

Original Research

Comparison Performances of Hybrid Sonocatalysis and Sonophotocatalysis on the Elimination of 2,4-Dichlorophenoxyacetic Acid in Water: Mineralization and Economic Analysis

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Abstract

This study compares the removal performances of sonocatalysis (SC) coupled with commercially available titanium dioxide (TiO₂, P25) and combined sonophotocatalysis (SPC) with H₂O₂ of 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide in aqueous media in batch experiments. A SC process (US/TiO₂) with 75 mg/L 2,4-D obtained 65.58±0.42% degradation, 7.84±1.3% mineralization, and 15.86±0.39% oxidation at a pH of 2, and a temperature of 35±1°C under optimum conditions after 360 minutes, whereas 82.24±2.91% degradation, 44.50±0.11% mineralization, and 55.11±0.35% oxidation were obtained after 360 minutes with SPC (US/UVA/TiO₂-H₂O₂), with the addition of an optimum 250 mg/L of H₂O₂. The synergistic index was calculated as 1.77 that indicated the positive effect of the combined system on degradation efficiency when compared with the individual processes. Total costs were obtained as 5072 USD/kg for SC and 4135 USD/kg for SPC, showing the cost efficiency of the hybrid SPC process in comparison to the SC process. The obtained results confirmed that the hybrid SPC process was more effective than the SC process in degrading and mineralizing 2,4-D for removal. Operation time was shorter, energy consumption was lower, and operation cost was lower when compared to the SC process.

Keywords: sonophotocatalysis, sonocatalysis, 2,4-dichlorophenoxyacetic acid, mineralization, energy consumption

Introduction

Pollution of surface and groundwater by pesticides and herbicides is considered to be one of the most serious water pollution problems caused by agricultural activities [1]. Currently, global pesticide usage to control pests is approximately 2 million tons to improve productivity and losses of agricultural products [2]. The presence of various pesticide residues in the aquatic environment, can cause detrimental effects on aquatic organisms and eventually human beings [3]. Among several pesticide compounds, 2,4-dichlorophenoxyacetic acid (2,4-D) is one of the world's most frequently used herbicides from the chlorinated phenoxy acids family due to its low cost, selectivity, effectiveness, and range of weed control [4, 5]. However, it has been reported that 2,4-D is a neurotoxic herbicide, meaning that it can be absorbed through the skin or can be inhaled, which could cause damage to liver, kidneys, muscles, and brain tissue [6, 7]. Besides, 2,4-D has been considered as a hormonal agent of toxicity II by the WHO and the US-EPA organizations [8]. In addition, the large volume of wastewater that is polluted with various chlorinated herbicides not only causes adverse effects on human health but also reduces the freshwater resources that are released back to the environment. Hence, the bio-refractory nature of 2,4-D requires development of novel treatment technologies to reduce its hazard to human health and the environment [9, 10].

Recently, several techniques have been used to eliminate 2,4-D from aqueous solution such as adsorption [11], biological degradation [12], electrochemical oxidation [13], photolysis and electrolysis [14], plasma-ozonation [15], heterogeneous photocatalysis [16], electro-Fenton [17], ozonation and thermal plasma [18]. In recent years, based on free oxidant radicals, advanced oxidation processes (AOPs) are the recommended treatment methods for high-chemical-stability and/or low-biodegradability wastewater organic and inorganic components that are resistant to conventional treatment methods [19-21]. Among various AOPs, the photodegradation process is a successful technique based on a catalyst such as titanium dioxide (TiO_2), zinc oxide, or others [22]. Further, ultrasonic degradation is another efficient technique used to treat aqueous solutions by causing rapid formation, growth, and strong collapse of cavitation bubbles, resulting in sonochemical impact occurring either due to pyrolytic decomposition within the bubbles or by the reduction and oxidation due to the generation of $\cdot\text{H}$ and $\cdot\text{OH}$ radicals [23, 24]. However, the individual advanced oxidation methods have many drawbacks including, insufficient transmission of light in water and limited reactive oxygen species (ROS) generation that prevents several applications [25, 26]. Currently, hybrid processes such as the combination of photocatalysis (PC) and sonolysis (S), called 'sonophotocatalysis' (SPC), have gained attention as a way to combine the advantages of the two processes

to degrade all kinds of compounds from water owing to easy operational, cheapness, and environmental friendly [27-30]. In the hybrid SPC process, uniform distribution of photocatalyst in water, enhancement of the catalyst surface area and catalytic activities, mass transfer increment, regeneration of active sites are the widely benefits of cavitation phenomenon that clearly explains the reason why SPC process is preferred [31-33].

Although the degradation and mineralization of 2,4-D using the combined ultrasound and photocatalysis processes has been studied in the literature [34-36], no one has attempted to understand the extensive mineralization, cost, and energy analyses of these hybrid SC and SPC processes on formulation-grade 2,4-D herbicide. This study presents great originality and novelty for certain reasons: (i) the detailed degradation and mineralization studies were presented by different analyses and methods, such as chemical oxygen demand (COD), total organic carbon (TOC), adsorbable organic halogen (AOX), high performance liquid chromatography (HPLC), and Fourier-transform infrared spectroscopy (FTIR) to demonstrate the feasibility of combined SPC as a more effective method than SC for the mineralization of commercial-grade 2,4-D herbicide under different operating conditions, (ii) the synergistic effect of combining energy-based AOPs was also evaluated to show the advantage of hybrid systems as compared with individual techniques, (iii) economic analyses and energy consumption were calculated for such hybrid processes in terms of engineering applications.

Materials and Methods

Chemicals

In the experiments, TiO_2 (Sigma-Aldrich Inc., St. Louis, MO; Art. No. 14021) was used as the catalyst. Commercial Amin EXT 500 SL 2,4-D amine salt $\text{C}_{10}\text{H}_{13}\text{C}_{12}\text{N}_3\text{O}_3$, MW 266.12 g/mol (equivalent to 500 g/L 2,4-D), which is the herbicide being removed by the treatment, was obtained from the Agrofarm® Company. Other chemicals such as NaOH (97%) and H_2SO_4 (97%), which were used to adjust the pH, were obtained from Merck (Darmstadt, Germany). All chemicals were used as received, without additional treatment. Purified water was used in all solutions and reaction mixtures (specific resistance 18.2 $\text{M}\Omega/\text{cm}$; Merck Millipore, Burlington, MA).

Experimental Procedures

An immersion-well photochemical reactor was used to study the SPC method (Fig. 1). The detailed information about hybrid reactor system was presented in our previous study Dikmen et al. [37]. Air was supplied into the system using a diffuser at a rate of 3.5 L/min. During the experiment, the reactor was run

in batch mode, and the reactor temperature was kept constant at $35 \pm 1^\circ\text{C}$ with a continuous water bath and a cold water pump. All S, PC, and SPC experiments were conducted using the same immersion-well reactor.

For the experiments, the desirable concentrations of 2,4-D solution were prepared daily in amber-glass volumetric flasks from a 1000 mg/L stock solution. The samples were centrifuged at 5000 rpm for fifteen minutes to remove TiO_2 from the solution and then filtered through a $0.45\text{-}\mu\text{m}$ syringe filter. Optimization of the conditions for SC and SPC was obtained by measuring the optical density (OD) of the samples at 283 nm, the maximum wavelength of 2,4-D, by means of a spectrophotometer (PharmaSpec UV-1700, Shimadzu, Japan). The percentage degradation of 2,4-D was calculated by using Eq. 1:

$$R (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where R is the percent 2,4-D removal, C_i and C_f are the initial and final 2,4-D concentration, respectively.

Analytical Methods

The absorbance spectrum of 2,4-D was analyzed by UV-Vis spectrophotometry (PharmaSpec UV-1700, Shimadzu, Japan). The TOC analysis was carried out using a TOC Combustion Analyzer (Lotix, USA). A Prominence LC-20A system (Shimadzu, Japan) was used to measure HPLC results. The FTIR analysis was performed using an IR-Affinity Prestige-21 (Shimadzu, Japan) to observe the changes in the functional

structure of the 2,4-D herbicide before and after the photocatalytic treatment. The COD was measured with commercial test kits (COD Merck 1.14541, 25-1500 mg/L Spectroquant test kit) using a Pharo100 visible spectrophotometer (Merck, Germany). A 3-mL sample was measured over 120 minutes at 150°C under thermoreactor Spectroquant TR 320 (Merck, Germany) treatment. When the sample contained hydrogen peroxide (H_2O_2), interference in COD determination was reduced by increasing the pH to above 10 to decompose the hydrogen peroxide to oxygen and water [38]. The AOX concentration analysis was carried out using a CL 10 (Behr, Germany) device. The pH and temperature measurements of all samples from the photocatalytic reactor were carried out using a pH meter (Orion Star A329 Thermo Scientific, USA) and a pH probe (8107UWMMMD ROSS pH/temperature electrode).

Results and Discussion

Preliminary Degradation Studies

The available mechanisms for the removal of commercial 2,4-D herbicide are P, S, sonophotolysis (SP), SC, SPC with TiO_2 , US, and UV irradiation. Treatment under UV irradiation, that is, P of the effluent, yielded only a 35% reduction in 2,4-D content after six hours of irradiation. Besides, degradation of the optimum loading of 50 mg/L 2,4-D subjected to US realized 39.6% efficiency in 360 minutes. Also, 51.2% decomposition of 2,4-D was obtained for an

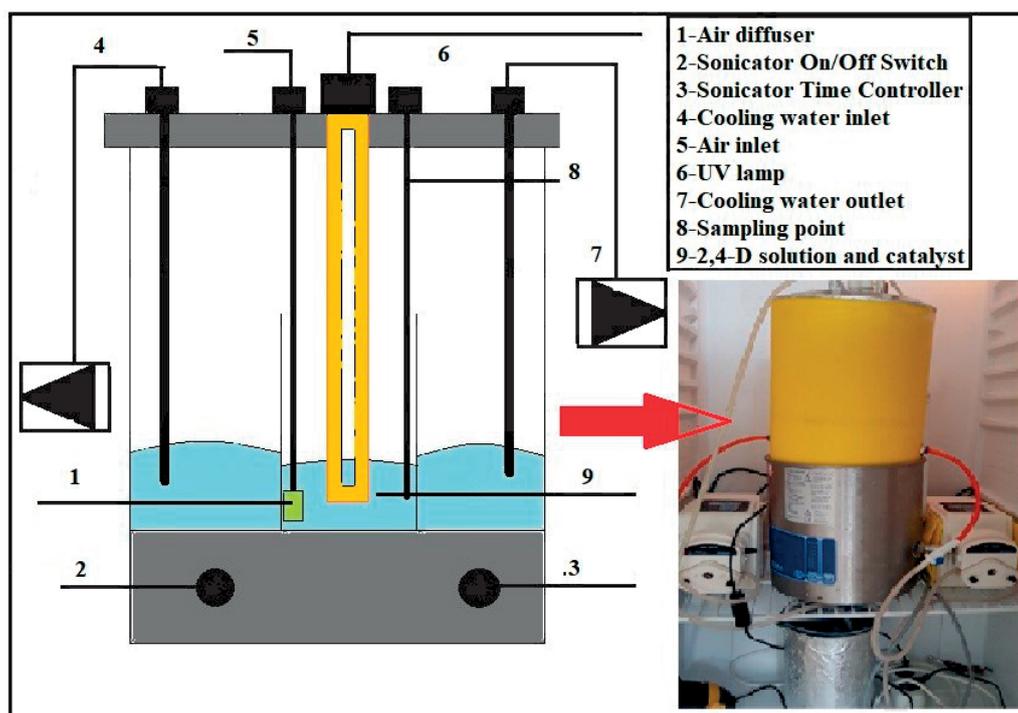


Fig. 1. Schematic diagram of the SPC reactor.

optimum loading of 50 mg/L 2,4-D in the SP process at the end of 360 minutes. The experiments revealed the importance of using UV and US together for 2,4-D degradation. As indicated in our previous study [39], 14.81% of the 2,4-D herbicide was initially removed (at time zero), and 37.14% 2,4-D herbicide adsorption had been achieved after 15 minutes with the TiO_2 catalyst. In addition, for the PC method, we achieved 81% of 2,4-D removal (10 mg/L) at 1.5 g/L P25 TiO_2 catalyst concentration and pH 5 in the presence of UV-A. Moreover, in our another study [40], 100% of the 2,4-D herbicide was removed at pH 2, 0.5 g/L TiO_2 , and 75 mg/L initial 2,4-D concentration after 60 minutes using spectrophotometric analyses of the SC method. Hence, the results revealed the importance of using a catalyst combined with US in the process. H_2O_2 is a strong oxidizing agent that promotes oxidation through the formation of additional reactive species (hydroxyl radicals) from H_2O_2 decomposition [41]. In present study, the higher 2,4-D degradation rate by SPC process could be explained by Kaur et al. [42] who stated in their study that 48.30% of a kind of pesticide cypermethrin was degraded in an aqueous solution using $\text{TiO}_2/\text{H}_2\text{O}_2$ mediated UV photocatalysis with 0.65 gL^{-1} TiO_2 and 179 mgL^{-1} of H_2O_2 in 3 h. Because H_2O_2 enabled to reduce the COD of the reaction mixture by oxidizing cypermethrin into free radical molecules which react with oxygen molecules resulted with the generation of peroxy radicals. Moreover, Ayare and Gogate [43] explained that the combination of H_2O_2 with US/UV could increase the oxidation rates due to enhanced concentration of $\cdot\text{OH}$ radicals caused by the increased charge separation due to higher acceptance of the photogenerated electrons. Our previous study [39] has also shown by spectrophotometric analyses that 100% of the 2,4-D herbicide was removed at pH 3, 1 g/L TiO_2 , 50 mg/L initial 2,4-D concentration, and 250 mg/L H_2O_2 concentration after 60 minutes.

2,4-D Degradation and Mineralization in Aqueous Solution

In the first step of this study, degradation of 2,4-D was investigated with SC and SPC processes to get information on the degradation kinetics of the parent pollutant (Fig. 2). In our previous studies [37, 40] a Taguchi statistical method was applied to optimize the effective parameters such as TiO_2 dosage (0-2 g/L), the initial pH (2-10), time (60-210 min), initial 2,4-D concentration (10- 100 mg/L) for SC process whereas TiO_2 dosage (0-1.5 g/L), the initial pH (3-9), time (60-180 min), initial 2,4-D concentration (25-100 mg/L) and H_2O_2 concentration (0-1000 mg/L) were used to optimize SPC process, respectively. In order to find the optimum conditions, 25 parameters (a total of 50 with the control set) for SC process and 16 parameters (a total of 32 with the control set) were tested for SPC process, respectively. The process parameters and their levels were selected according to previous studies in the

literature. In the present study, the degradation of 2,4-D versus operation time was investigated by fixing the pH at 2 and 3, using 75 and 50 mg/L 2,4-D concentration, and 0.5 and 1 g/L TiO_2 concentration for the SC and SPC processes, respectively depending on findings in our previous studies [37, 40]. The HPLC analyses showed that the degradation efficiency of 2,4-D at 360 minutes was $65.6 \pm 0.42\%$ for SC and $82.3 \pm 2.91\%$ for SPC (Fig. 2). As shown in Fig. 2, no significant difference was observed in the degradation efficiency of 2,4-D between the SC and SPC processes until the 200th minute. It is thought that faster degradation of the 2,4-D herbicide can be connected to the chlorine atoms in its structure, which is discussed in the FTIR spectra section of this study. It has been observed that there is tension in the chlorine bond for both processes that can be thought to cause rapid degradation [44]. Moreover, there was a 17% difference between the 200th and 360th minutes when the SC and SPC processes were compared (Fig. 2). Amalraj and Pius [45] stated that the presence of UV with catalyst enables an increase in the oxidative power of the $\cdot\text{OH}$ radicals that is known to be strong enough to oxidize 2,4-D into CO_2 , H_2O , and other mineral compounds. AOX is a general parameter that indicates the total amount of halogenated organics and recent studies have focused on the generation of AOX from wastewater treatment of AOPs [46]. Some studies informed that AOX formation was related to the free chlorine (e.g., Cl_2 , HClO or ClO^-) chlorination of organics during AOPs [47, 48]. Because toxic, chlorinated 2,4-D herbicide was chosen to be degraded in this study, it was necessary to examine the AOX changes of that target pollutant. As seen in Fig. 3, AOX removals were 57.1% for SC and 72% for SPC. Pinto et al. [49] studied atrazine pesticide, and they stated that the residual toxicity was probably due to the presence of toxic, chlorinated degradation products. Okcu et al. [39] reported that the removal of AOX in the first mineralization experiment, without hydrogen peroxide, was 77.67%, while, in the experiments with H_2O_2 , it reached a maximum of 79.14% after 24 hours.

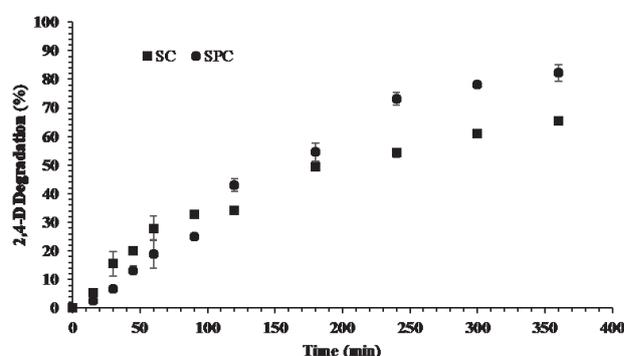


Fig. 2. 2,4-D degradation percentage (%) of sonocatalytic (SC) and sonophotocatalytic (SPC) processes (for SC: pH 2, $C_{2,4-D} = 75 \text{ mg/L}$, $C_{\text{TiO}_2} = 0.5 \text{ g/L}$; for SPC: pH 3, $C_{2,4-D} = 50 \text{ mg/L}$, $C_{\text{TiO}_2} = 1 \text{ g/L}$).

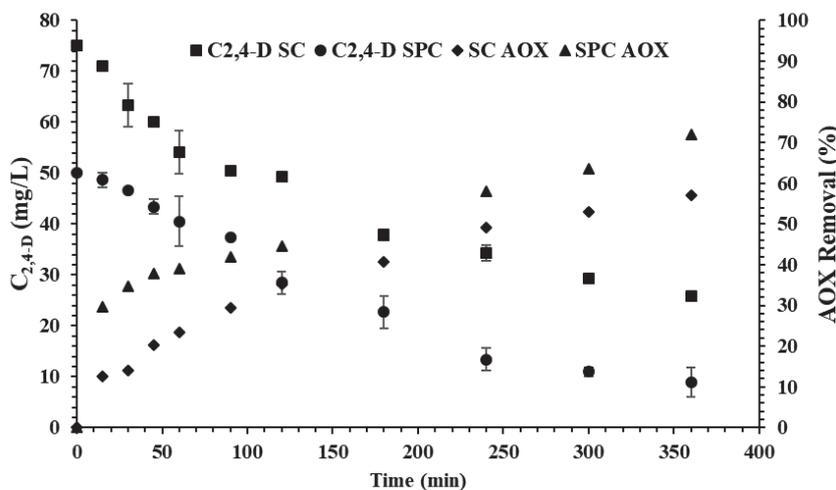


Fig. 3. 2,4-D concentration profile during the SC (■) and SPC (●) processes, AOX removal (%) profile for SC (◆) and SPC (▲) processes (for SC: pH 2, $C_{2,4-D} = 75$ mg/L, $C_{H_2O_2} = 0.5$ g/L; for SPC: pH 3, $C_{2,4-D} = 50$ mg/L, $C_{H_2O_2} = 1$ g/L).

In the current experiment, higher AOX removal with the SPC process is thought to be due to the presence of UV irradiation together with H_2O_2 . As shown in Fig. 3, percentage removal of AOX continued to increase against decreased 2,4-D concentration in the SC and SPC processes. Both SC and SPC processes were completed at the end of 360 minutes, due to an overheating problem with the reactor systems.

The COD and TOC parameters were measured to investigate the mineralization of 2,4-D. A decrease in the COD indicates the mineralization or degradation degree of an organic species in aqueous solution, and it defines the total oxygen quantity required to oxidize organic matter to CO_2 and H_2O [50, 51]. The chemical structure of the target pollutant is expected to be modified at the end of the oxidation that results in a decrease in the COD of the compound in aqueous solution [39]. With the six-hour SC and SPC processes, removal of $7.84 \pm 1.3\%$ and $44.5 \pm 0.11\%$ TOC were achieved, respectively. In SC, the maximum COD concentration was $15.9 \pm 0.4\%$ in 300 minutes, corresponding to a TOC concentration of $7.25 \pm 0.59\%$ (Fig. 4). Likewise, in 300 minutes, the maximum COD concentration was $55.1 \pm 0.35\%$, which corresponds to a TOC concentration of $37.8 \pm 0.78\%$ with SCP. The COD decreased 40% with SC after 300 minutes and 23% with the SPC process in 60 minutes. This issue, as stated by Okcu et al. [39], could be due to toxic by-product accumulation after 300 minutes, which is the key point wherein the COD value reached the maximum removal for both SC and SPC processes, and after which COD removal efficiency dropped sharply. When the COD removal efficiencies were compared between the SC and SPC processes, SPC achieved higher removal efficiency due to its hybrid property with UV and H_2O_2 . Sathishkumar et al. [52] reported that norflurazon was treated for 300 minutes, and they obtained 58% removal efficiency for SPC and 17% for SC processes, respectively. Shokri [53], stated that acid red 14 dye

was treated with both the SC and SPC methods. As the result of the experiments at 50 mg/L, they observed 25.4% reduction of COD in SC and 55.5% of COD in SPC in 180 minutes. The summary of the comparison of SPC process with other methods for the removal of 2,4-D is presented in Table 1.

FTIR Spectra

FTIR analysis produces a spectral range of 650 to 4000 cm^{-1} , which gives information about the changes in the functional structure of the 2,4-D herbicide occurring after six hours of SC and SPC processes. In Figs S1-S3, there are important peaks in the 2,4-D herbicide within the 650 to 4000 cm^{-1} range. Fig. S2 shows the changes in the FTIR spectrum of the 2,4-D herbicide after 30, 120, and 360 minutes of the SC process. Also, the FTIR spectra of 2,4-D herbicide after 30, 120, and 360 minutes of the SPC process are given in Fig. S3. Differences in the FTIR spectra of the treated and untreated pesticide solutions indicate the degradation of the organic bonds of the pesticides [60]. The peaks in the FTIR spectrum that were obtained after the SC and SPC processes in this study are compared in Table 2 with studies in the literature that have similar peaks to define the degradation of 2,4-D herbicide. In the literature, degradation of the C-O bond in the aromatic chain is defined to be the most important oxidation indicator for phenoxy herbicides [66]. In this study, the FTIR results showed that C-O bonds were observed at 1234 cm^{-1} and 1119 cm^{-1} in the SC and SPC processes, respectively, which is considered to be evidence of oxidation of the parent 2,4-D compound.

Synergistic Effect Study

The interaction of the combined advanced oxidation process (S and PC) was quantified by synergy index (SI) that was calculated based on the pseudo-first-order

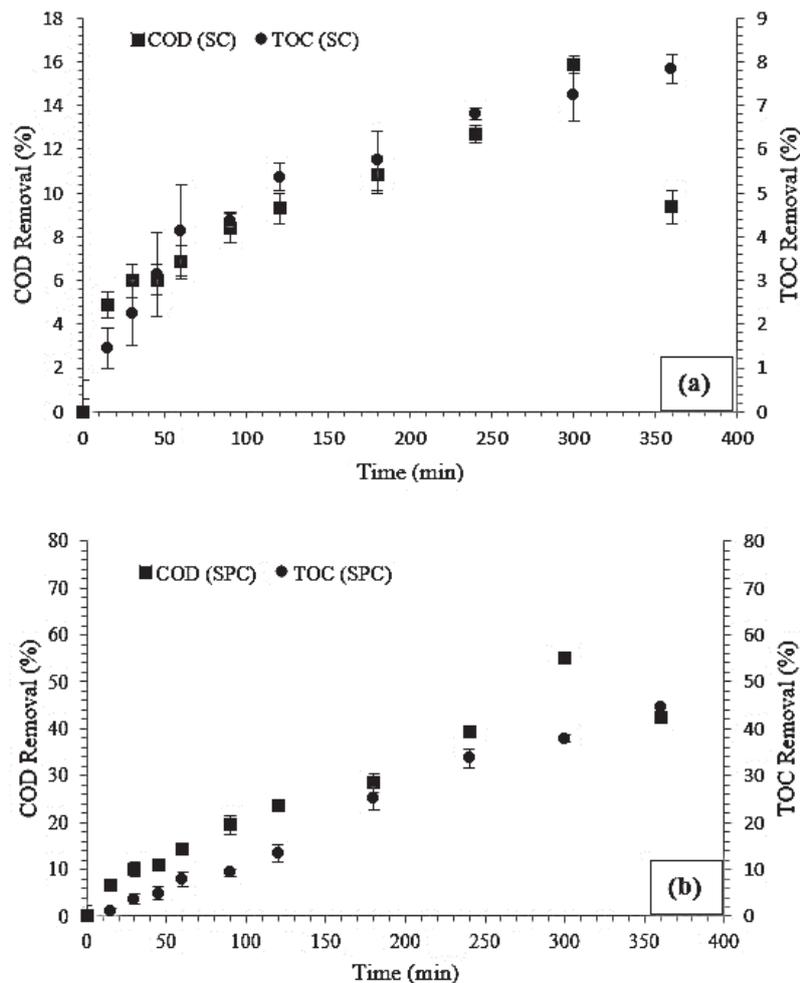


Fig. 4. a) COD removal (%) in SC (■) and TOC removal (%) in SC (●), b) COD removal (%) in SPC (■) and TOC removal (%) in SPC (●) (for SC: pH 2, $C_{2,4-D} = 75$ mg/L, $C_{TiO_2} = 0.5$ g/L; for SPC: pH 3, $C_{2,4-D} = 50$ mg/L, $C_{TiO_2} = 1$ g/L)

rate constant and second-order kinetics constant of hybrid AOPs [67]. The synergy index, which is the ratio of the SPC rate constant to the sum of the rate constants of the individual processes (Eq. 3) [67, 68]:

$$\text{Synergistic effect}(s) = \frac{k_{SPC}}{k_S + k_{PC}} \quad (3)$$

where k_{SPC} , k_S , and k_{PC} are the apparent rate constant of SPC, S, and PC processes, respectively.

Synergistic effect values greater than 1.0 show a positive effect [69]. As shown in Table 3, the synergistic index was calculated as 1.77, and results for the degradation of 2,4-D indicated that the combined system has a positive effect on degradation efficiency when compared with the individual processes. Samantha et al. [68] obtained the synergistic index as 1.61, and [70] reported lower synergy level (0.99) for the treatment of vinasse with US-UV/TiO₂ for COD removal. It is clear that the reaction rate constant of the SPC process is greater than that of the sum of the rate constants of the individual processes; $k_{SPC} > k_S + k_{PC}$. The reason for the efficient treatment performance

of hybrid SPC was thought to be the prevention of suspended catalyst nanosized agglomerations due to the propagation capability of ultrasound throughout the method. Hence, the surface area of catalysts was increased, which resulted in increased generation of additional free •OH radicals due to this effect in the reaction mixture [71]. Besides, the catalyst surface could be cleaned continuously by the ultrasonic waves, preventing pollutant accumulation and that of their intermediates produced during degradation [72].

Energy Consumption and Cost Analysis of the SC and SPC Processes

The electrical energy consumed by the SC and SPC processes constitutes a significant part of the operating cost. EEO is a figure of merit defined by [73] as the amount of energy (kWh m⁻³) required to degrade 90% of a target pollutant in 1 m³ of water.

For a batch reaction, E_{EO} (kW energy amount consumed per process) is calculated by using the following Eq. (4) [49]:

Table 1. Comparison of 2,4-D removal degradation and mineralization efficiencies between SPC and other AOPs in the literature.

Process	2,4-D concentration	Time	Removal efficiency	References
US/UV/TiO ₂ /H ₂ O ₂	50 mg/L	360 min	84% 2,4-D, 55% COD, and 45% TOC	Present study
US/Ag ₃ PO ₄ /TiO ₂	10 mg/L	60 min	98.4% 2,4-D	[54]
US-EP/nZVI	50 mg/L	140 min	91% 2,4-D, 92% COD, and 88% TOC	[55]
UV/TiO ₂ /NCP (natural zeolite)	6 mg/L	95 min	58% 2,4-D by UV, and 31% 2,4-D by visible light	[56]
WO ₃ /NaNbO ₃ -coupled photocatalysts	10 mg/L	180 min	18% TOC	[57]
Anodic oxidation (AO) and electro-Fenton (EF) using a boron-doped diamond (BDD) anode.	20 mg/L	120 min	92% 2,4-D and 69% TOC	[17]
Electrooxidation (EO) and Oxone	40 mg/L	180 min	100% 2,4-D and 69% TOC	[58]
UVA/P25 TiO ₂ /H ₂ O ₂	25 mg/L	180 min	100% 2,4-D, 82% COD, and 56% TOC	[16]
Three-dimensional electrode (2D and 3D) reactors with graphite (G)/b-PbO ₂ anode.	100 mg/L	100 min	88% 2,4-D and 92% COD using 2D and 70% 2,4-D and 75% COD using 3D electrode	[59]

Table 2. FTIR spectra of the degradation of 2,4-D in SC and SPC processes.

Process Type	Literature Results Wavenumber (cm ⁻¹)	In this study Wavenumber (cm ⁻¹)	Assignment	References
SC	770–870	870	Calcium carbonate bands	[61]
SC	693	684	C — Cl stretching	[62]
SC	1234	1250	O — H coupled with C — O	[63]
SPC	1435–1475	1450	C = C vibration of the aromatic ring	[61]
SPC	693	710	C — Cl stretching	[62]
SPC	770–870	860	Calcium carbonate bands	[61]
SPC	2344	2340	C ≡ C stretching	[64]
SPC	1119	1130	C — OH stretching	[65]

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C_0}{C_f}\right)} \quad (4)$$

The above equation is related to the L-H model first-order kinetic:

$$\ln\left(\frac{C}{C_0}\right) = -k_{app}t \quad (5)$$

Table 3. Synergy index for hybrid systems and individual processes.

S Synergy index	k (1/min)	
	PC	SPC
0.00017 1.77	0.00133	0.00266

With the combination of Eq. (4) and the L-H model first-order kinetic, Eq. (5), E_{EO} can be expressed as:

$$E_{EO} = \frac{38.4 \times P}{V \times k_{app}} \quad (6)$$

Eq. (6) (E_{EO}) is used to determine the electrical energy model of each ideal batch reactor for SC and SPC. Total consumed energy of the SC process (US-TiO₂) and the SPC process (US/UV-TiO₂) with H₂O₂ is presented in Table 4.

Advanced oxidation processes largely depend on electrical energy, which tends to be one of the major contributors to the operating cost a significant factor in the selection of the most economical wastewater treatment process [74, 75].

Eq. (7) and Eq. (8) were used to measure the overall operating costs of SC and SPC degradation of 2,4-D herbicide under optimum conditions. The operating

Table 4. Effect of SC and SPC reactors on the electrical energy per order (E_{EO}).

Experimental Conditions						
Process type	Initial concentration (mg/L)	TiO ₂ concentration (g/L)	Process time (min)	H ₂ O ₂ concentration (mg/L)	pH	E_{EO} (kWh/m ³ /order)
SPC	50	1	60	250	3	7797
SC	75	0.5	60	-	2	10791

costs per kilogram (kg) of COD elimination from the 2,4-D herbicide in wastewater were calculated in terms of US dollars (USD), using the experimental results [30, 76]. In the both equations, energy consumption is the sum of the energy requirements of the peristaltic pump (40 W), the US reactor (120 W), the air pump (3 W) and the UV-A lamp (36 W only for the SPC reactor).

$$\text{Total consumed energy (kWh)} = \frac{\text{Consumed power (W)} \times \text{Reaction time (dk)}}{(1000 \times 60)} \quad (7)$$

$$\text{Total operating cost} \left(\frac{\text{USD}}{\text{kg}} \right) = \frac{\text{Total consumed energy (kWh)} \times \text{Unit energy cost (USD/kWh)}}{(C_{\text{initial COD}} - C_{\text{final COD}}) \left(\frac{\text{mg}}{\text{L}} \right) \times \text{Treated volume (V)} \times 10^6 \left(\frac{\text{mg}}{\text{kg}} \right)} \quad (8)$$

As shown in Table 4, E_{EO} values of 7797 and 10791 kWhm⁻³ were obtained for the SPC and SC processes, respectively. Rahman et al. [77] stated in their study that based on the time required to achieve more than 90% of COD from treated palm oil mill effluent, the electrical energy calculated for the combination of processes (sonolysis and photocatalysis) was 1342.25 kWh/m³ for a US power of 20 W. According to those results, the SPC process was found to be more efficient not only reduces the COD concentration to the permissible standard discharge limits but also reduces the energy consumption, showing the advantages of the hybrid system in the energy efficiency aspect Rahman et al. [77]. According to Table 5, the SPC process with US-UV/TiO₂/H₂O₂ had a potential

for a higher percentage of rapid organic matter removal compared to the treatment process with US-TiO₂. As shown in Table 5, the hourly energy consumption amounts of the SC and SPC processes were 0.810 kW 0.990 kW, respectively. In the SPC process, H₂O₂ was used in addition to the SC process to obtain higher efficiency in the removal of 2,4-D. Total costs were 5072 USD/kg for SC and 4135 USD/kg for SPC, showing the cost efficiency of the hybrid SPC process in comparison to the SC process.

Conclusions

The degradation and mineralization analyses of 2,4-D herbicide by SC and combined SPC with H₂O₂ were done in this study. A SC process (US-TiO₂) with 75 mg/L 2,4-D obtained 65.58±0.42% degradation, 7.84±1.3% mineralization, and 15.86±0.39% oxidation at a pH of 2, and a temperature of 35±1°C under optimum conditions after 360 minutes, whereas 82.24±2.91% degradation, 44.50±0.11% mineralization, and 55.11±0.35% oxidation were obtained after 360 minutes with SPC (US/UVA/TiO₂-H₂O₂), with the addition of an optimum 250 mg/L of H₂O₂. The US/UVA/TiO₂-H₂O₂ process was more effective as a batch SPC process in terms of cost and efficiency per kg of COD removal from wastewater. The obtained results verified that a hybrid SPC process can achieve effective degradation and mineralization with shorter operation time and lower energy consumption, thus with lower operation cost as compared to the SC process. Therefore, on the basis of these results, it is concluded that the hybrid SPC is more appropriate than the SC for 2,4-D herbicide removal.

Table 5. Cost analysis for 2,4-D herbicide removal in SC and SPC reactors.

	2,4-D herbicide concentration (mg/L)	Catalyst concentration (g/L)	TiO ₂ cost (USD/g)	H ₂ O ₂ concentration (mg/L)	H ₂ O ₂ cost (USD/L)	pH	COD removal (mg/L)	Reaction time (min)	Total power consumed per mg 2,4-D removal (kWh)	Total cost (USD/kg)
SC	75	0.5	1.14	-	-	2	20	300	0.81	5071.740
SPC	50	1.5	3.42	250	0.209	3	30	300	0.99	4135.229

1. The working volume of both reactors is 1 L. 2. Total energy consumed (P)-198 W (includes energy for electronic magnetic stirrer (8.5 W), US bath (120 W), air pump (3 W), peristaltic pump (30 W) and UV lamp (36 W) 3. Unit cost of power 12.52 US cents/kWh in 2022 4. TiO₂ price is 202 EUR for 100 G (Sigma-Aldrich®) 5. H₂O₂ (30 %) price is 25.20 EUR for 1 L.

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Conflict of Interest

The authors declare no conflict of interest.

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Supporting Materials

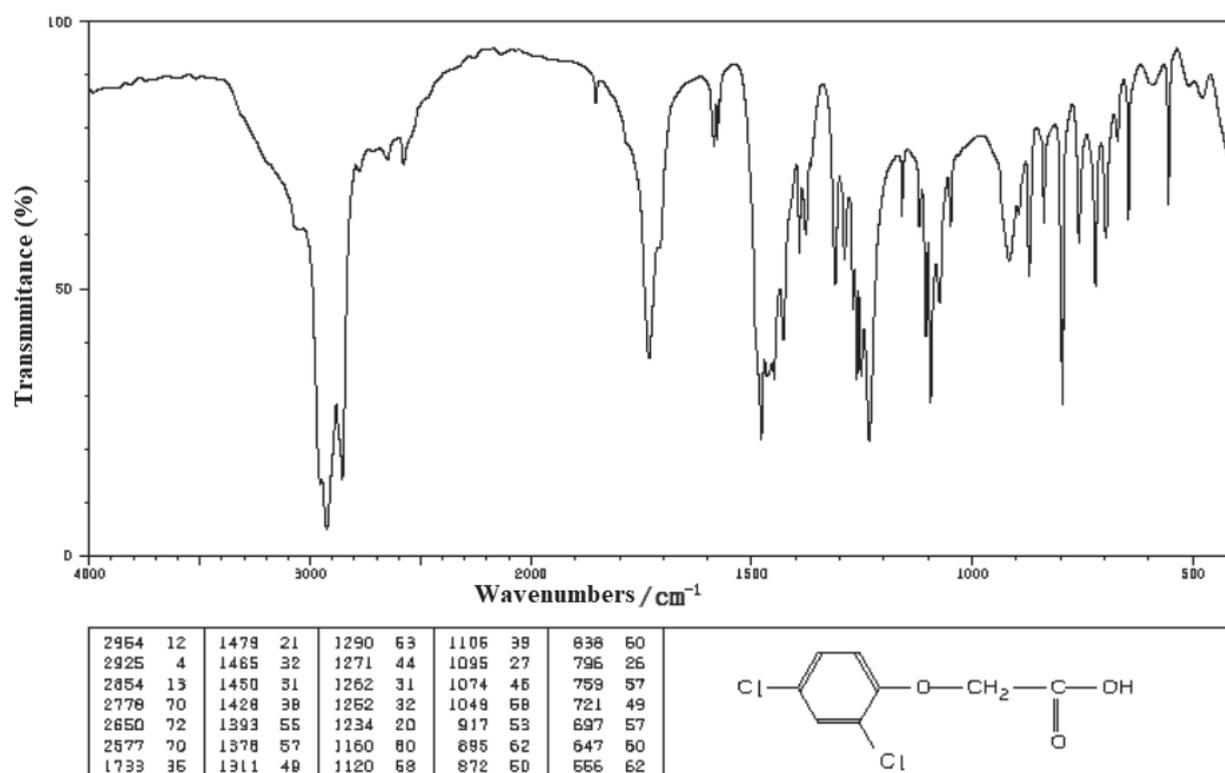


Fig. S1. FTIR spectrum of the original 2,4-D herbicide.

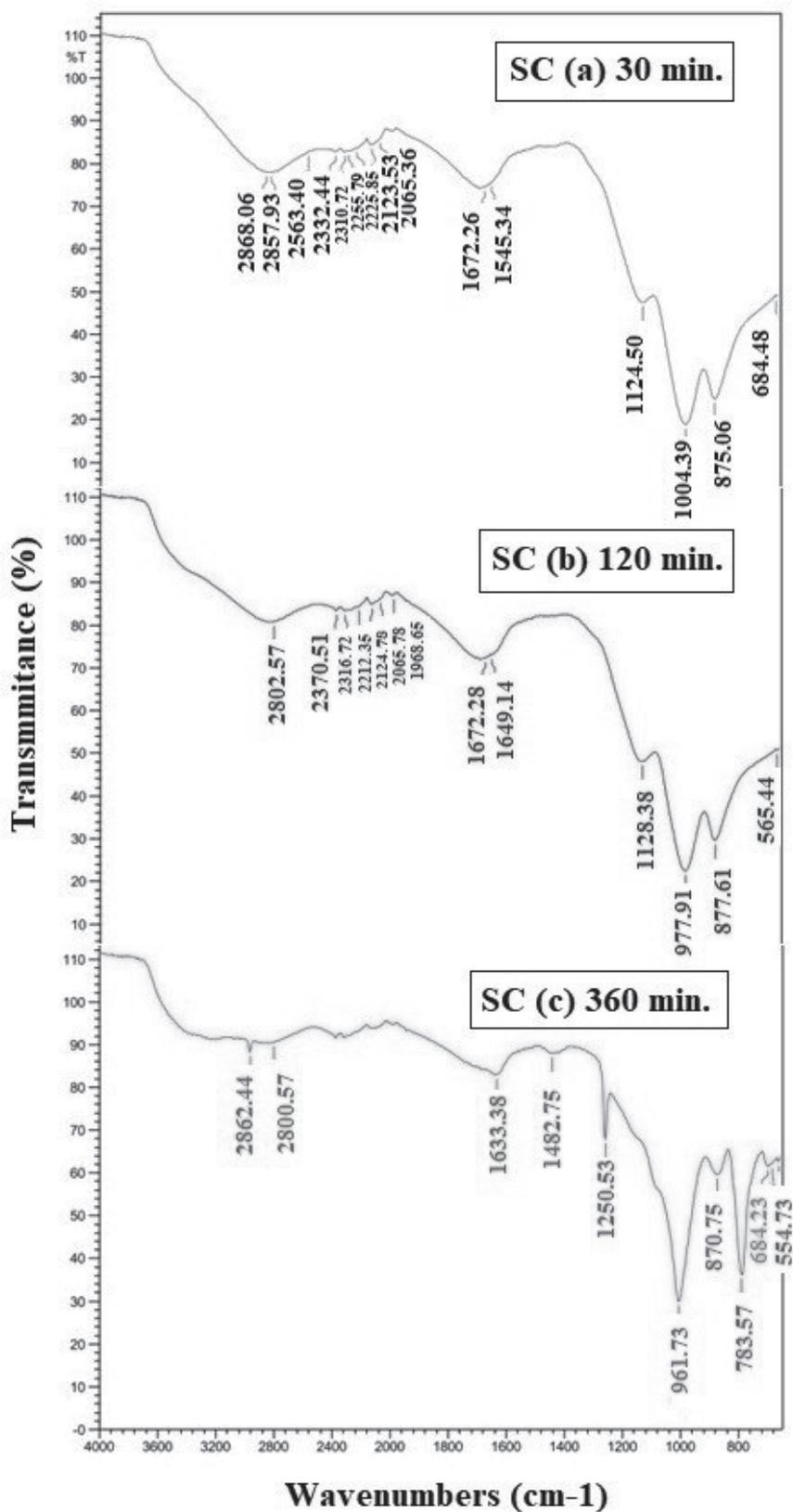


Fig. S2. SC FTIR results a)30 min. b)120 min. c)360 min.

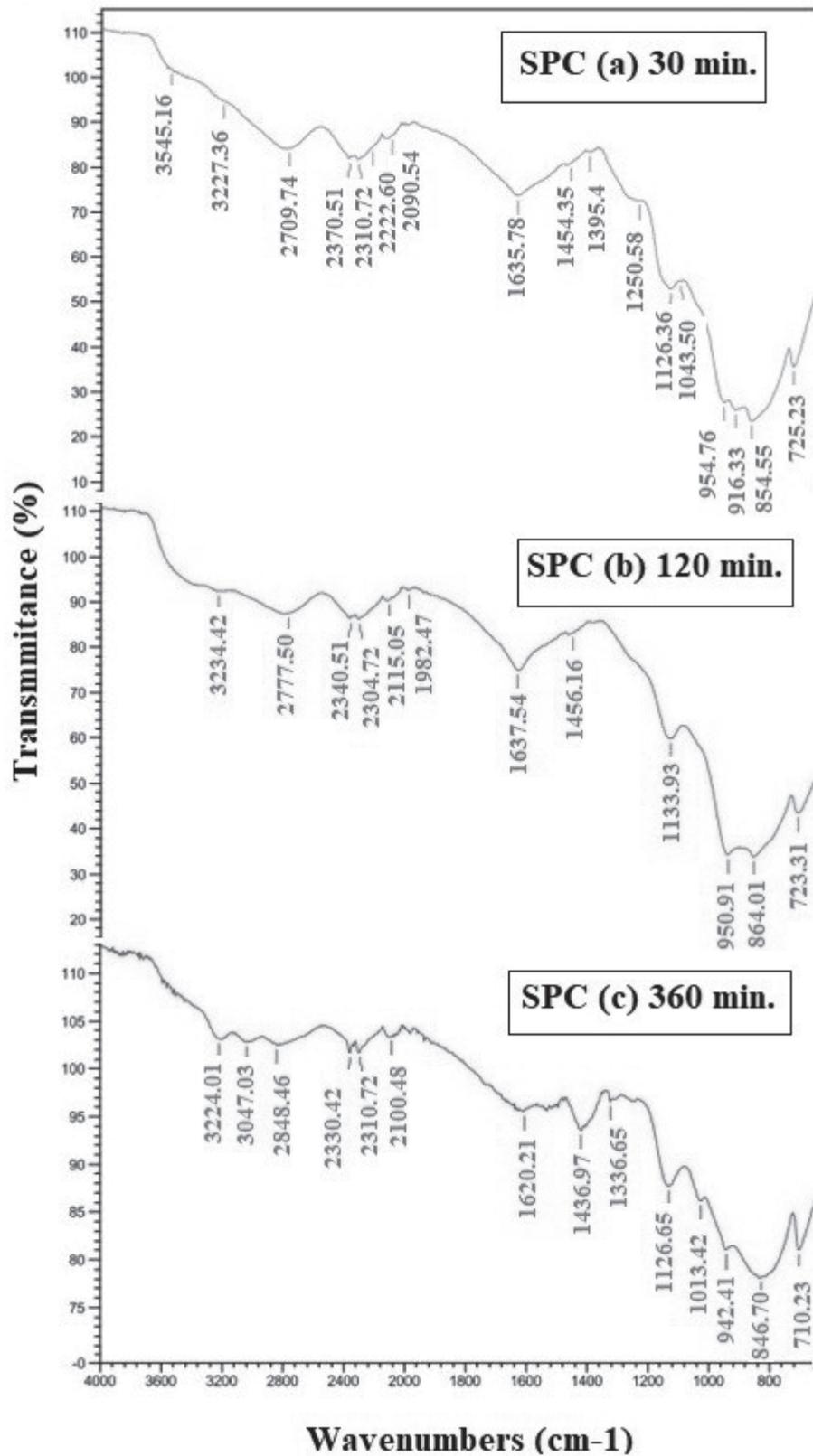


Fig. S3. SPC FTIR results a)30 min. b)120 min. c)360 min