in interferences in their removal by various treatment such as precipitation, ion exchange etc. Further, it might also impart elevated leach ability and higher mobility to cationic contaminants from the conditioned wastes i.e. waste immobilized in cement or other matrices and can adversely influence the quality of the final form of waste. From this research, the comparison of US with Fenton system and US with H_2O_2 with different frequency has been shown on Figure 2.1 and Figure 2.2.

Figure 2.1 was presented the effect of frequency of ultrasound on the percentage degradation of EDTA (2%) with time in the presence of Fenton reagent alone. The percentage degradation of EDTA with time using H_2O_2 on Figure 2.2 has shown the effect of frequency on the percentage degradation of EDTA was increase with the time. From the comparisons of the kinetics of EDTA degradation it can be concluded that higher frequency of ultrasound and Fenton reagent favour faster kinetics of degradation.

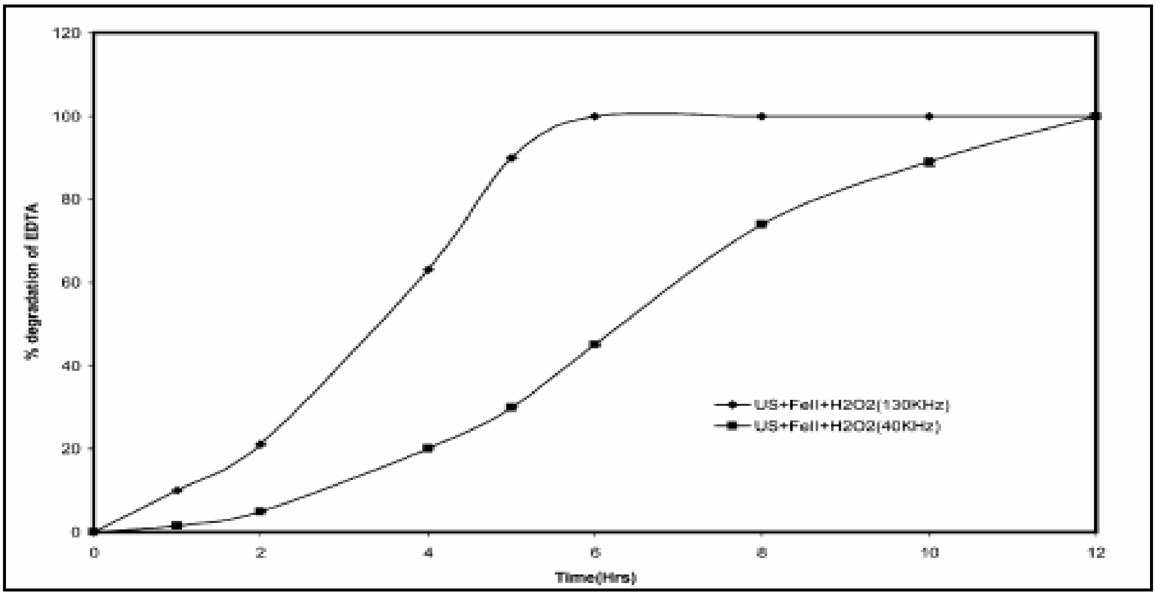


Figure 2.1 Effect of frequency on the ultrasonic degradation of EDTA (2%) using Fe(II) and H_2O_2 (Chitra *et al*., 2004)

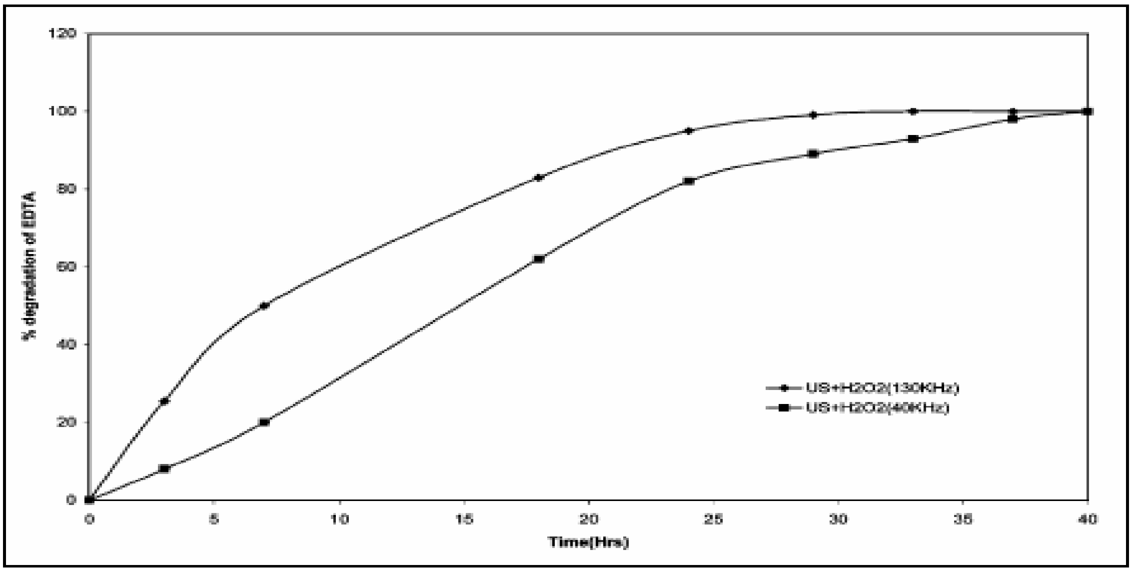


Figure 2.2 Effect of frequency on the ultrasonic degradation of EDTA (2%) using H_2O_2 (Chitra *et al*., 2004)

2.2 Advanced Oxidation Processes (AOPs)

Advanced chemical oxidation processes make use of (chemical) oxidants to reduce COD/BOD levels, and to remove both organic and oxidisable inorganic components. The processes can completely oxidize organic materials to carbon dioxide and water, although it is often not necessary to operate the processes to this level of treatment. A wide variety of advanced oxidation processes are available; (i) Chemical oxidation processes using hydrogen peroxide, (ii) the ozone & peroxide, hypochlorite, Fenton reagent etc, (iii) ultra-violet enhanced oxidation such as UV/ozone, UV/hydrogen peroxide, UV/air , and (iv) wet air oxidation and catalytic wet air oxidation (where air is used as the oxidant).

Advanced oxidation processes are particularly appropriate for effluents containing refractory, toxic or non-biodegradable materials. The processes offer several advantages over biological or physical processes, including process operability, unattended operation, the absence of secondary wastes and the ability to handle fluctuating flow rates and compositions. However, advanced oxidation processes often have higher capital and operating costs compared with biological treatment. The most suitable variant for each application is chosen on the basis of the chemical properties of the effluent.

For many years, the removal of harmful organic pollutants from waters and wastewaters has been investigated by a variety of chemical processes. Among them, oxidations by several agents such as UV radiation, Fenton’s reagent, or ozone, have been used successfully (Blake, 1997). The resistance of some persistent chemicals to these oxidants has forced the development of new methodologies known as advanced oxidation processes (AOPs), which employ a combination of several oxidants. The main task of AOPs is to enhance free radicals in aqueous solutions. One of the most frequently used AOPs is based on the ultraviolet photolysis of hydrogen peroxide (H_2O_2/UV), where radiation below 400 nm is capable of photolyzing the H_2O_2 molecule. The accepted mechanism for hydrogen peroxide photolysis is cleavage of the molecule into hydroxyl radicals with the quantum yield of two $OH^{\bullet}$ radicals per quantum of radiation absorbed.

2.3 Sodium Dodecylbenzene Sulfonate (SDBS)

Surfactants (also called surface active agents or wetting agents) are organic chemicals that reduce surface tension in water and other liquids (Tchobanoglous, 1991). Besides that, surfactants are compounds composed of both hydrophilic and hydrophobic or lipophobic groups. In view of their dual hydrophilic and hydrophobic nature, surfactants tend to concentrate at the interfaces of aqueous mixtures: the hydrophilic part of the surfactant orients itself towards the aqueous phase and the hydrophobic part orients itself away from the aqueous phase into the second phase.

Figure 2.3 shows the molecular structure of the SDBS. The hydrophobic part of a surfactant molecule is generally derived from a hydrocarbon containing 8 to 20 carbon atoms (e.g. fatty acids, paraffin, olefins, and alkyl benzenes). The hydrophilic portion may ionise in aqueous solutions (cations, anionic) or remain un-ionise (non-ionic). The surfactant that was used in this study is sodium dodecylbenzene sulfonate (SDBS); the representatives of LAS will be use.

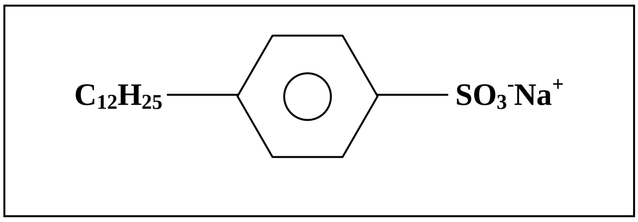


Figure 2.3 SDBS molecule structure

2.4 Previous Treatment of SDBS

Anionic are only used as detergents, they are widely applied in many fields of technology and research. They have been successfully employed to enhance the efficacy of the active ingredient in pharmaceutical and agriculture formulations, in cosmetics and biotechnological and other industrial processes (Cserhati *et al*., 2002). SDBS is one of the surfactant that are usually using as a solutions in some studied.

Like in new studied of degradation of SDBS in water by ultrasonic irradiation by Manousaki *et al.* (2004). They were investigated about the potential of using ultrasonic irradiation for removal of SDBS from the aqueous solutions. Experiments was performd at initial concentrations of 15, 30 and 100 mg/L, ultrasonic frequencies of 20 and 80 kHz, applied power values of 45, 75 and 150W and liquid bulk temperatures of 20, 40 and 60 °C. At the conditions in question, SDBS conversion has found to decrease with increasing temperature and initial solute concentration and decreasing power and frequency. Investigations using the radical scavenger's 1-butanol and KBr revealed that SDBS degradation proceeds through radical reactions occurring predominately at the bubble–liquid interface and, to a lesser extent, in the liquid bulk. Addition of NaCl or H_2O_2 had little or even an adverse effect on SDBS conversion. (Manousaki *et al*., 2004). They had been made a several conclusions for this studies, there are:

a) Low frequency ultrasound is capable of degrading SDBS in relatively dilute synthetic solutions. Hydroxyl radical-mediated reactions occurring at the gas–liquid interface appear to be the prevailing degradation mechanism.

b) Treatment performance can be maximized choosing optimal operating conditions. The water matrix is also likely to affect performance due to the presence of compounds that may act as radical inhibitors or promoters as well as change the physicochemical properties of the solution.

c) Ultrasonic treatment alone may not be suitable for decontaminating completely complex wastewaters of high organic load.

2.5 Critical Micelle Concentration (CMC)

A fundamental property of surfactants is their ability to form micelles (colloidal-sized clusters) in solution. This property is due to the presence of both hydrophobic and hydrophilic groups in each surfactant molecule. It is the formation of micelles in solution, which gives surfactants their excellent detergency and solubilisation properties. When dissolved in water at low concentration surfactant molecules exist as monomers. The hydrocarbon chain, which is incapable of hydrogen bonding, disrupts the normal water structure in its vicinity. The resultant high entropy 'structured water', which surrounds the chain, increases the free energy of the system. The free energy can be minimized if the hydrocarbon chains are partially or totally removed from contact with water, by either adsorption onto or absorption into organic matter. At higher concentrations, the system's free energy can also be reduced by the aggregation of the surface-active molecules into clusters (micelles) with the hydrophobic groups located at the centre of the cluster and the hydrophilic head groups towards the solvent. The concentration of surfactant at which the thermodynamics of the surfactant- solvent system favours micelle formation was called the critical micelle concentration (Haigh, 1996).

CHAPTER 3

METHODOLOGY

3.1 Introduction

High Performance Liquid Chromatography (HPLC), Total Organic Carbon (TOC) and pH analyses used to investigate the effects of sonochemical degradation of wastewater containing anionic surfactant (below CMC). From the TOC analysis it is to see the contents of organic and oxygen on this experiment. The others analysis like HPLC analyses, the peak area are used to calculate the concentration of SDBS versus the sonication time. The pH has taken to show the acidity or alkali of the SDBS at the end of experiment.

3.2 Materials

Sodium dodecylbenzene sulfonate (SDBS), H_2O_2 and Fenton reagent are supplied by Scharlau Chemise S.A. The initial concentration for SDBS is a 100 μM at 30˚C, H_2O_2 is a 0.1 M and Fe^{2+} is a 0.01 M has been used.

3.3 Experimental Set-up and Procedures

3.3.1 Sonication Experiment

Sonication experiment performed in ultrasonic cleaning bath of frequency 40 kHz from Ultrasonic system; model BRANSON 5510 of power 500 Watt respectively. The samples has been taken and placed inside the ultrasonic bath to make a directed sonication. Constant temperature was maintained at 30˚C with a temperature control system provided in the instrument. The first pH value for this experiment must be equal to 3 only for Fenton reagent involved. In all cases, 6 L of SDBS aqueous solution were prepared daily and subjected to ultrasonic irradiation. The pH value of the original SDBS solution was about 7-7.5. Runs were discontinued periodically to remove 25 ml samples that were analysed by means of high performance liquid chromatography (HPLC) and TOC analysis.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

Sonochemical degradation of wastewater containing anionic surfactant (SDBS) in the presence of H_2O_2 and Fenton reagent were investigated. Therefore, in this chapter were concluded all the results and discussion about the effect of TOC removal, SDBS concentration and pH profile and also the discussion about the characteristic of this SDBS had been made.

4.2 Effect of homogeneous catalyst

4.2.1 TOC profiles

Sonication of three different treatments which is the effected of US alone, US with H_2O_2 and US with Fenton reagent in this experiment were performed. This resulted in an initial TOC is 21.6 mg/L respectively. All experiments used a temperature of 30°C, 40 kHz, 500 W and a sonication time of 120 min. During sonication, the concentration of SDBS was measured at 0, 1, 2, 5, 10, 20, 30, 45, 60, 90 and 120 mins.

To quantify the overall degradation of SDBS, the percentage of TOC removal of the solutions was measured as a function of sonication time. Figure 4.1 shows the normalized TOC-time profiles during the sonication of SDBS with different treatments. It can be seen that there was much difference at TOC removal for those three different treatments. For instance, for US alone resulted in almost 12% TOC removal after 120 min of sonication, and 55% and 62% TOC removals were achieved at US + H_2O_2 and US + Fenton respectively after 120 min of sonication.

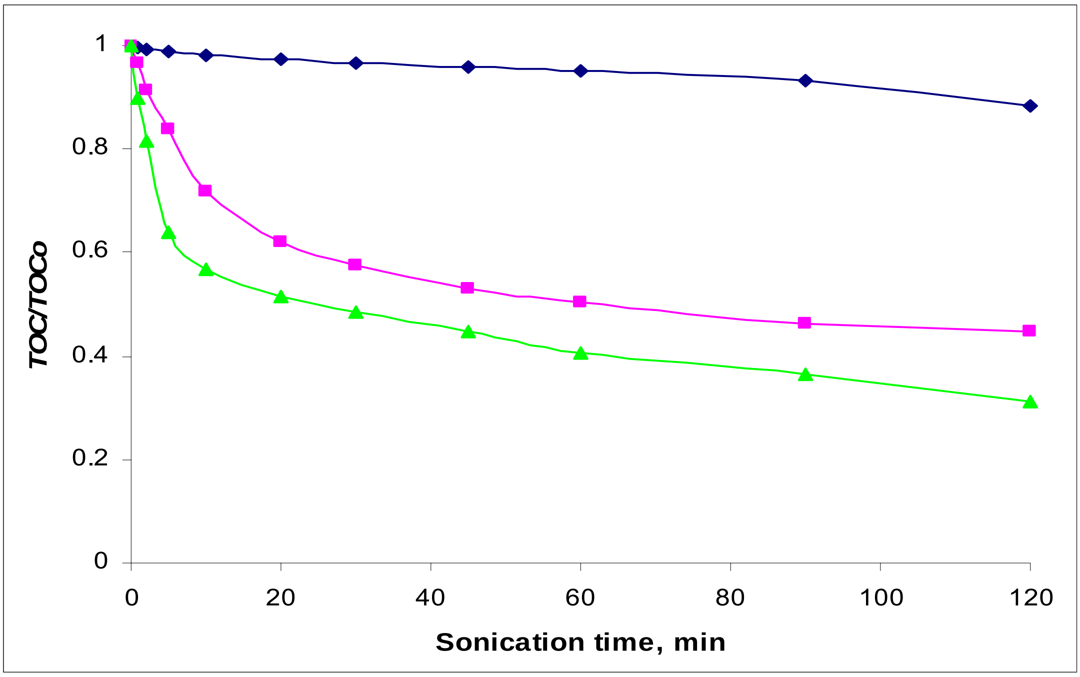


Figure 4.1 Graph of Normalised TOC-time for SDBS at **-●-** US alone, **-■-** US + H_2O_2 and **-▲-** US + Fenton

According to Ashokkumar *et al.* (2003), hydrogen peroxide can be produced by application of ultrasound alone; however the amount may be significant. So for US alone its can be seen from the graph, the degradation rate was decrease slowly. This is because, SDBS is an anionic surfactant of negligible volatility, and direct pyrolisis of

SDBS within the bubble can be expected to be insignificant. So that, in these researched the formation of OH radical is the significant effect involved in this treatment.

For the further experiment, Hydrogen peroxide can be added to this process as an initiator to increase OH radical concentration in the solution. As a result, the degradation rate of the solution changed more directly. Because of that, the surfactant more degradable and the values of C becomes less. To enhance the efficiency of degradation, a more effective utilisation of OH radicals is desirable. It is expected that addition of Fe (II) will regenerated •OH as shown as Equation 1,

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{-} + HO\bullet \qquad (1)$$

Thus accelerating the rate of degradation and thereby increasing the efficiency of ultrasonic degradation, its can be seen from the graph for US + Fenton.

4.2.2 SDBS concentration profiles

Sonication of different treatment such as H_2O_2 and Fenton reagent were performed. All experiments used a temperature of 30°C, 40 kHz, 500 W and a sonication time of 120 min. During the sonication, the concentration of SDBS was measured at 0, 1, 2, 5, 10, 20, 30, 45, 60, 90, and 120 mins. To quantify the overall degradation of SDBS, the concentration removal of the solutions was measured as a function of the sonication time. From the Figure 4.2 it shows the graph of concentration removal during the sonication of SDBS with different treatment. It can be seen that there was much difference at concentration removal for those different treatments. For instance, US alone resulted in almost 76% concentration removal after 120 min of sonication, and 77% and 81% concentration removals were achived at US + H_2O_2 and US + Fenton respectively after 120 min of sonication.

From the Figure 4.2, it can be seen that the concentration of SDBS decreased directly with increasing sonication time. It can be observed that the values of molecules weight decreased after 120 min of sonication. Papadaki et al., 2004 who studied the effect of low frequency (20 kHz) ultrasonic irradiation on the removal of various solutions reported that the degradation of SDBS (at initial concentration of 1 g/L) results in the formation of lower molecule weight compounds and is accompanied by low total oxidation rates. In parallel, water sonolysis results in the formation of hydrogen peroxide. However, the presence of Fe^{2+} ions at concentrations as low as about 10^{-3} g/L generally increase the rate of uncatalysed sonolytic degradation. They also added that this is attributed to iron being capable of readily decomposing hydrogen peroxide in a Fenton-like process to form reactive hydroxyl radicals as well as being an effective oxidation catalyst.

From Figure 4.2 also, within the first 30 min it can be seen that the concentration of SDBS decrease rapidly, this is because at this stage the probability of OH radicals attack on SDBS molecules increase with formation of OH radicals. Then, after 30 min until 120 min, the concentration of SDBS decrease almost constant, this is because the OH radicals become slower to attack the SDBS molecules and the another factors were the formation of OH radicals more slowly and maybe more short organic compounds form at the end of treatment. The highest of degradation rate (d[SDBS] / dt) of SDBS with different treatment achieved by using US + Fenton treatment which is 0.68 μM/min followed by using US + H_2O_2 and US alone, which is 0.52 μM/min and 0.44 μM/ min.

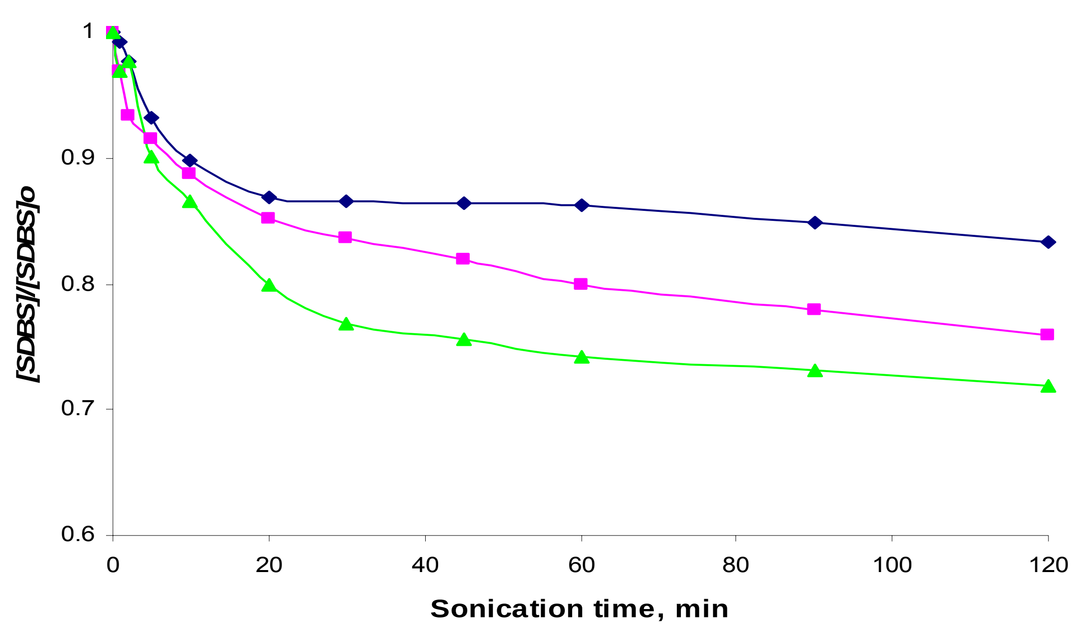


Figure 4.2 Graph of Normalised Concentration-time for SDBS at 30 °C with 230nm. -●- US alone, -■- US + H_2O_2 and -▲- US + Fenton

4.2.3 pH profiles

Sonication of different treatments which is H_2O_2 and Fenton were performed. In this research, the pH profile is not the crucial parameters to be determined. This is because; the pH change is often monitored to see the pH profiles or trend during the reaction processing. Figure 4.3 shows the normalised pH profiles during the sonication of SDBS at different reagents. From pH profiles, it can be seen that the pH solution dropped from its initial value within the 10-30 min of sonication and then remained almost constant through the course of reaction up to 120 min. These results imply that SDBS sonolysis is accompanied by the formation of organic acids from organic material and that their concentration remains quite stable (Papadaki et al., 2004).

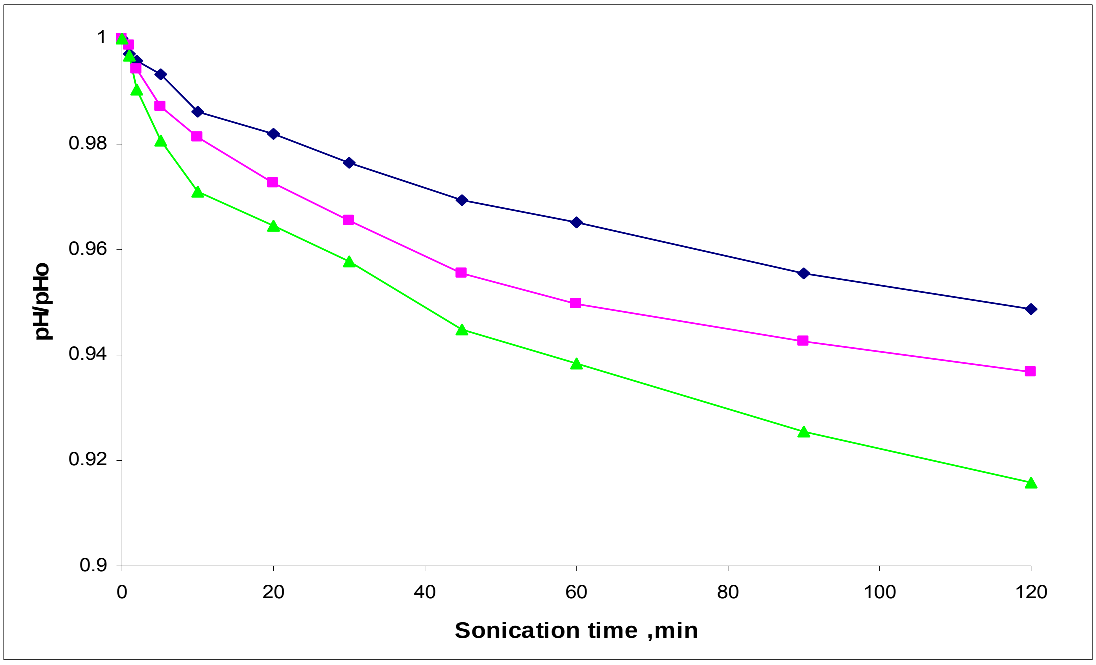


Figure 4.3 Graph of Normalised pH-time for SDBS at 30 °C, 40 kHz and 500 W. -●- US alone, -■- US + H_2O_2 and -▲- US + Fenton

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

The conclusion drawn from this study can be summarized that the main degradation of SDBS at below CMC proceeds via a reaction with OH radicals and since SDBS is anionic surfactant of negligible volatility, direct pyrolysis of SDBS can be expected to be insignificant. Therefore, the formation of OH radicals is the significant effect involved in this treatment. From the discussion, by using the US + Fenton treatment appears to be the highest in terms of % TOC removal which is 67% and followed by the others two treatment which is US + H_2O_2 and US alone treatment have been achieved at 55% and 12%. .

The initial degradation rate (d[SDBS]/dt, within the first 30 min) increases by using the US + Fenton treatment which is 0.68 μM/min followed by US + H_2O_2 and US alone were achieved at 0.52 μM/min and 0.44 μM/min respectively. This could be explained due to the fact that using Fenton reagent can increasing the probability OH radicals attack on SDBS molecules, thus the leading to increased degradation rates and the end of treatment maybe more short organic compounds were formed. Thus as the actual conclusion, by using US + Fenton treatment is more effective to used for treat wastewater than US + H_2O_2 and US alone.

There are several recommendations that can be improved for the further research on sonication degradation of SDBS which is needed to research more in different concentration of H_2O_2 and Fenton reagent to see the enhancement to SDBS degradation in the presence of various reagents. The use of higher frequency of ultrasound may give a significant effect to the overall degradation of SDBS as it is one of the factors that affect the cavitation process. Lastly but not least, for the further investigations are needed to understand the mechanisms involved in all treatments.

APPENDICES

SECTION A: DATA

i) Table for US alone

Sonication Time	**0**	**1**	**2**	**5**	**10**	**20**	**30**	**45**	**60**	**90**	**120**
TOC	21.6	21.55	21.41	21.36	21.23	21.00	20.90	20.72	20.56	20.10	19.10
	21.6	21.43	21.35	21.28	21.23	21.09	20.70	20.64	20.63	20.06	19.18
	21.6	21.52	21.42	21.47	21.23	20.81	20.860	20.78	20.49	20.12	19.08
Ph	7.2	7.18	7.17	7.15	7.10	7.07	7.03	6.98	6.95	6.88	6.83
	7.2	7.19	7.17	7.14	7.11	7.08	7.03	6.99	6.95	6.88	6.84
	7.2	7.18	7.16	7.15	7.11	7.07	7.03	6.99	6.97	6.87	6.83
[SDBS]	98.6433	97.8547	96.3695	91.9738	88.6542	85.7145	85.3899	85.2390	84.1980	83.7144	82.2560
	99.5487	97.2049	96.4399	92.6709	88.7322	85.6972	85.7234	84.2498	84.0720	83.4000	82.3560
	98.0454	97.5432	97.0985	91.0237	88.0587	86.9176	87.9098	85.9871	85.1520	84.4654	82.2067

ii) Tables for US with H_2O_2

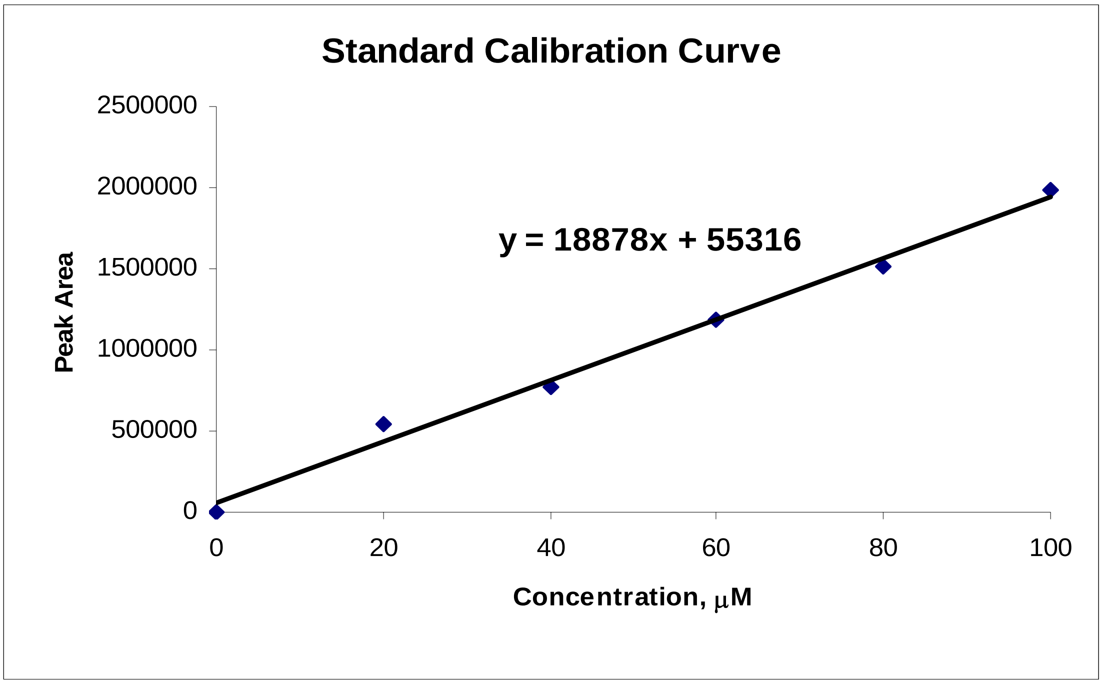
Sonication Time	**0**	**1**	**2**	**5**	**10**	**20**	**30**	**45**	**60**	**90**	**120**
TOC	21.6	20.84	19.71	18.13	15.47	13.40	12.46	11.43	10.92	9.97	9.69
	21.6	20.80	19.69	18.10	15.38	13.41	12.46	11.40	10.90	9.90	9.66
	21.6	20.76	19.73	18.18	15.50	13.35	12.48	11.33	10.82	9.95	9.69
Ph	6.96	6.95	6.92	6.87	6.83	6.77	6.72	6.65	6.61	6.56	6.52
	6.97	6.94	6.93	6.87	6.83	6.78	6.71	6.65	6.60	6.55	6.52
	6.96	6.95	6.92	6.87	6.83	6.77	6.72	6.66	6.60	6.54	6.51
[SDBS]	95.6751	92.6548	89.2584	87.6158	84.9562	81.5043	80.0033	78.3214	76.5238	74.4985	72.5621
	95.7162	93.0509	89.6754	88.0087	84.9562	81.6943	80.9990	78.3543	76.6139	74.5007	72.2769
	97.6809	92.7578	89.3432	87.5132	84.5432	82.3783	81.3421	77.3098	77.0938	73.0998	73.6691

iii) Table for US with Fenton reagent.

Sonication Time	**0**	**1**	**2**	**5**	**10**	**20**	**30**	**45**	**60**	**90**	**120**
TOC	21.6	19.43	17.62	13.82	12.23	11.14	10.45	9.67	8.79	7.89	6.78
	21.6	19.93	17.67	13.09	12.13	11.10	10.54	9.68	8.55	7.82	6.77
	21.6	20.01	17.70	14.02	12.24	11.15	10.47	9.67	8.74	7.83	6.78
Ph	3.09	3.08	3.06	3.03	3.00	2.98	2.96	2.92	2.90	2.86	2.83
	3.09	3.08	3.06	3.04	3.01	2.98	2.97	2.93	2.90	2.85	2.82
	3.09	3.08	3.05	3.03	3.01	2.99	2.96	2.93	2.89	2.86	2.83
[SDBS]	87.9422	85.2596	82.9524	79.2007	76.3514	70.2589	67.5739	66.4523	65.3255	64.3257	63.2755
	87.9542	85.2696	81.9534	79.2010	76.3632	71.2605	67.5743	66.4698	66.5651	63.9097	63.03755
	87.8998	85.2601	82.9698	78.2023	76.3625	71.2479	68.6679	65.0032	65.3417	64.0032	62.9755

iv) Table below shows the data of standard calibration curve for SDBS

Concentration (μM)	**Peak Area**
0	0
20	541323
40	777719
60	1184821
80	1512651
100	1978635



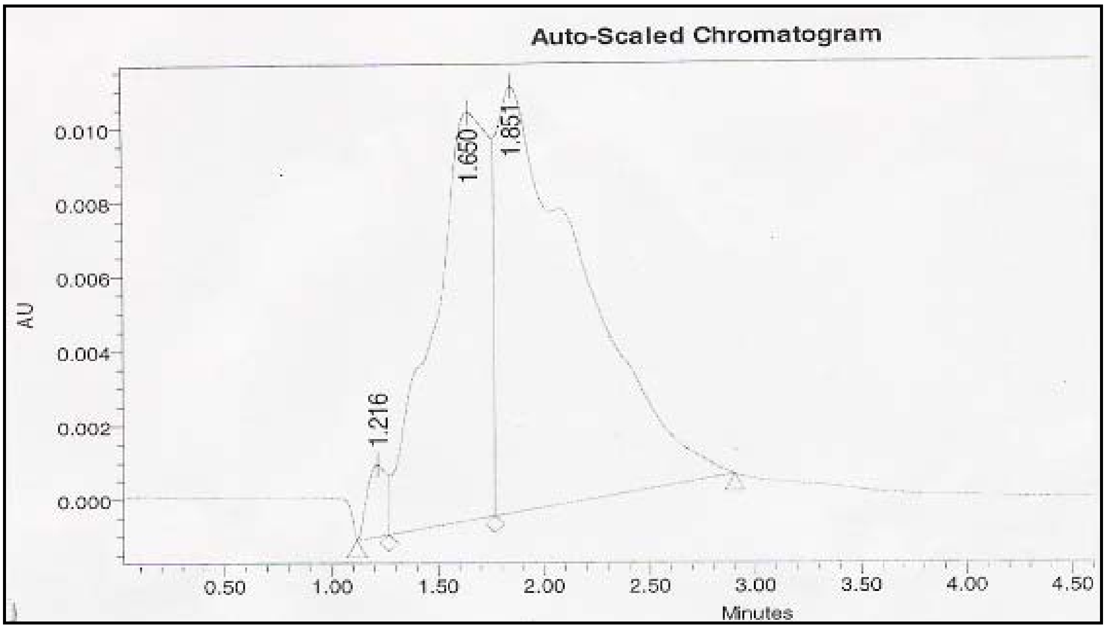
v) Figure shows the standard calibration curve for SDBS

vi) Tables below show the data of [SDBS] for US alone, US + H_2O_2 and US + Fenton analysis.

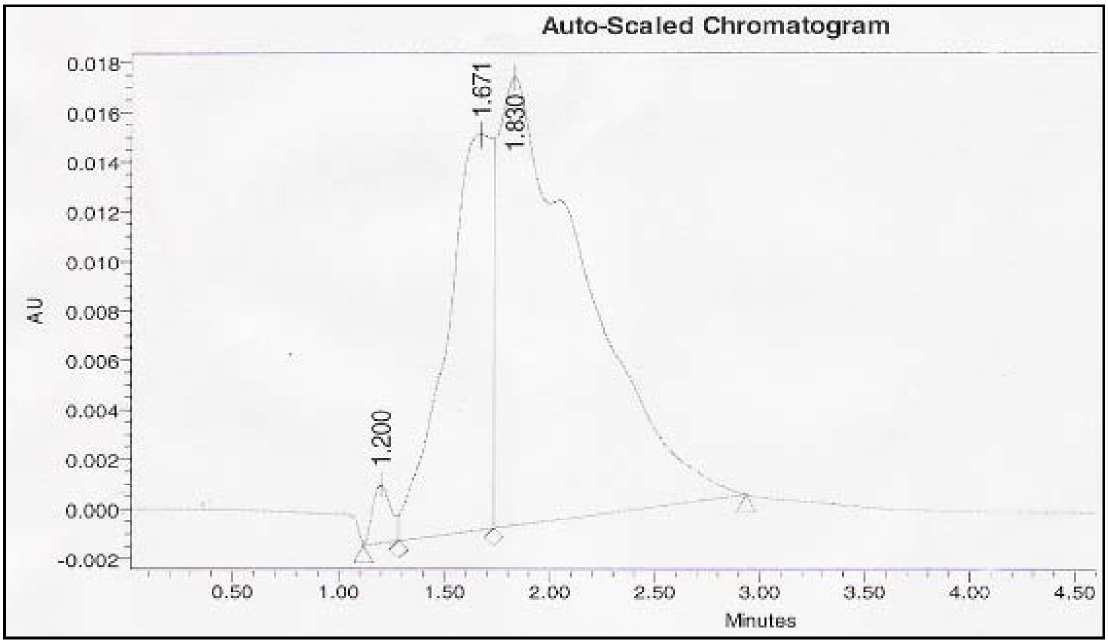
TIME, min	US alone		US + H_2O_2	
	Peak Area	[SDBS], µM	Peak Area	[SDBS], µM
0	1917504	98.6433	1861471	95.6751
1	1902617	97.8547	1804453	92.6548
2	1874579	96.3695	1740336	89.2584
5	1791597	91.9738	1709327	87.6158
10	1728930	88.6542	1659119	84.9562
20	1673434	85.7145	1593954	81.5043
30	1667307	85.3899	1565618	80.0033
45	1664458	85.2390	1533867	78.3214
60	1662815	85.1520	1499932	76.5238
90	1635676	83.7144	1461699	74.4985
120	16081445	82.2560	1425143	72.5621

TIME, min	US + Fenton	
	Peak Area	[SDBS], µM
0	1715489	87.9422
1	1664847	85.2596
2	1621291	82.9524
5	1550467	79.2007
10	1496678	76.3514
20	1381664	70.2589
30	1330976	67.5739
45	1309803	66.4523
60	1288531	65.3255
90	1269657	64.3257
120	1249831	63.2755

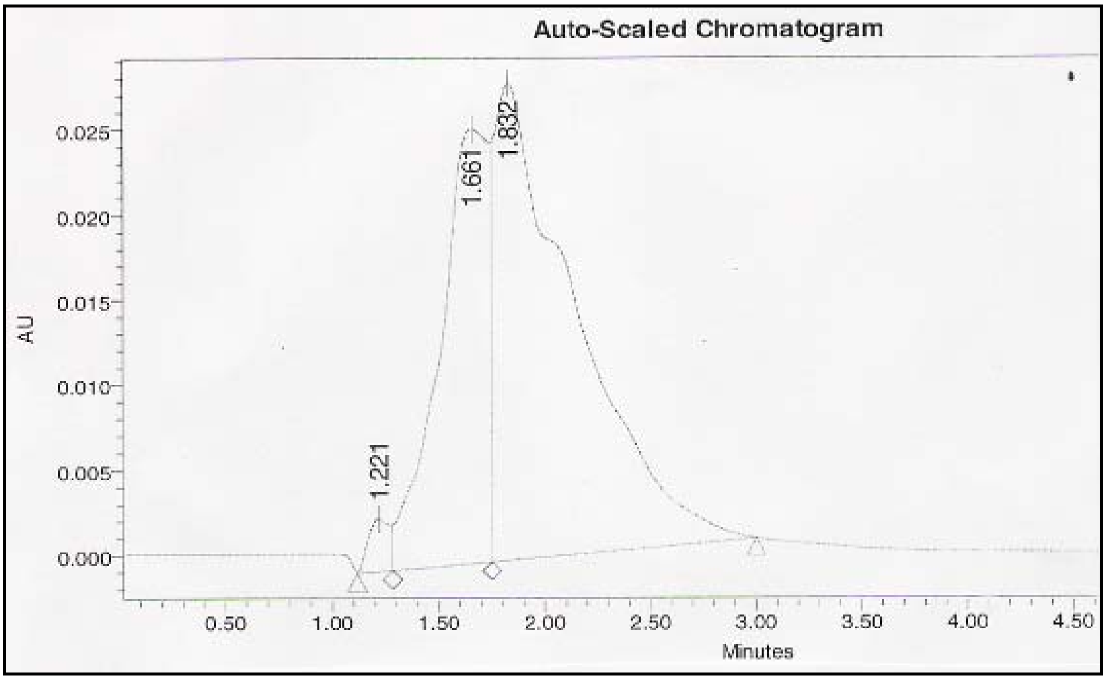
SECTION B: CHROMATOGRAM GRAPH



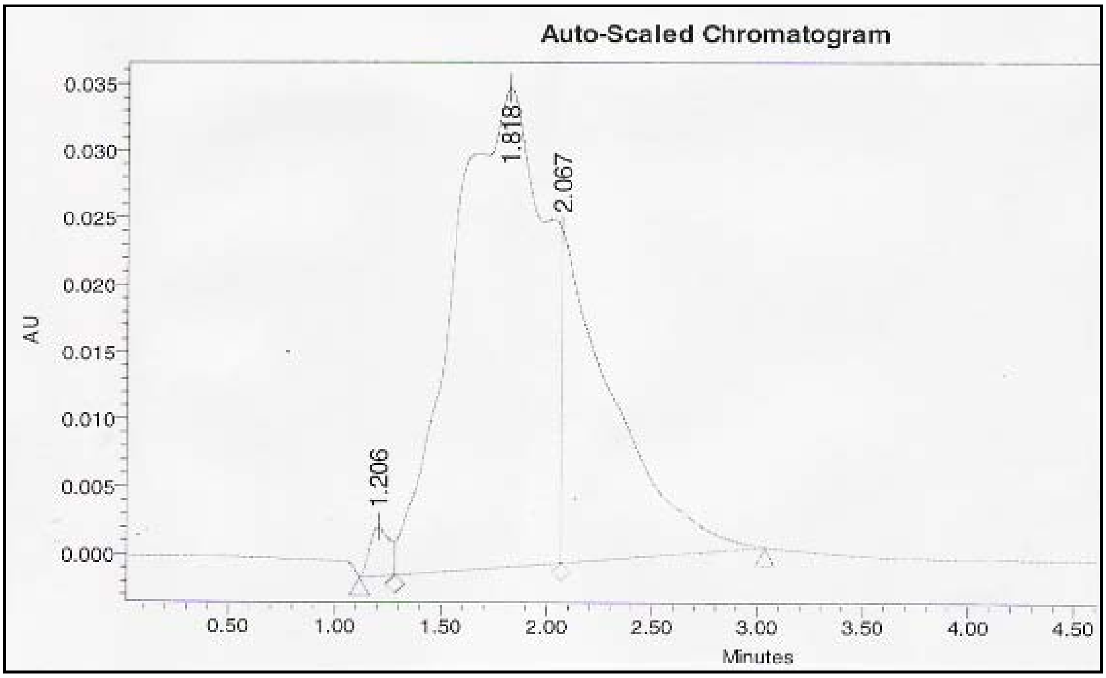
i) Chromatogram graph for standard 20 μM at 230nm.



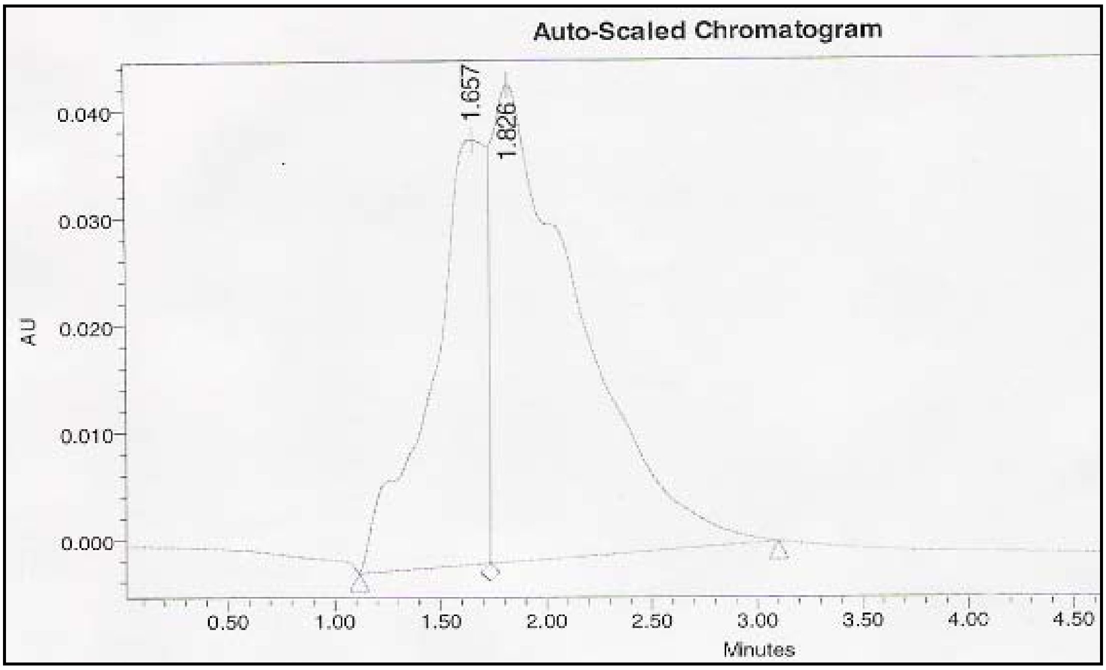
ii) Chromatogram graph for standard 40 μM at 230nm.



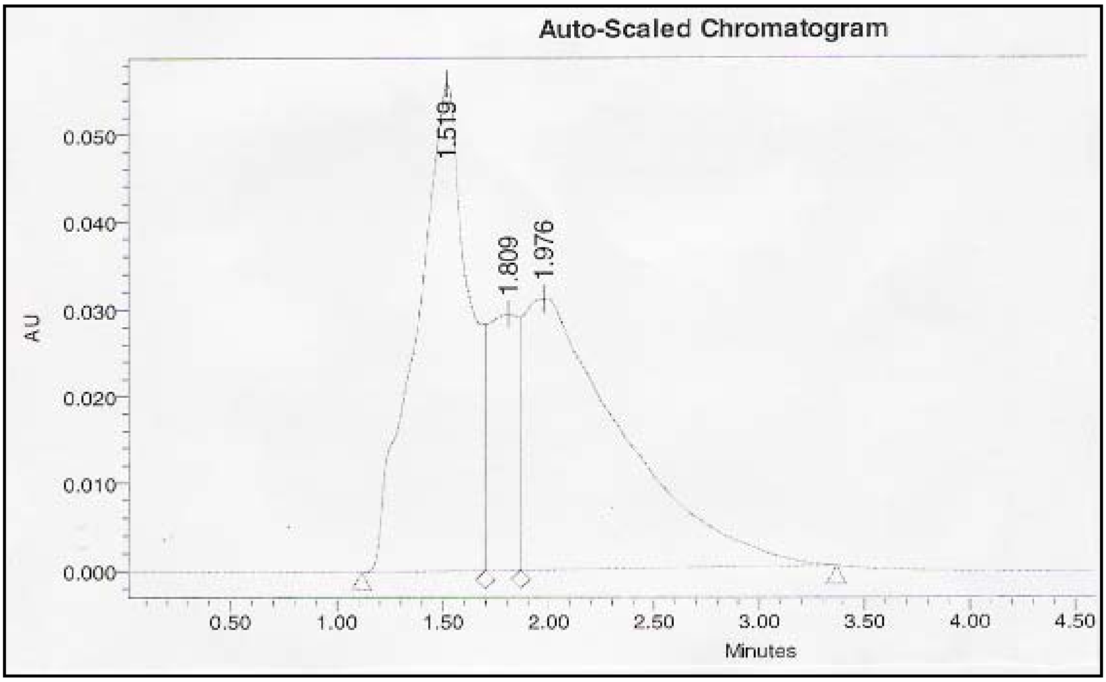
iii) Chromatogram graph for standard 60 μM at 230nm.



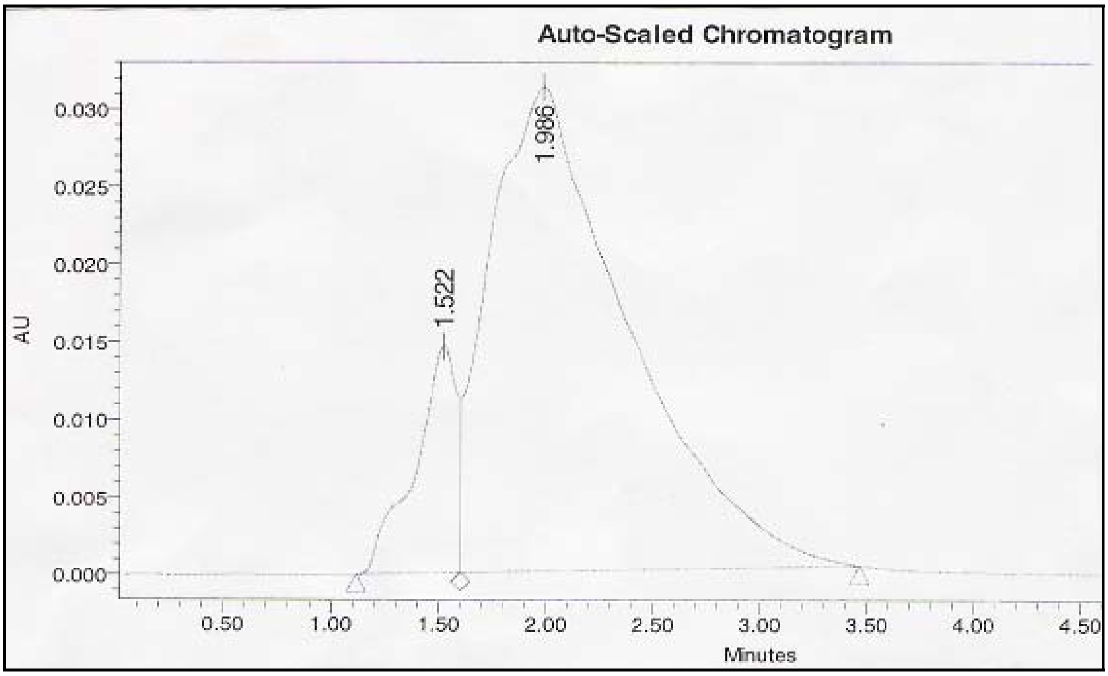
iv) Chromatogram graph for standard 80 μM at 230nm.



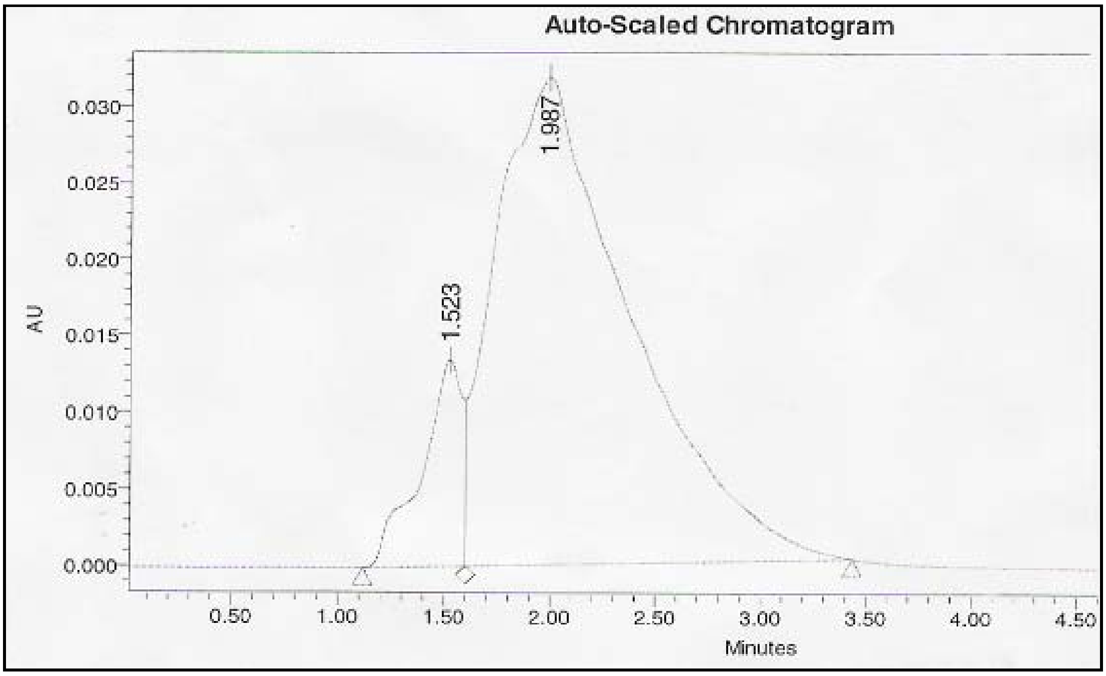
v) Chromatogram graph for standard 100 μM at 230nm.



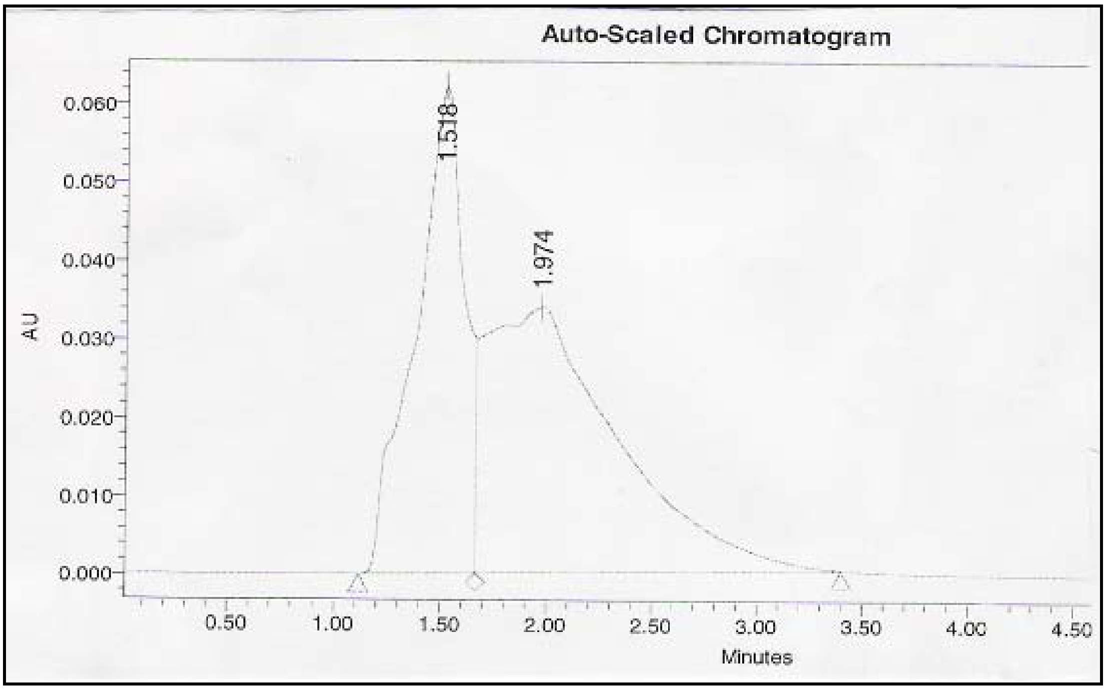
v) Chromatogram graph for US alone at 0 min at 30 °C and 230nm.



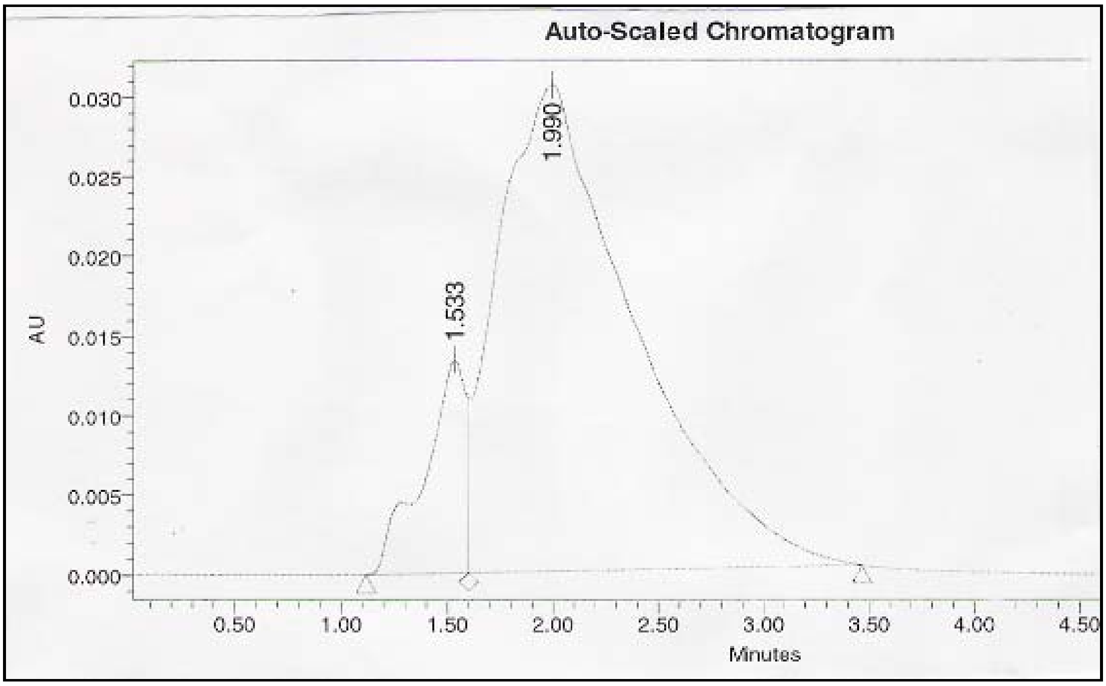
vi) **Chromatogram graph for US alone at 1 min at 30 °C and 230nm.**



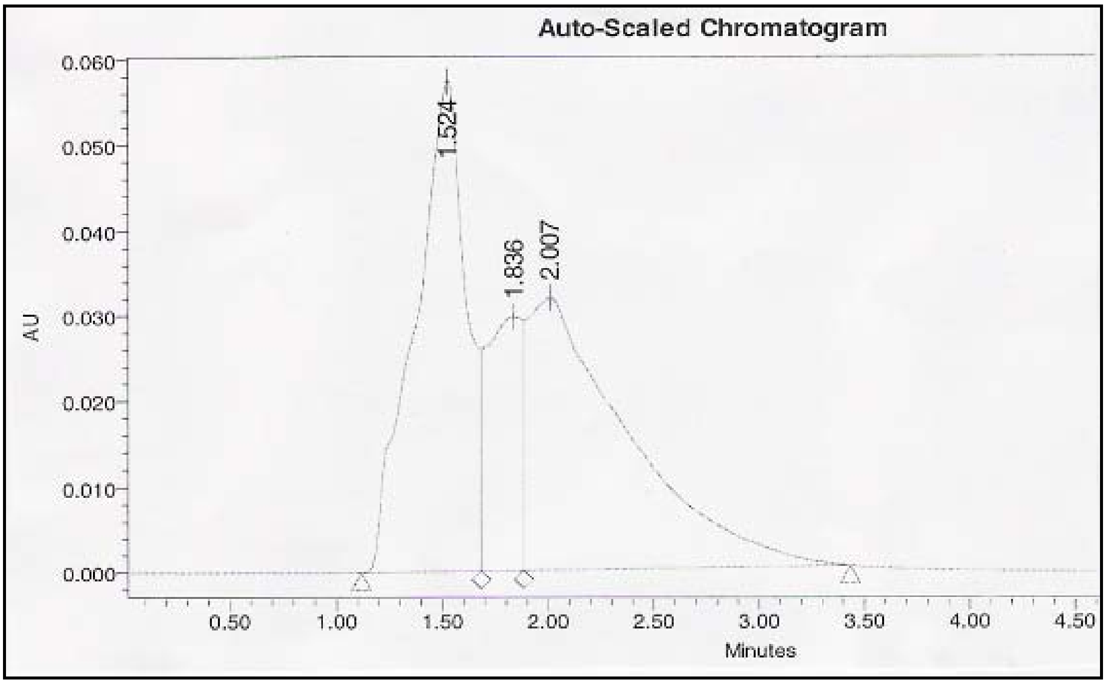
vii) Chromatogram graph for US alone at 2 min at 30 °C and 230nm.



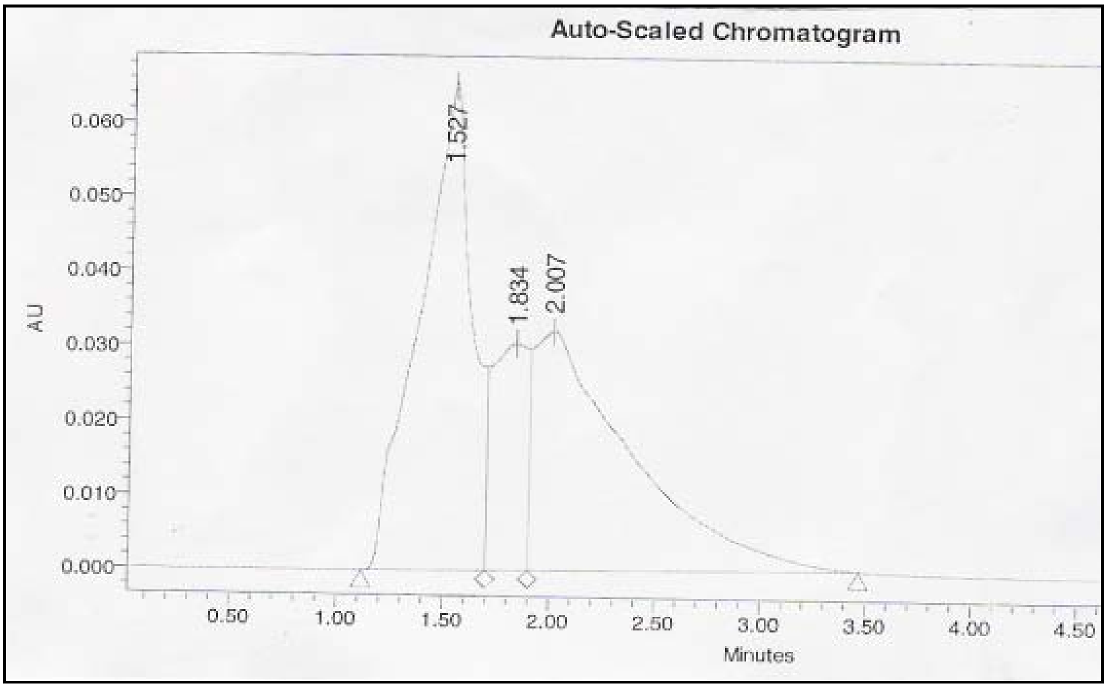
viii) Chromatogram graph for US alone at 5 min at 30 °C and 230nm.



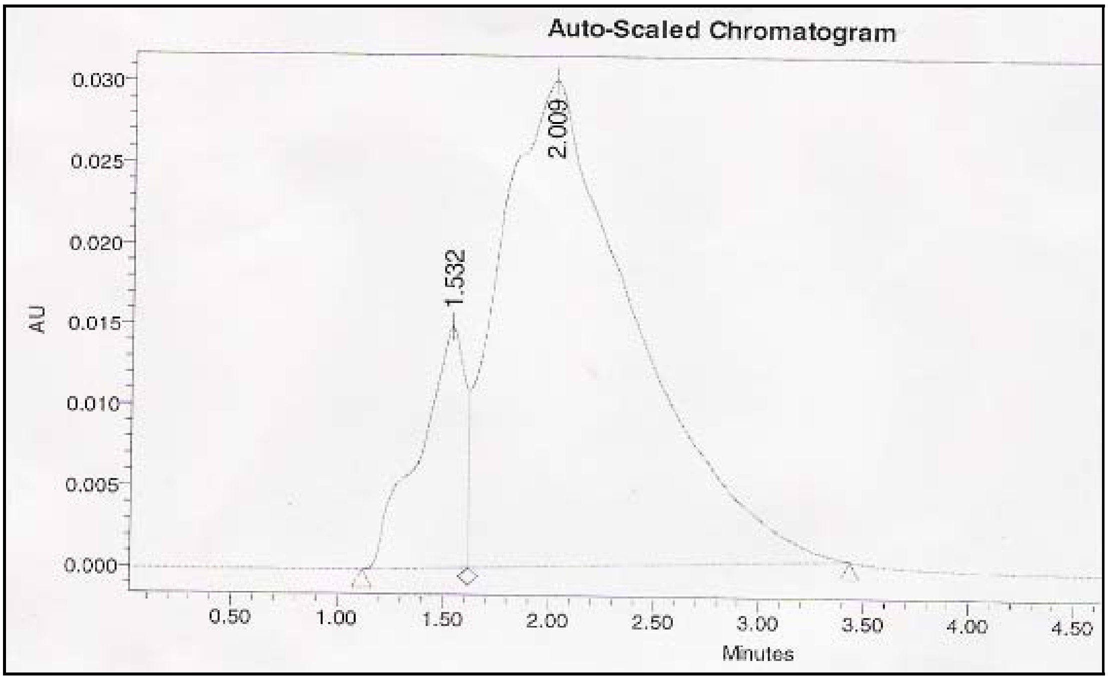
ix) Chromatogram graph for US alone at 10 min at 30 °C and 230nm.



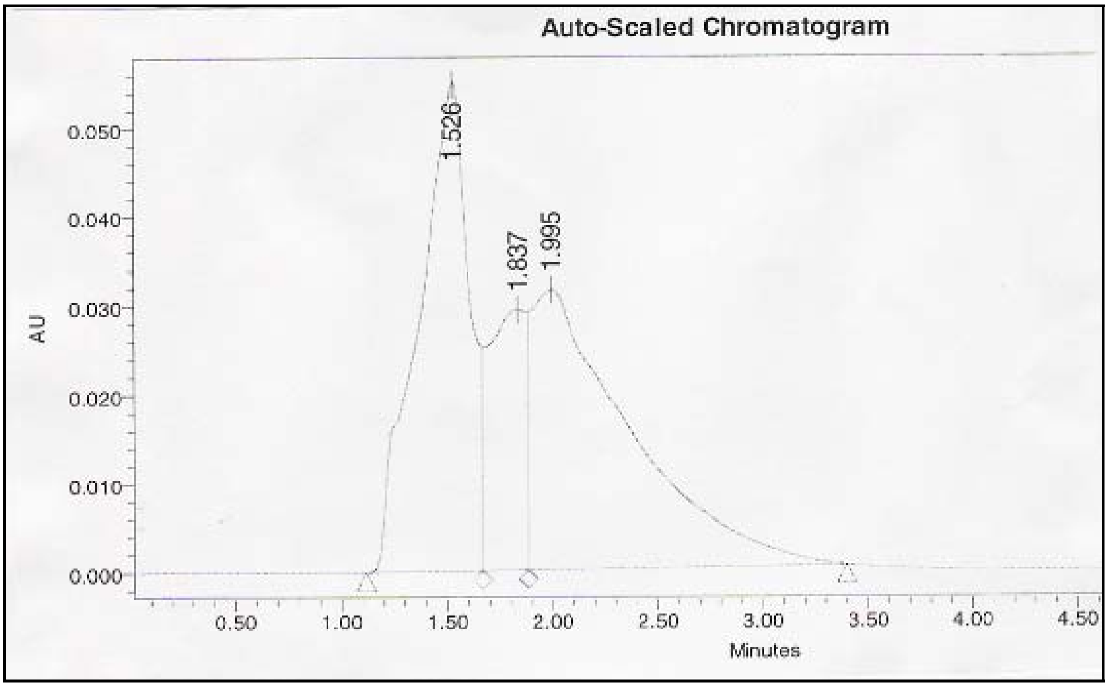
x) Chromatogram graph for US alone at 20 min at 30 °C and 230nm.



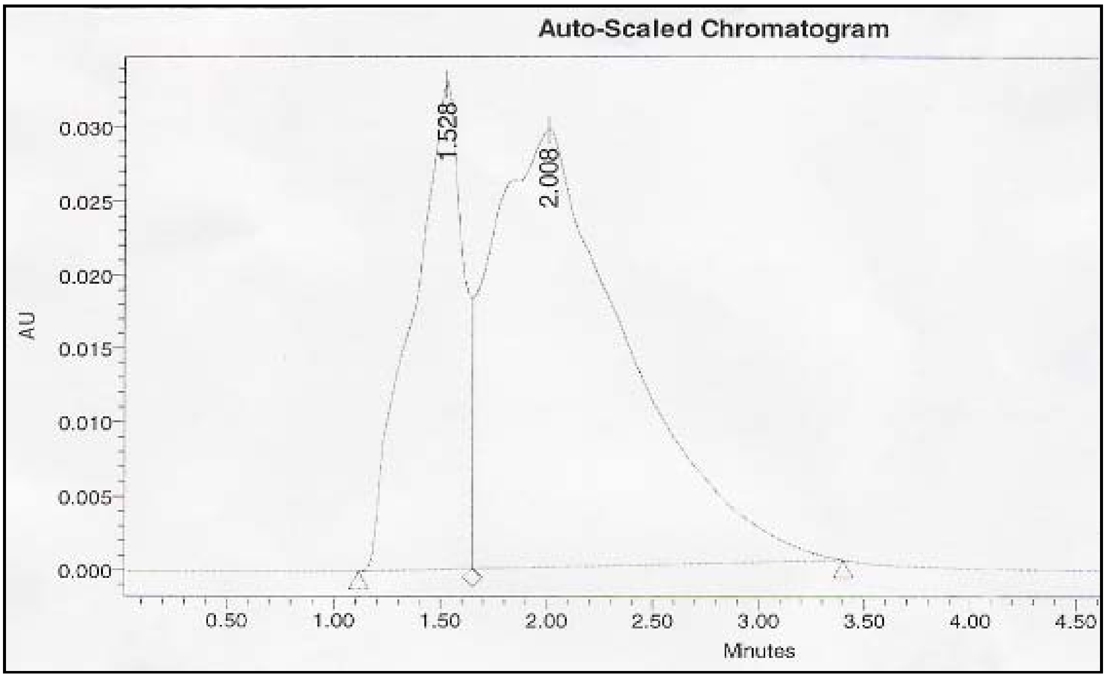
xi) Chromatogram graph for US alone at 30 min at 30 °C and 230nm.



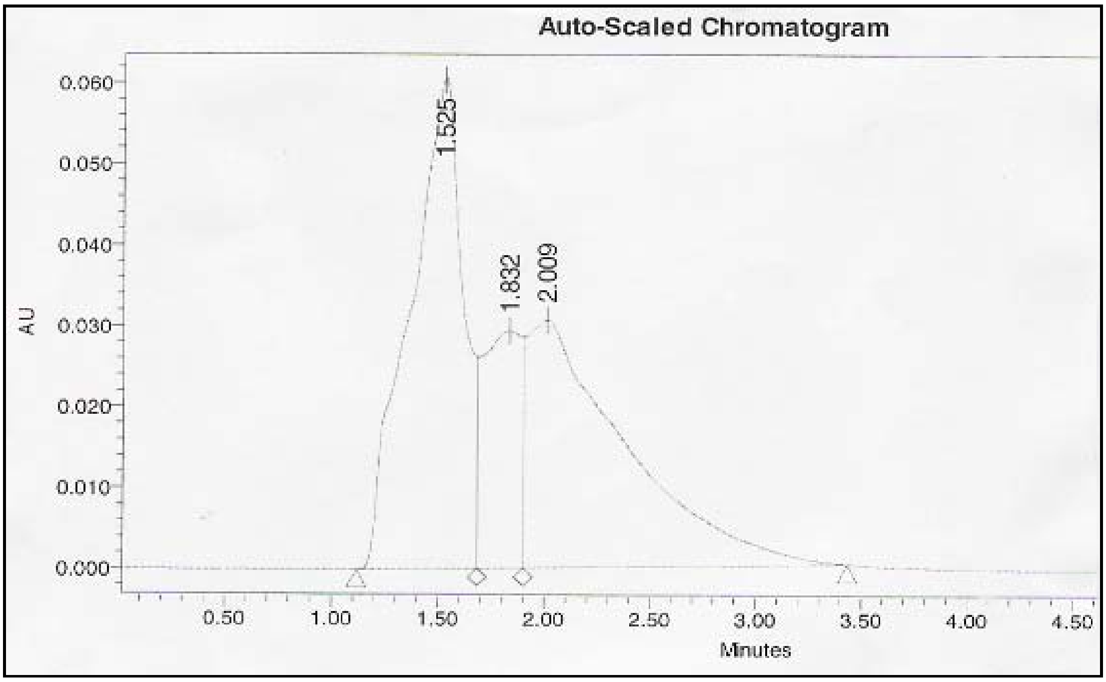
xii) Chromatogram graph for US alone at 45 min at 30 °C and 230nm.



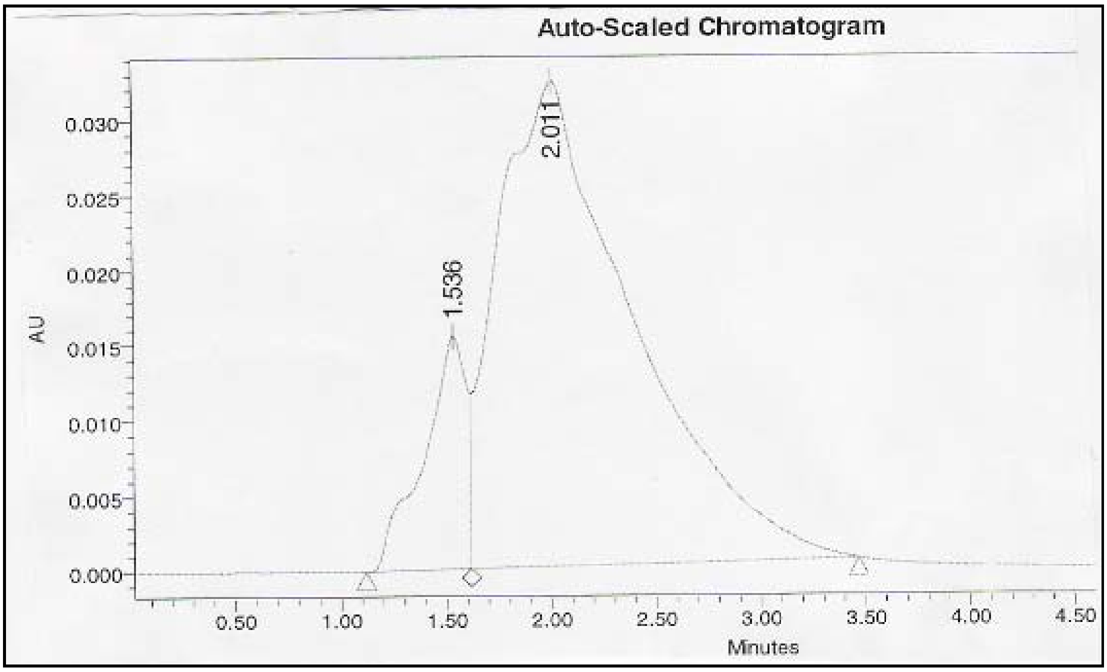
xiii) Chromatogram graph for US alone at 60 min at 30 °C and 230nm.



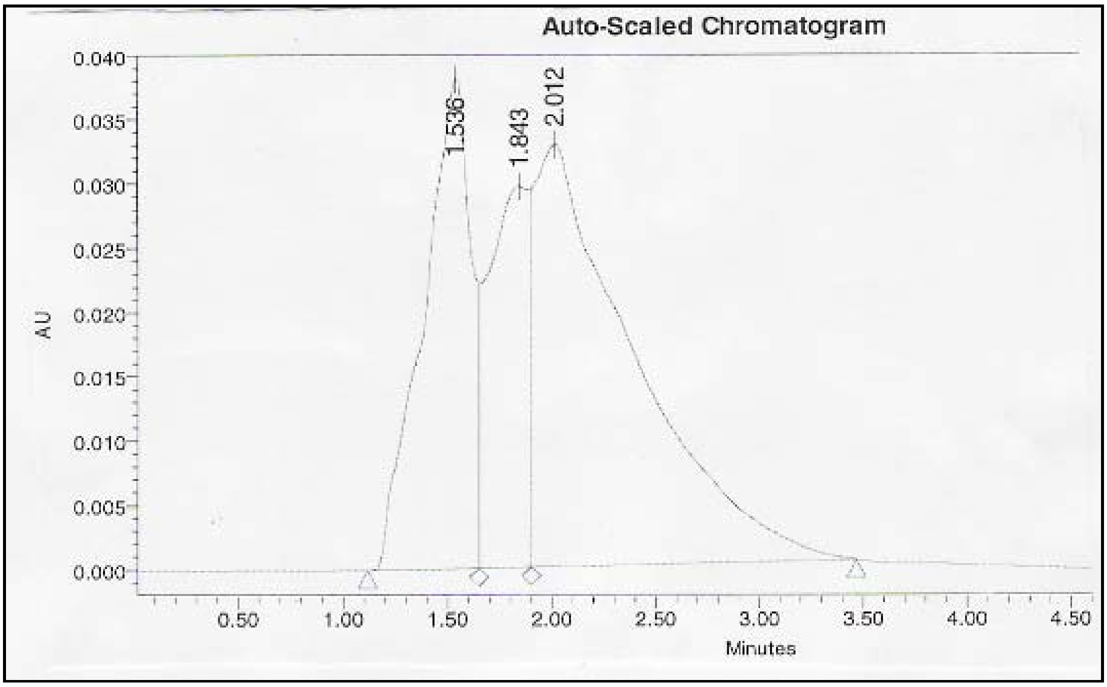
xiv) Chromatogram graph for US alone at 90 min at 30 °C and 230nm.



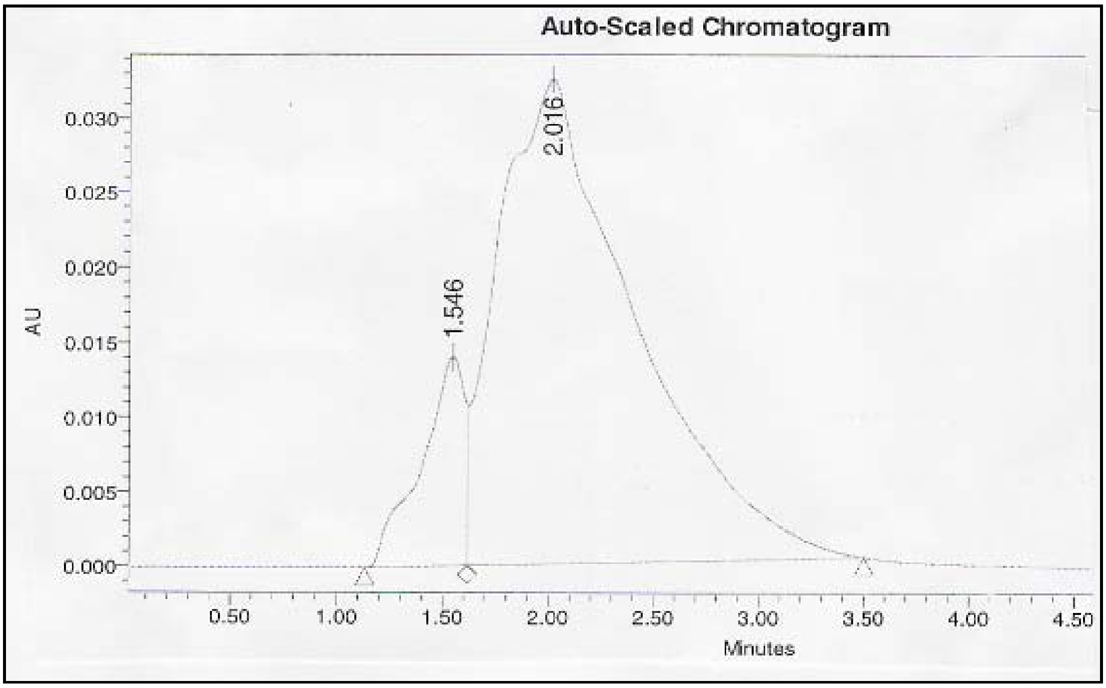
xv) Chromatogram graph for US alone at 120 min at 30 °C and 230nm.



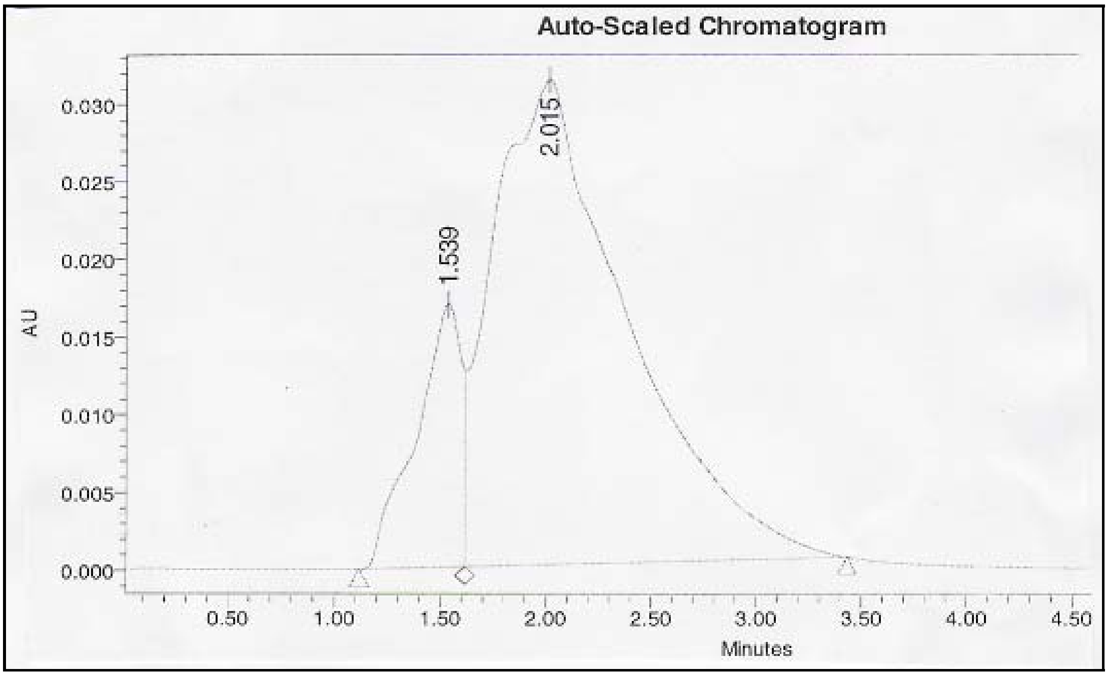
xvi) Chromatogram graph for US + H_2O_2 at 0 min, 30 °C and 230nm.



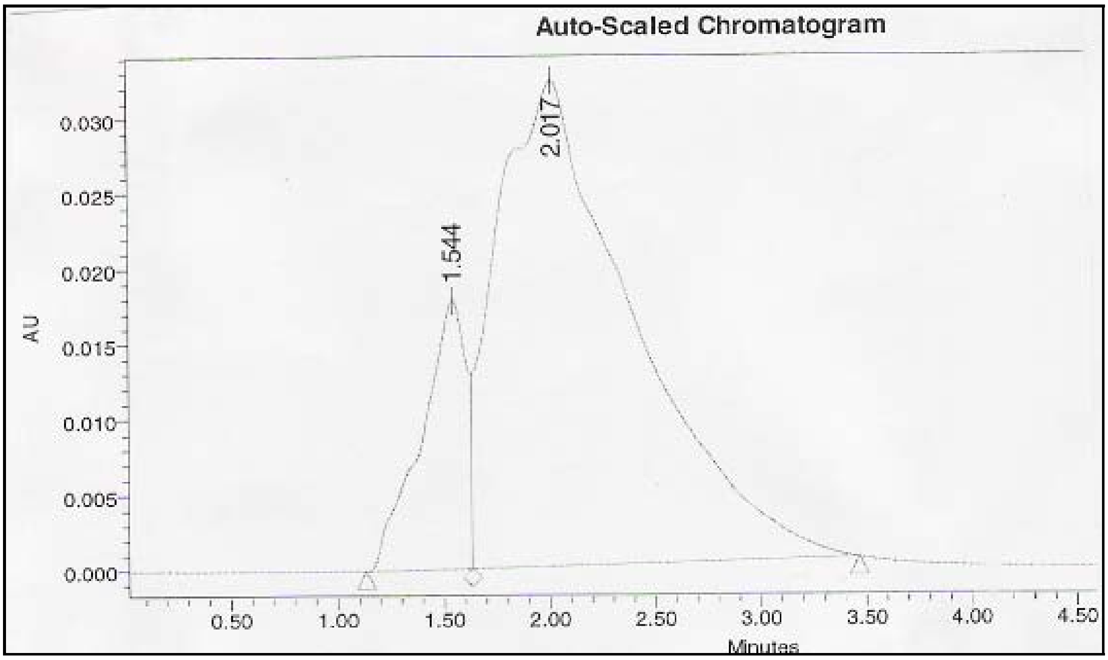
xvii) Chromatogram graph for US + H_2O_2 at 1 min, 30 °C and 230nm.



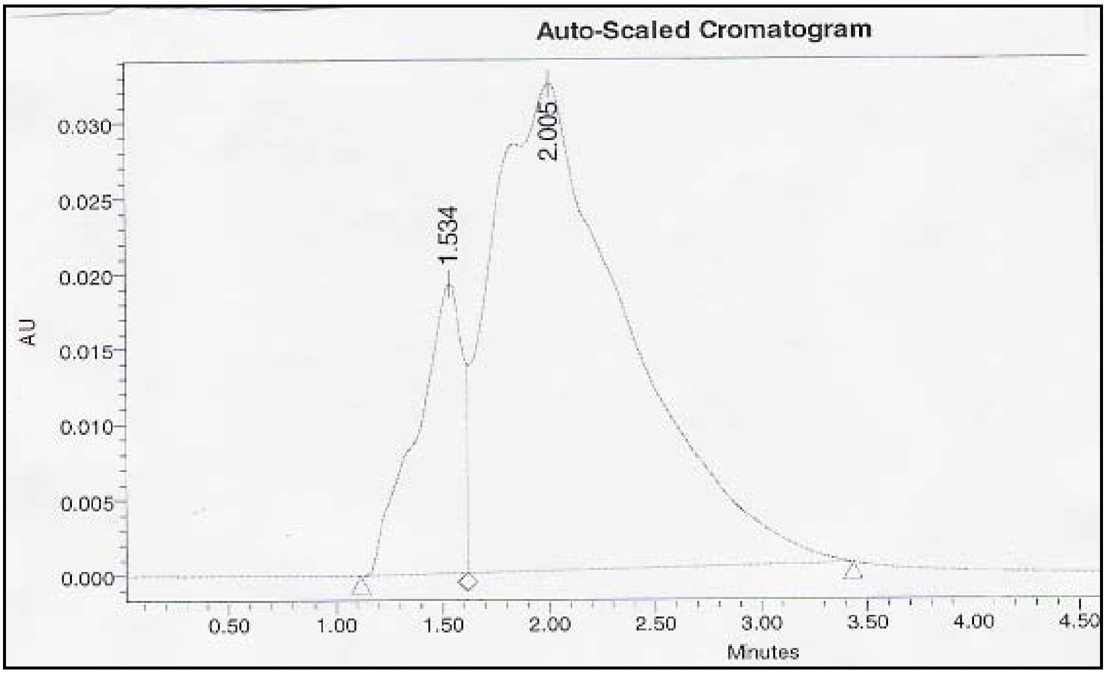
xviii) Chromatogram graph for US + H_2O_2 at 2 min, 30 °C and 230nm.



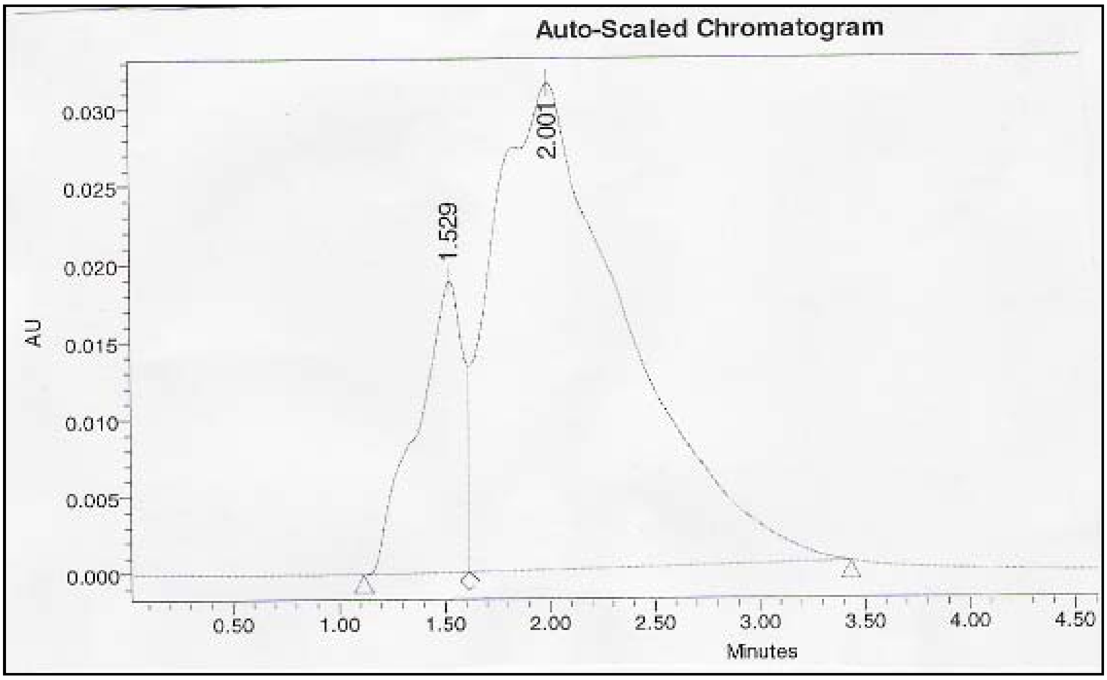
xix) Chromatogram graph for US + H_2O_2 at 5 min, 30 °C and 230nm.



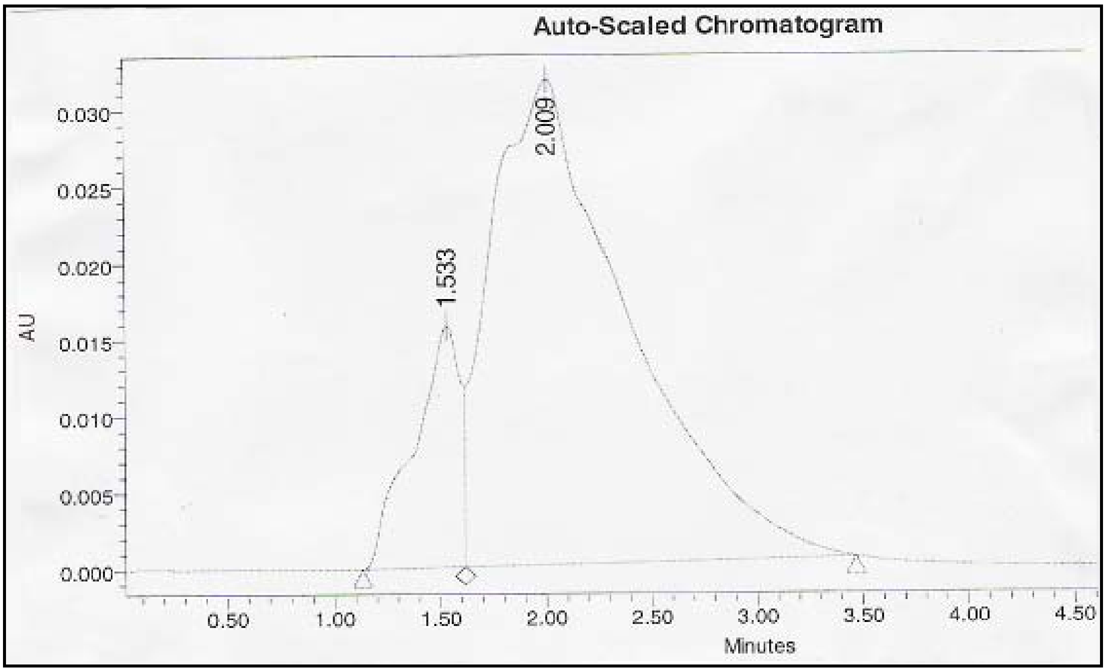
xx) Chromatogram graph for US + H_2O_2 at 10 min, 30 °C and 230nm.



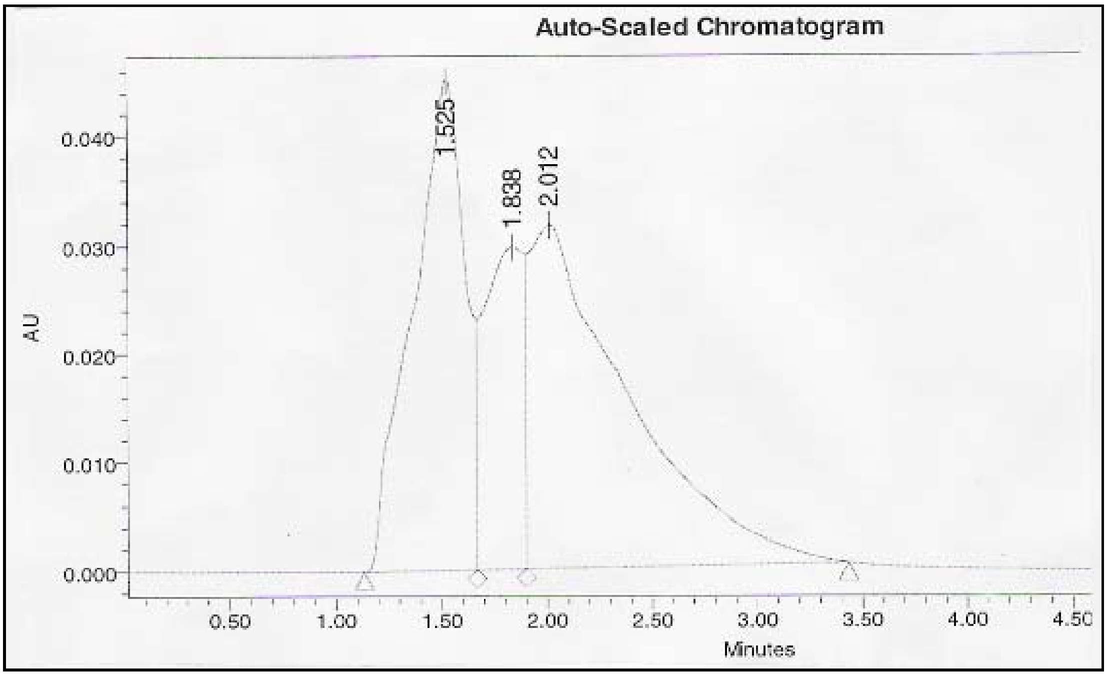
xxi) Chromatogram graph for US + H_2O_2 at 20 min, 30 °C and 230nm.



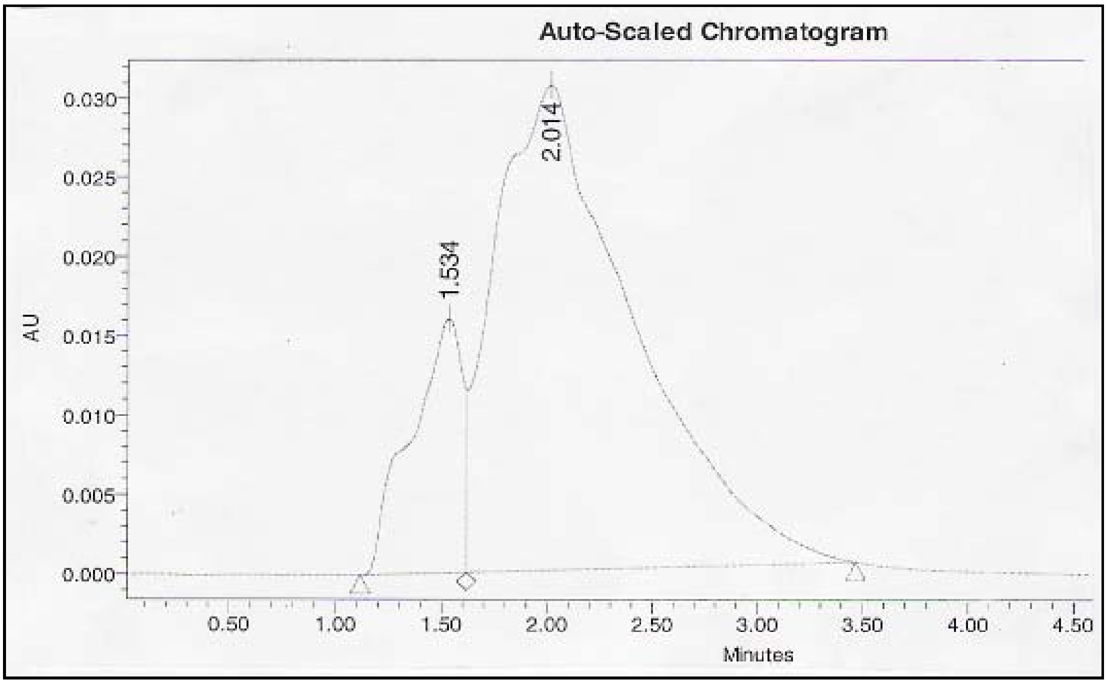
xxii) Chromatogram graph for US + H_2O_2 at 30 min, 30 °C and 230nm.



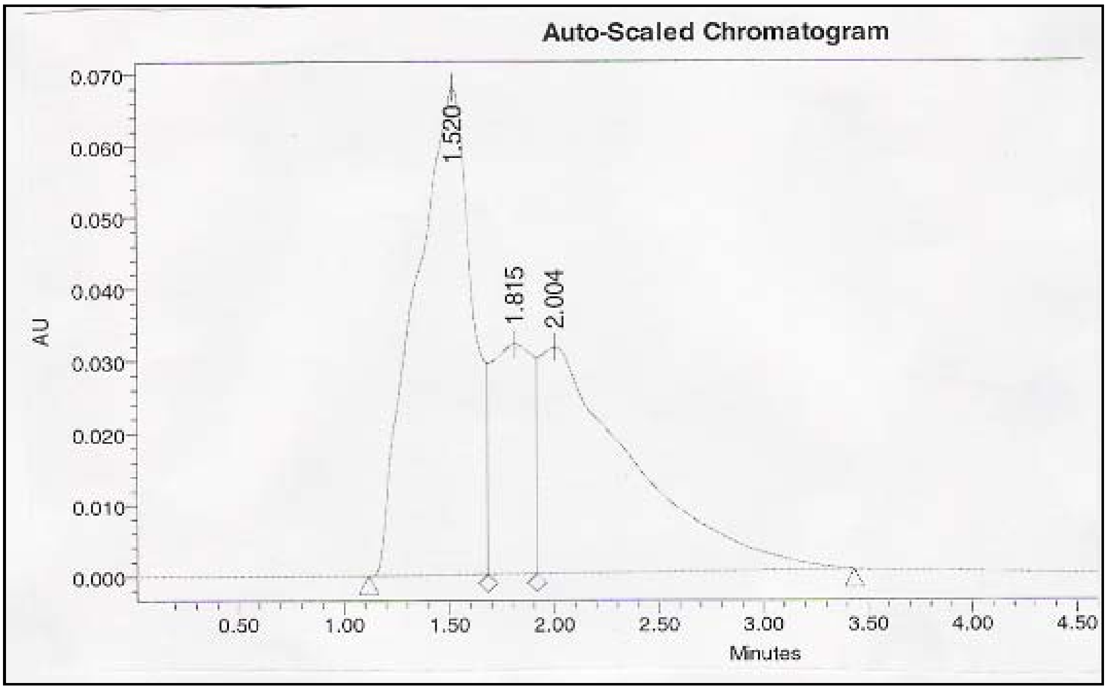
xxiii) Chromatogram graph for US + H_2O_2 at 45 min, 30 °C and 230nm.



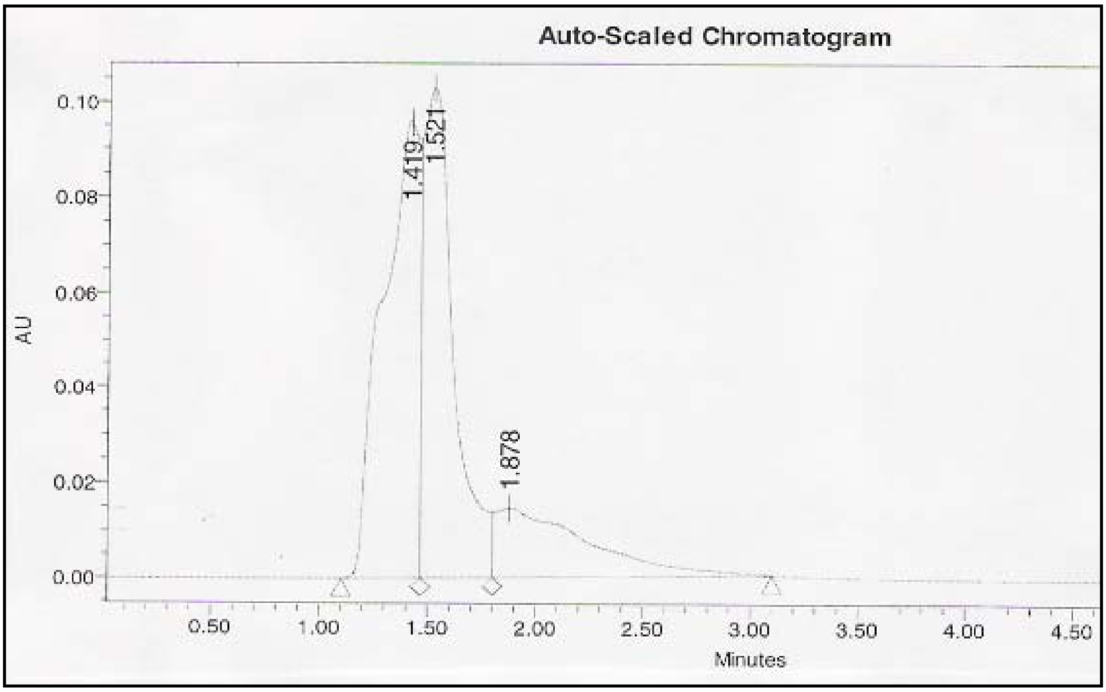
xxiv) Chromatogram graph for US + H_2O_2 at 60 min, 30 °C and 230nm.



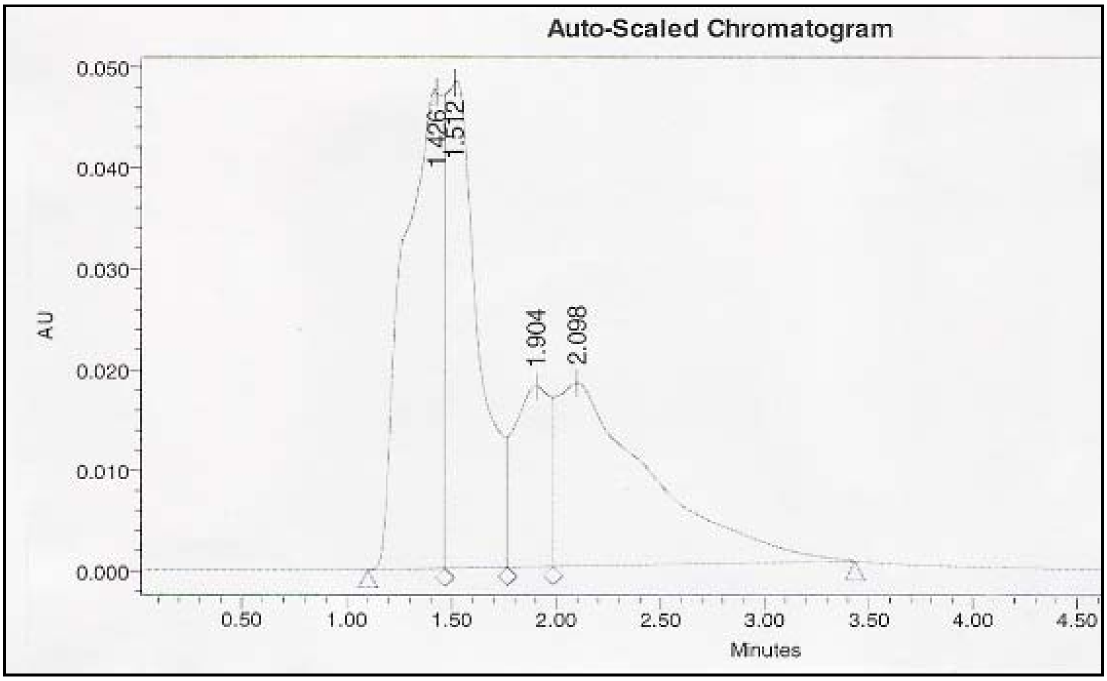
xxv) Chromatogram graph for US + H_2O_2 at 90 min, 30 °C and 230nm.



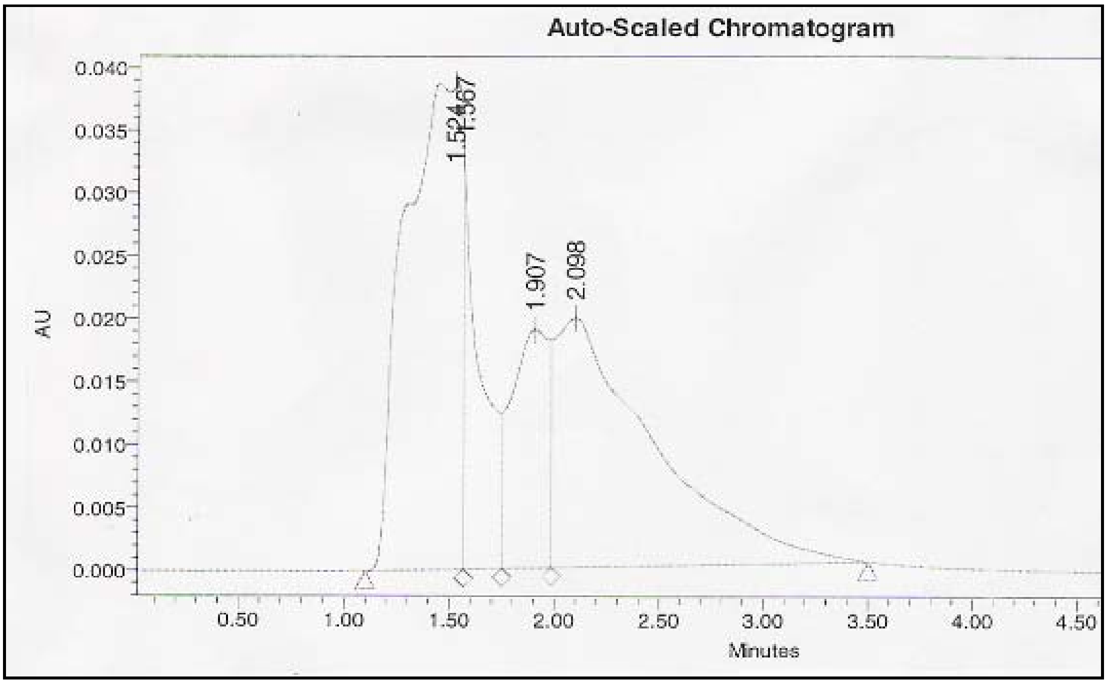
xxvi) Chromatogram graph for US + H_2O_2 at 120 min, 30 °C and 230nm.



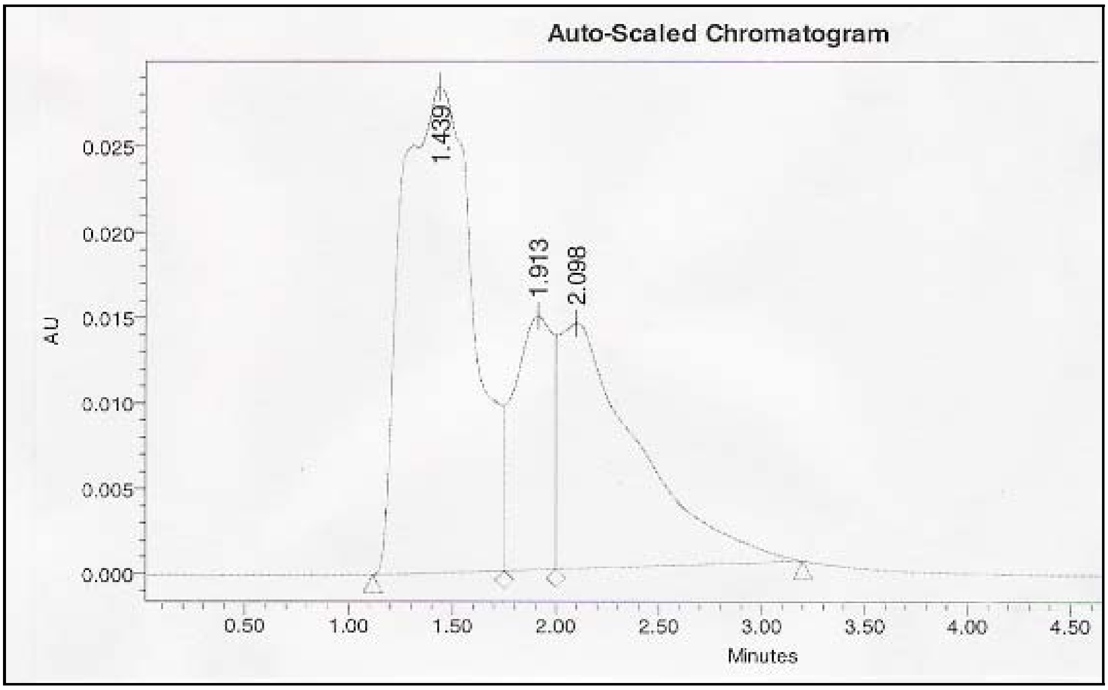
xxvii) Chromatogram graph for US + Fenton at 0 min, 30 °C and 230nm.



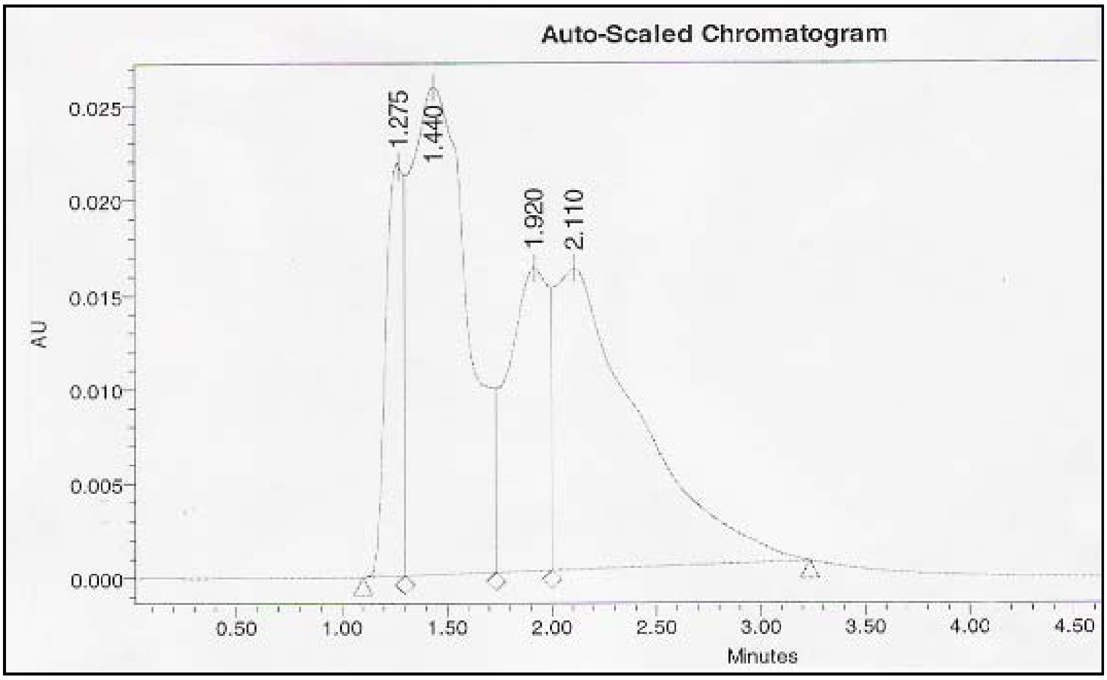
xxviii) Chromatogram graph for US + Fenton at 1 min, 30 °C and 230nm.



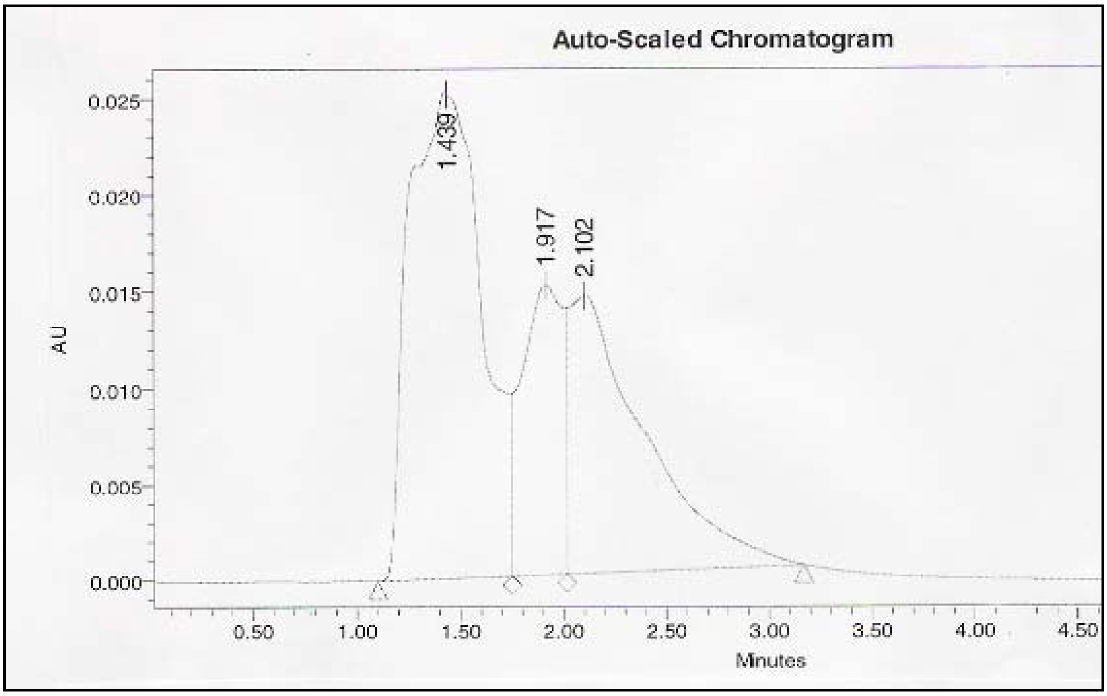
xxix) Chromatogram graph for US + Fenton at 2 min, 30 °C and 230nm.



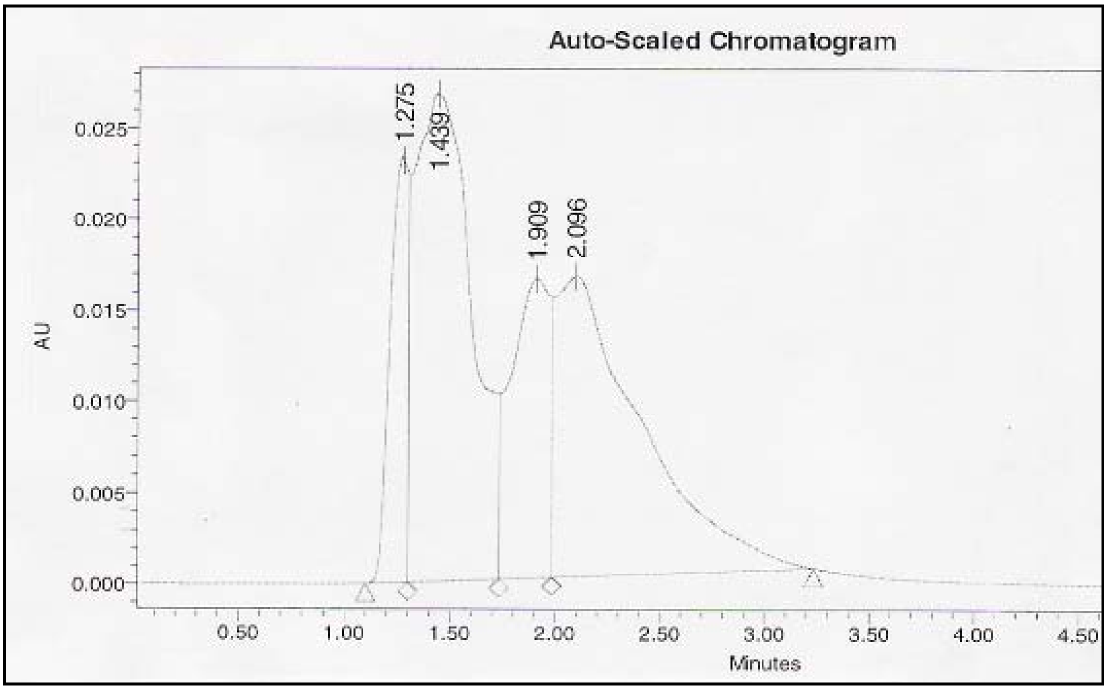
xxx) Chromatogram graph for US + Fenton at 5 min, 30 °C and 230nm.



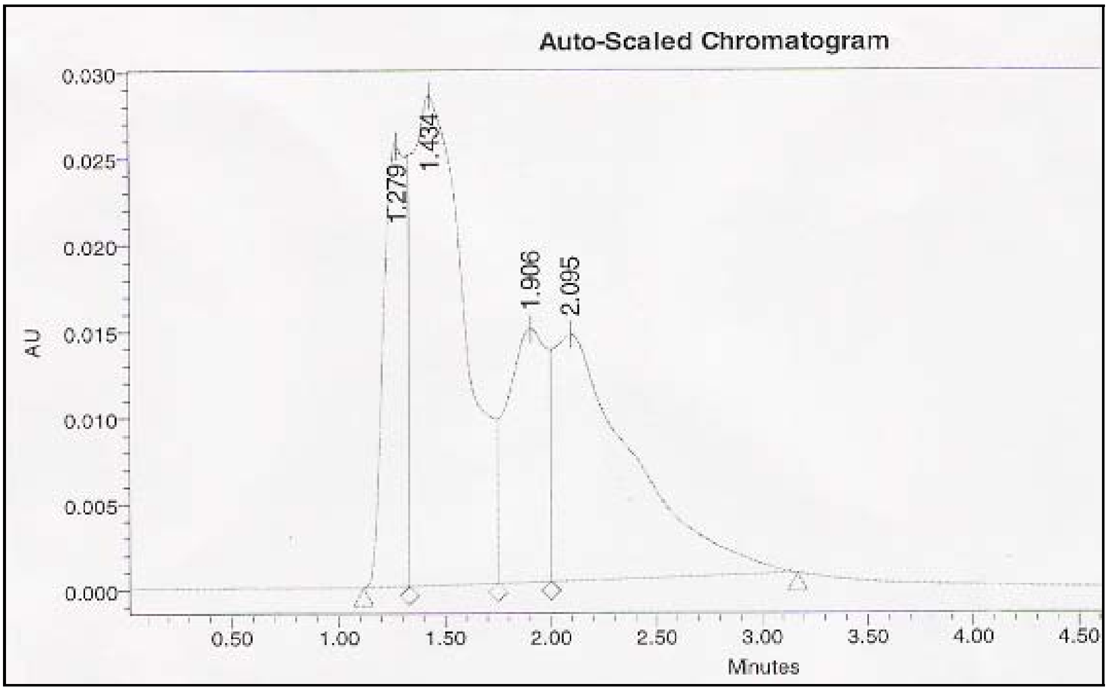
xxxi) Chromatogram graph for US + Fenton at 10 min, 30 °C and 230nm.



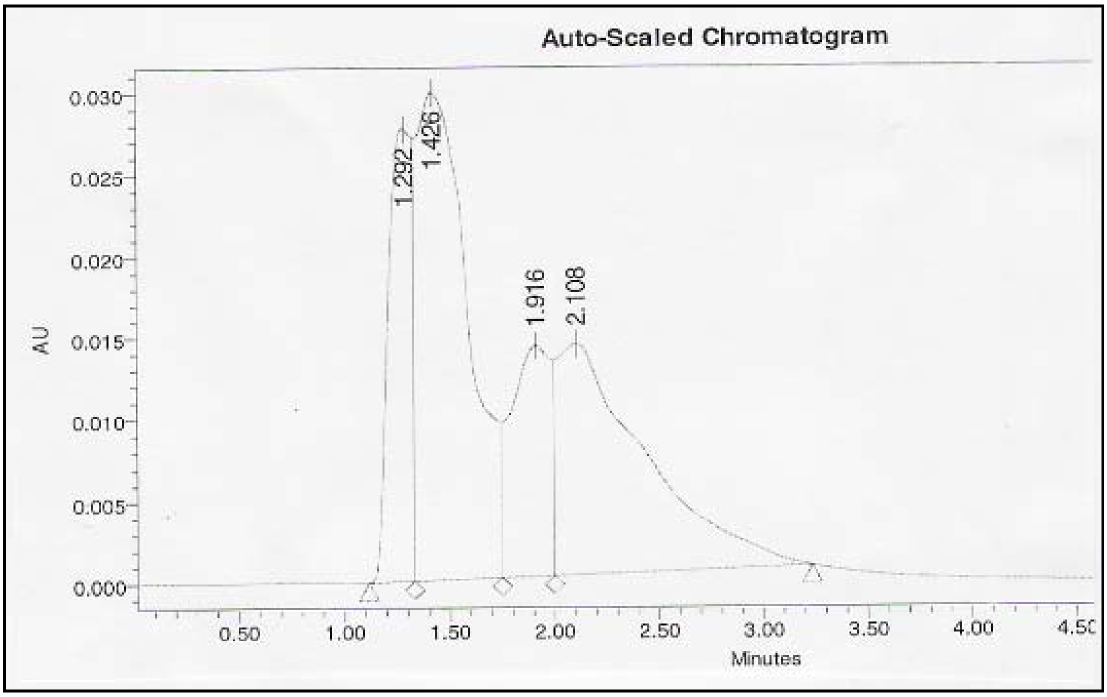
xxxii) Chromatogram graph for US + Fenton at 20 min, 30 °C and 230nm.



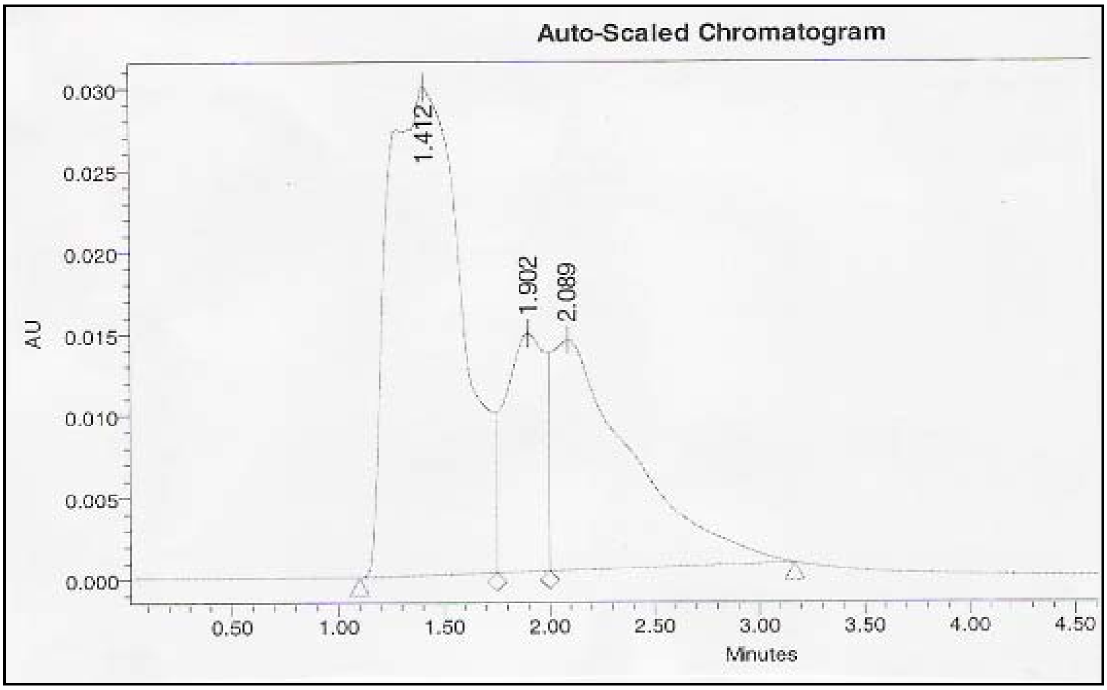
xxxiii) Chromatogram graph for US + Fenton at 30 min, 30 °C and 230nm.



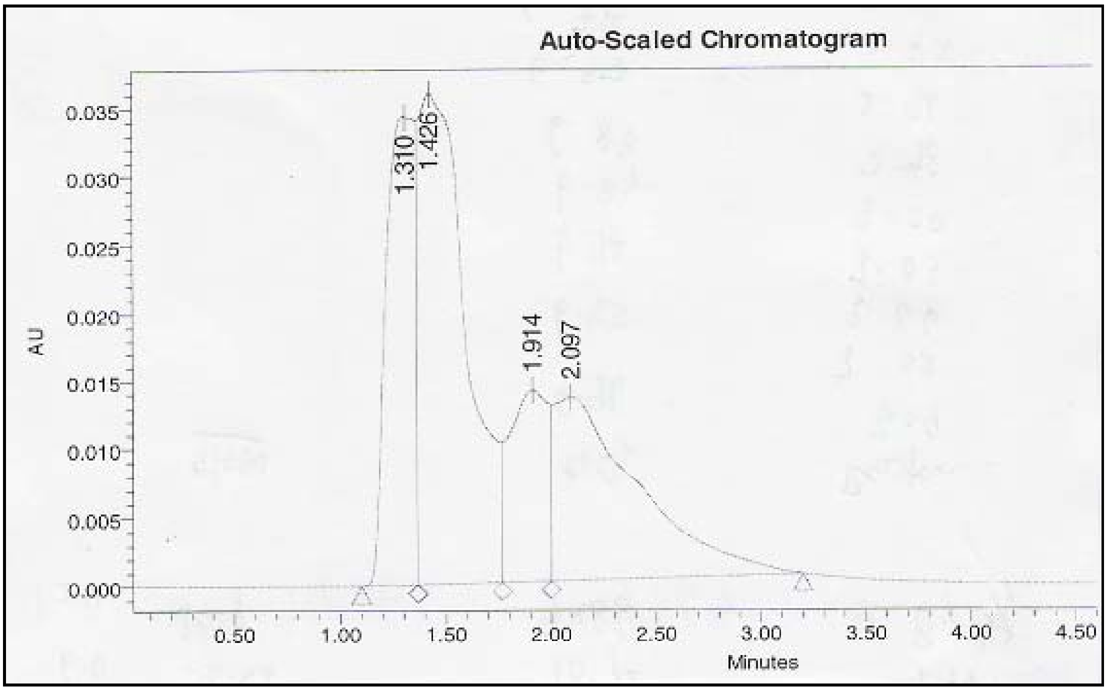
xxxiv) Chromatogram graph for US + Fenton at 45 min, 30 °C and 230nm.



xxxv) Chromatogram graph for US + Fenton at 60 min, 30 °C and 230nm.



xxxvi) Chromatogram graph for US + Fenton at 90 min, 30 °C and 230nm.



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UTM/RMC/F/0024 (1998)

UNIVERSITI TEKNOLOGI MALAYSIA

BORANG PENGESAHAN
LAPORAN AKHIR PENYELIDIKAN

TAJUK PROJEK : THE EFFECT OF HOMOGENEOUS CATALYST FOR THE DEGRADATION OF SODIUM DODECYLBENZENE SULFONATE IN WATER BY MEANS OF ULTRASONIC IRRADIATION

Saya DR MOHD ARIFFIN BIN ABU HASSAN
(HURUF BESAR)

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TANDATANGAN KETUA PENYELIDIK

DR MOHD ARIFFIN B ABU HASSAN
Nama & Cop Ketua Penyelidik

Tarikh : 10/05/2006

CATATAN : **Jika Laporan Akhir Penyelidikan ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh laporan ini perlu dikelaskan sebagai SULIT dan TERHAD.*

UNIVERSITI TEKNOLOGI MALAYSIA
Research Management Centre

PRELIMINARY IP SCREENING & TECHNOLOGY ASSESSMENT FORM
(To be completed by Project Leader submission of Final Report to RMC or whenever IP protection arrangement is required)

1. **PROJECT TITLE IDENTIFICATION** :

The effect of homogeneous catalyst for the degradation of Sodium Dodecylbenzene Sulfonate in water by means of ultrasonic irradiation Vote No: 75199

2. **PROJECT LEADER** :

Name :
DR MOHD ARIFFIN BIN ABU HASSAN

Address :
Chemical Engineering Department, Faculty Of Chemical and Natural Resources Enginnering,
Universiti Teknologi Malaysia, 81310 Skudai.

Tel : 07-5535485 Fax : 07-5581463 e-mail : m.ariffin@fkkksa.utm.my

3. **DIRECT OUTPUT OF PROJECT** *(Please tick where applicable)*

Secientific Research	Applied Research	Product/Process Development
☐ Algorithm	☐ Method/Technique	☐ Product / Component
☐ Structure	☐ Demonstration / Prototype	☐ Process
☐ Data		☐ Software
☐ Other, please specify	☐ Other, please specify	☐ Other, please specify

4. **INTELLECTUAL PROPERTY** *(Please tick where applicable)*

☐ Not patentable
☐ Patent search required
☐ Patent search completed and clean
☐ Invention remains confidential
☐ No publications pending
☐ No prior claims to the technology

☐ Technology protected by patents
☐ Patent pending
☐ Monograph available
☐ Inventor technology champion
☐ Inventor team player
☐ Industrial partner identified

5. LIST OF EQUIPMENT BOUGHT USING THIS VOT

6. STATEMENT OF ACCOUNT

a)	APPROVED FUNDING	RM : 15,000.00
b)	TOTAL SPENDING	RM : 14,817.16
c)	BALANCE	RM : 182.84

7. TECHNICAL DESCRIPTION AND PERSPECTIVE

Please tick an executive summary of the new technology product, process, etc., describing how it works. Include brief analysis that compares it with competitive technology and signals the one that it may replace. Identify potential technology user group and the strategic means for exploitation.

a) Technology Description

The application of ultrasound (US) for the destruction of organic pollutants has recently drawn much attention. Ultrasound irradiation is one of the processes that have been used widely for wastewater treatment. The presence of homogeneous catalyst to the ultrasonic irradiation will lead to the improvement of the overall efficiency of the SDBS degradation due to higher production of OH radicals.

b) Market Potential

Ultrasonic treatment of wastewater containing anionic surfactant is one of the promising alternative treatment methods that need to be explored. From the mechanisms point of view of the ultrasonic irradiation for wastewater treatment, it is hoped that further research can be done for other type of wastewater.

c) Commercialisation Strategies

8. RESEARCH PERFORMANCE EVALUATION

a) FACULTY RESEARCH COORDINATOR

Research Status	( )	( )	( )	( )	( )	( )
Spending	( )	( )	( )	( )	( )	( )
Overall Status	( )	( )	( )	( )	( )	( )
	Excellent	Very Good	Good	Satisfactory	Fair	Weak

Comment/Recommendations :

…………………………………………… Name : ………………………………………

Signature and stamp of
JKPP Chairman

Date : ………………………………………

b) RMC EVALUATION

Research Status	( )	( )	( )	( )	( )	( )
Spending	( )	( )	( )	( )	( )	( )
Overall Status	( )	( )	( )	( )	( )	( )
	Excellent	Very Good	Good	Satisfactory	Fair	Weak

Comments :-

Recommendations :

☐ Needs further research

☐ Patent application recommended

☐ Market without patent

☐ No tangible product. Report to be filed as reference

……………………………………………….. Name : ………………………………………

Signature and Stamp of Dean / Deputy Dean Date : ……………………………………….
Research Management Centre