

Supporting Information

Photocatalytic hydrogen driven (Pd-C\UV\H₂) advanced reduction process (ARP) for dechlorination and degradation of chlorotoluron in aqueous environment

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Materials and methods.

Test S1. Materials

Chlorotoluron (analytical grade according to ACS, 98%), delivered by Combi-Blocks, USA, and deionized (DI) water (Direct-Q® Water Purification System - Merck Millipore) were utilized for the preparation of CHL solutions. Sodium sulfite (analytical grade, Merck, Germany) was utilized as a reducing agent. Sodium hydroxide solution and sulfuric acid (VI) solution (98%), were purchased from POCH S.A., Poland to adjust the pH. In the catalytic activity, commercially available catalyst – a palladium (unreduced) on activated carbon (5%) (Thermo Scientific, USA) was used. Typically, the Pd/C catalyst is prepared by conventional impregnation approach [1].

Palladium-Matrixmodifier Standard ($c(\text{Pd}) = 10 \pm 0.2 \text{ g/L}$, $(\text{Pd}(\text{NO}_3)_2/\text{HNO}_3$, ca. 15%), Merck, Germany) was used as mother solution, to prepare calibration solutions for the inductively coupled plasma (ICP-OES) technique for analysis of Pd leaching. In order to examine how ionic species influence on the CHL reduction, different salts such as, sodium chloride, iron (III) chloride, sodium nitrate and nitrite, sodium sulfate and sodium carbonate (> 98 %, POCH S.A., Poland) were utilized. The effect of dissolved organic matter on CHL degradation was examined via humic acid sodium salt (97%, Angene, China). Methanol (99.8 %) used for quenching experiments was obtained from POCH (Poland). The high-performance liquid chromatography (HPLC) analysis used acetonitrile (99.9%) as an eluent component, purchased from Fischer Chemical (USA). All samples were introduced to chromatographic system after filtering via a hydrophilic PTFE syringe filter of 0.45 μm size (Alchem, Poland).

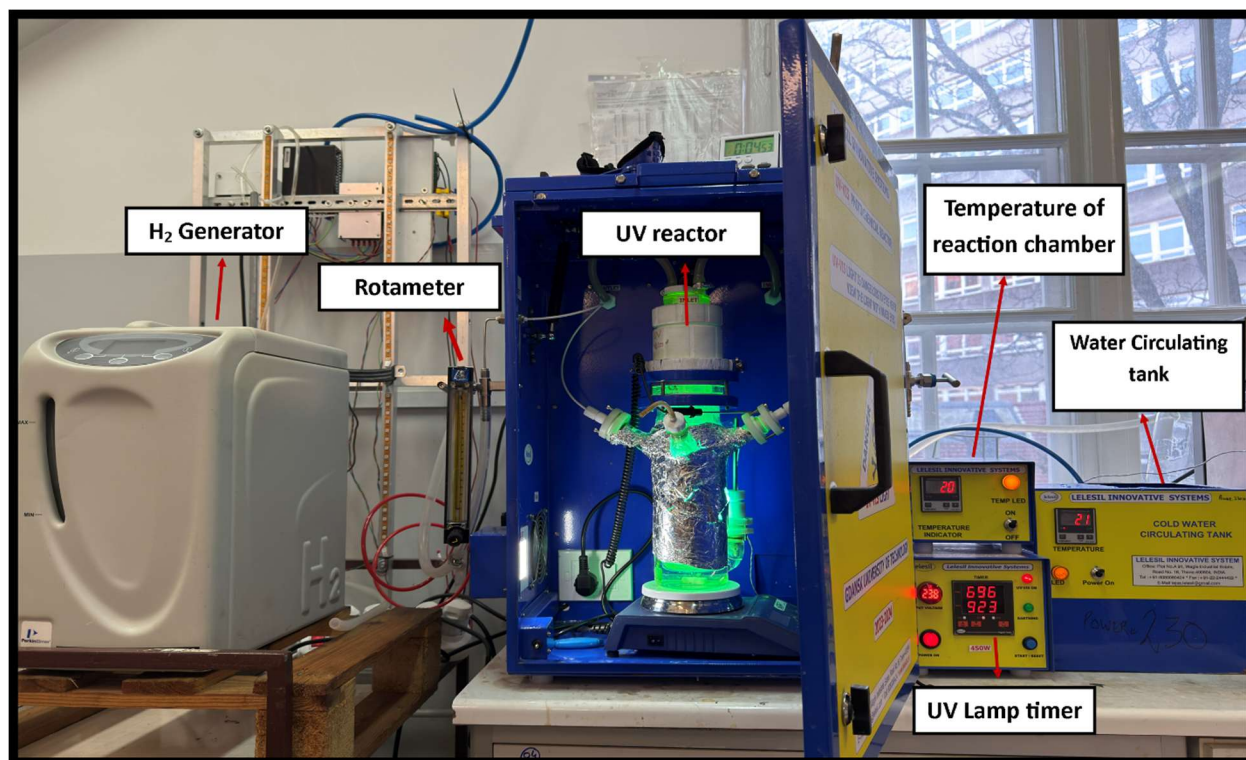


Fig. S1. Real image of experimental system.

Text S2. Characterization of Pd catalyst (SEM, EDS, XRD, XPS)

Scanning electron microscopy (SEM, FEI Quanta 250) equipped with the energy dispersive spectrometer (EDS, Ametek, Berwin) were performed to examine the morphology and crystalline phases and chemical composition of the Pd-C catalyst surface of fresh and after (1st, 5th) cycle, respectively. The crystalline phases of fresh Pd-C were examined via X-ray diffraction (XRD) on a PANalytical X'Pert PRO X-ray diffractometer used with Cu K α radiation. The system was operated under 40 kV and 40 mA, with a scan step size of 0.0167 $^\circ$ and a duration per step of 10.16 s. Furthermore, a UHV method with a 128-channel hemispherical analyzer was utilized to obtain X-ray photoelectron spectroscopy (XPS, Omicron NanoTechnology) investigation. The analysis of XPS were done in an high vacuum environment, below 1.1×10^{-8} mbar, at ambient condition. A source of Mg K \pm X-rays were used to excite the photoelectrons and the X-ray anode was powered at 15 keV and 300 W. The binding energy values were referenced to the C1s peaks' position (284.6 eV) resulted from surface contaminants.

Text S3. Ultra-high performance liquid chromatography (UHPLC) analysis

Separation was carried out in ultra-high performance liquid chromatography (UHPLC) Nexera XS system (USA). The study used a system with controller SCL-40 (Shimadzu, Japan), degassing unit SGU-405, solvent delivery module LC-40D XS, auto sampler SIL-40C XS, photo diode array detector SPD-M40, column oven CTO-40C and an Agilent chromatographic column (Zorbax C-18, 150×4.6 mm, 3.5 μ m). The degraded CHL samples were filtered by syringe filter. CHL samples were analyzed with an eluent ratio of 60% water and 40% acetonitrile (99.9%, Fischer Chemical, USA). Besides, flow rate was set at 1 mL/min, temperature was 20 $^\circ$ C, and detection wavelength of 241 nm was used. Samples were injected (10 μ L) using an

autosampler. The CHL retention time was determined through standard solutions, and a 5-point external calibration curve was prepared for determination of CHL concentration in process samples.

Text S4. Control of Pd leaching into water – ICP-OES analysis

The Pd concentration in post-processed model solutions was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) in a Shimadzu ICPE-9820-Plasma Atomic Emission Spectrometer (Shimadzu, Japan). Calibration standards from 0–200 µg/L were prepared from the Palladium-Matrixmodifier Standard. Prior to analysis, samples were prepared by mixing treated CHL solution (after 60 min) and 5% HNO₃ solution at 1:1 (v/v) ratio, and experiments were performed using falcon tubes with 10 ml volume. Furthermore, the argon gas (Air Liquide, Poland) with the purity of 99.995% was used for ICP-OES. Subsequently, the samples were introduced into the ICP instrument via autosampler (AS-10). Emission intensity in the ICP-OES signal was measured at 340.458 nm for Pd [2]. At selected wavelength, the limit of detection (LOD) of the ICP-OES method for Pd was 49.6 µg/L (defined as signal to noise ratio equal to 3).

Text S5. Identification of degradation by-products – gas chromatography coupled with mass spectrometry (GC-MS)

A gas chromatograph with mass spectrometer (GC-MS, model QP2010SE, Shimadzu, Japan) was utilized to run the chromatographic examination of degradation intermediates. The dispersive liquid-liquid microextraction (DLLME) approach was performed to prepare the CHL degradation samples for analysis. Furthermore, for separation a RTX®-100-DHA (Restek) capillary column (100 m x 0.25 mm ID x 0.5 µm df) was used. Helium carrier gas flow through the column was 1 mL/min, and the injection port temperature was maintained at 300 °C.

Temperature program was starting at 35 °C for five minutes, then at a rate of 20 °C/min to 300 °C, and lastly by isothermal separation for 20 min at 300 °C. The mass spectrometer's ion source]and the interface temperature were 200 °C and 300 °C respectively. The MS mass scan range extended from 34 m/z to 350 m/z [3–5].

Text S6. Anion identification/quantification by ion chromatography

Chloride ions concentration was determined by ion chromatography (Dionex Aquion, Thermo Scientific, USA) equipped with a Dionex IonPac™ AS22 column (4 × 250 mm), suppressor Dionex Anion Self-Regenerating (Dionex ASRS™ 300 × 4mm) AutoSuppression™ Recycle Mode and a AS-DV automated sampler. The CHL samples were analyzed at following conditions: 1.2 mL/min flow rate of eluent (4.5 mM Na₂CO₃/1.4 mM NaHCO₃) was set, column temperature of 30 °C, injection volume (injected by means of autosampler) 10 µL, and applied current was 31 mA.

Text S7. Response surface method

An analysis of the CCD experimental outcomes was conducted by predicted model of the empirical second-order polynomial equation (Eq. 1S) [6]:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \epsilon \quad \text{Eq. (1S)}$$

where Y = predicted response value of CHL degradation effectiveness; β_0 represents the overall mean response or intercept constant. X_1 , X_2 and X_3 are independent variables. β_1 , β_2 and β_3 are the model coefficient, and ϵ is the random error.

Table 1S

Experimental factors and their levels.

Factors	Symbols (Factor)	Levels				
		-a	Low (-1)	Central (0)	High (+1)	+a
H ₂ (L/h)	X ₁	2	2.41	3	3.59	4
Pd-C	X ₂	1	1.61	2.5	3.39	4
pH	X ₃	2	4.03	7	9.97	12

Table 2S. Condensed Fukui indices for radical attack on the CHL molecule.

Atom	f_k^0
1 H	0.032
2 H	0.033
3 H	0.024
4 C	-0.020
5 C	0.087
6 C	0.098
7 H	0.042
8 C	0.092
9 H	0.035
10 C	0.056
11 C	0.131
12 H	0.038
13 C	0.047
14 Cl	0.093
15 N	0.065
16 H	0.024
17 C	-0.006
18 O	0.033
19 N	0.031
20 C	-0.011
21 H	0.012
22 H	0.002
23 H	0.023
24 C	-0.006
25 H	0.006
26 H	0.020
27 H	0.020

Results and Discussion.

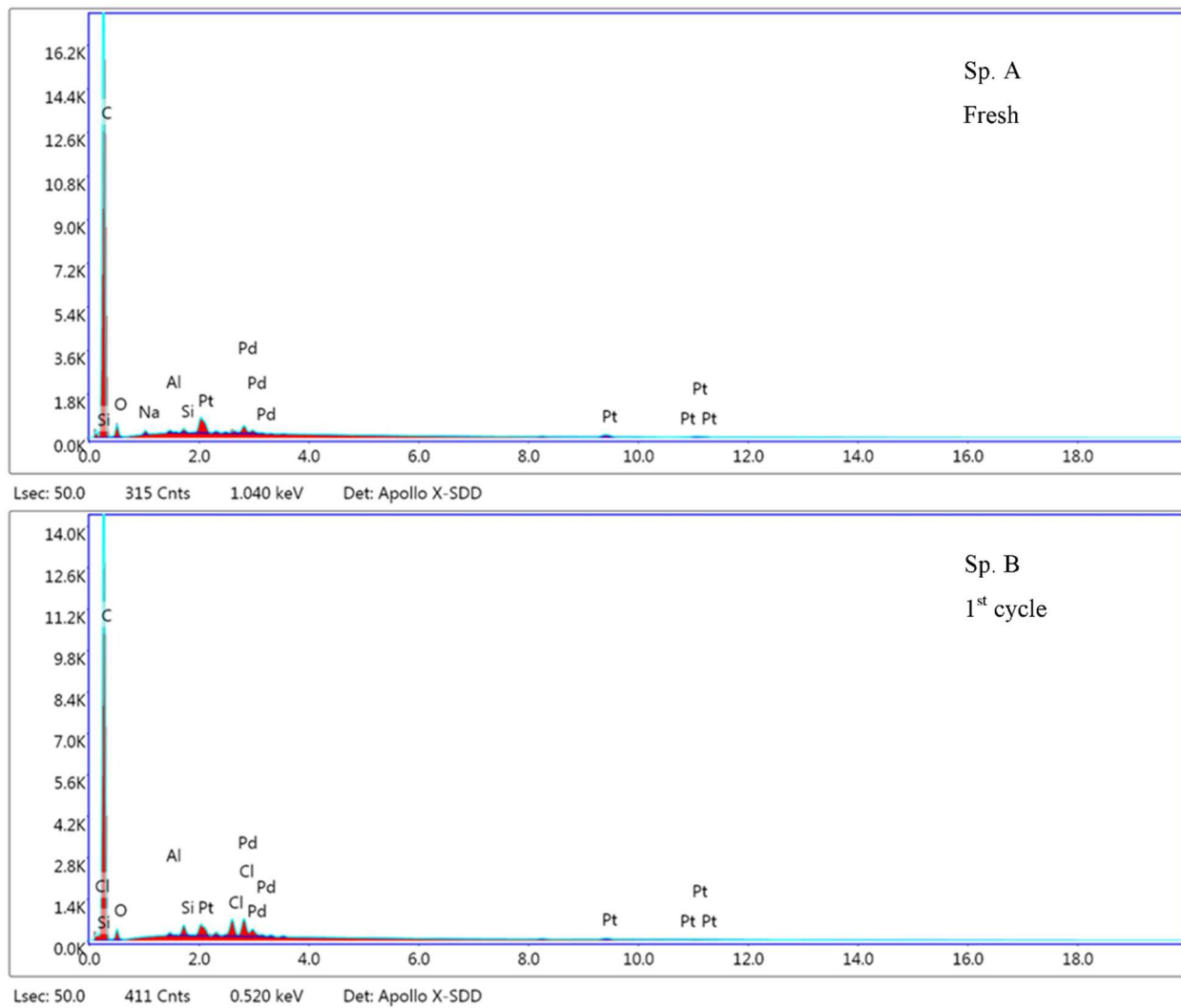


Fig. S2. EDS images of fresh and after 1st cycle of Pd-C catalyst.

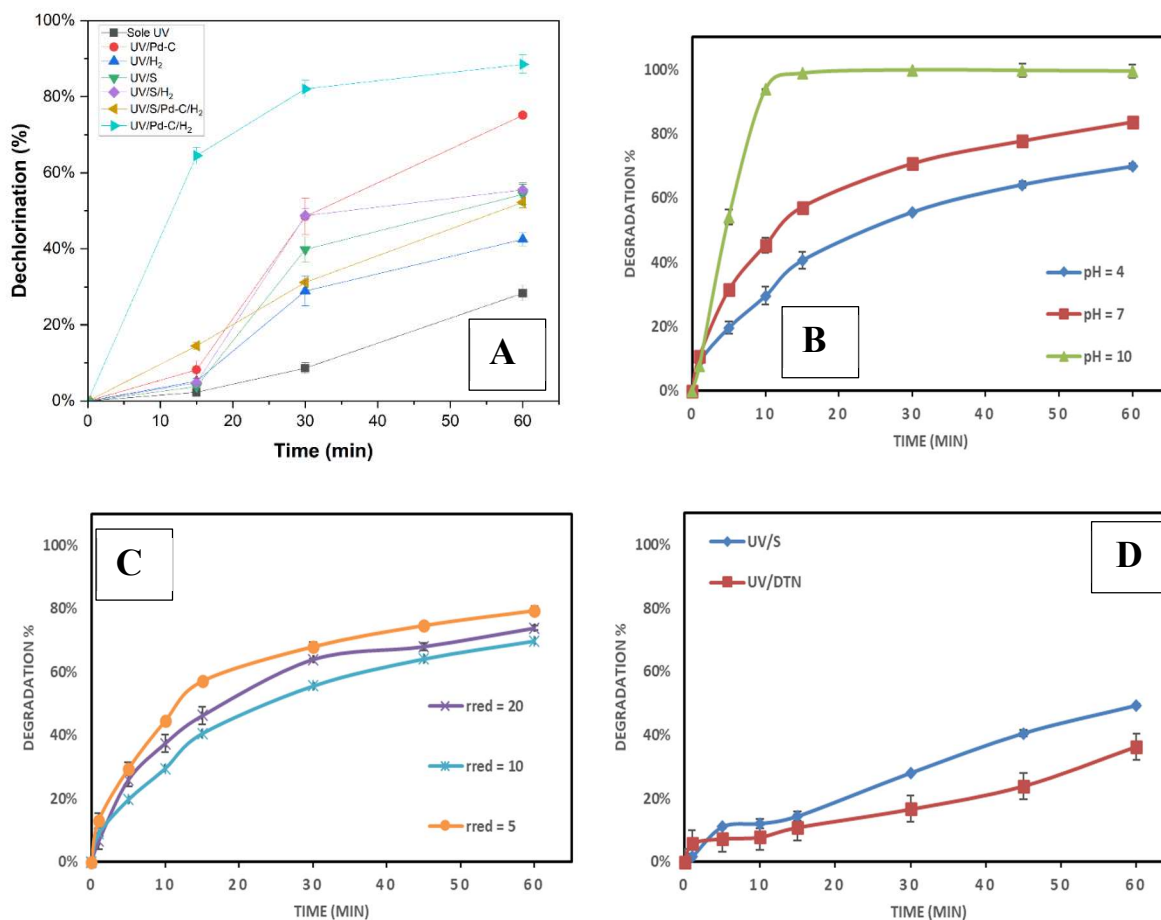


Fig. S3. (a) Dechlorination of CHL via different processes at conditions of Pd-C:CHL = 2:2, $r_{red} = 10$, $H_2 = 2L/h$, CHL = 20 mg/L and pH = 7. (b) effect of sulfite ($r_{red} = 10$) at different pH on UV/Pd-C/H₂ process (condition: Pd-C:CHL = 4:2, $H_2 = 4L/h$), (c) effect of sulfite concentration on UV/Pd-C/H₂ (condition: Pd-C:CHL = 4:2, $H_2 = 4L/h$ and pH = 4) process. (d) degradation of CHL via the two different (UV/SO₃²⁻ and UV/S₂O₄²⁻) processes at $r_{red} = 10$ and pH = 4.

Table 3S. Matrix of central composite design; factors, experimental and predicted responses

Run	A:H ₂	B:Pd-C	C:pH	Actual degradation (%)	Predicted degradation (%)
1	2.41	3.39	9.97	98.30	97.42
2	3.00	2.50	7.00	96.40	96.40
3	3.00	2.50	7.00	95.10	96.40
4	3.59	1.61	4.03	96.10	95.39
5	3.00	4.00	7.00	99.50	100.07
6	3.00	1.00	7.00	92.50	92.74
7	3.00	2.50	2.00	95.80	97.04
8	2.00	2.50	7.00	94.90	95.09
9	2.41	1.61	4.03	95.00	93.82
10	2.41	1.61	9.97	92.80	93.06
11	3.00	2.50	7.00	96.80	96.40
12	3.59	1.61	9.97	94.50	94.63
13	3.59	3.39	9.97	99.80	98.99
14	3.00	2.50	12.00	95.10	95.77
15	3.00	2.50	7.00	96.50	96.40
16	3.00	2.50	7.00	96.00	96.40
17	4.00	2.50	7.00	97.80	97.72

18	3.00	2.50	7.00	96.90	96.40
19	2.41	3.39	4.03	98.40	98.18
20	3.59	3.39	4.03	99.90	99.75

Table 4S. Coded levels and values of experimental design

Source	Sum of Squares	*df	Mean Square	F-value	p-value	
Model	75.22	3	25.07	49.08	< 0.0001	significant
A-H ₂	8.35	1	8.35	16.34	0.0009	
B-Pd-C	64.91	1	64.91	127.05	< 0.0001	
C-pH	1.96	1	1.96	3.84	0.0676	
Residual	8.17	16	0.5109			
Lack of Fit	5.99	11	0.5441	1.24	0.4304	not significant
Pure Error	2.19	5	0.4377			
Cor Total	83.39	19				

*Degree of freedom

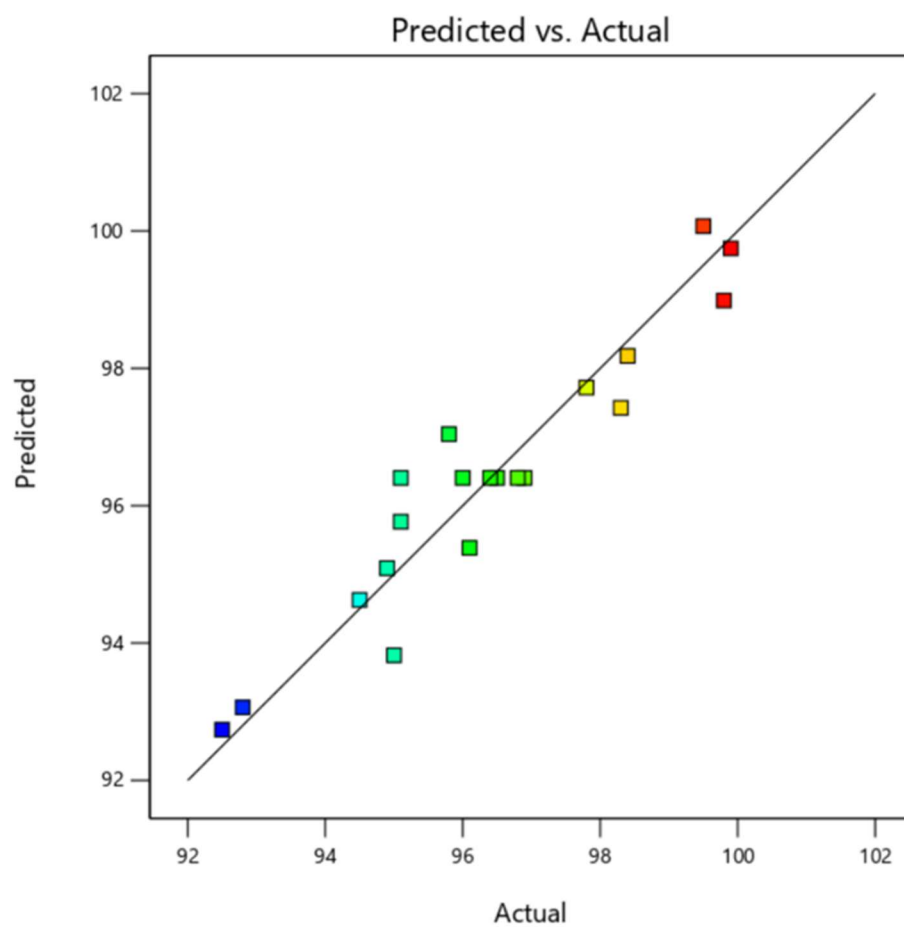


Fig. S4. Plot of actual vs predicted degradation (%) values for UV/Pd-C/H₂ process in degradation efficiency of CHL.

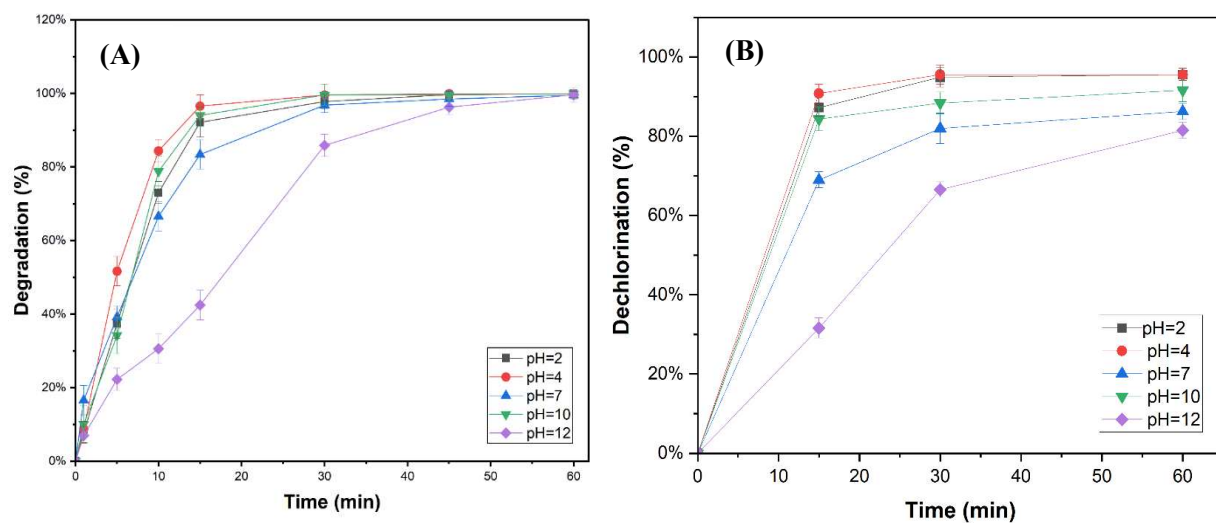


Fig. S5. Effects of pH on (a) degradation rates and (b) dechlorination through the UV/Pd-C/H₂ process. Conditions: CHL concentration: 20 mg/L, H₂ = 2 L/h and Pd-C:CHL = 2:1 (or 4:2).

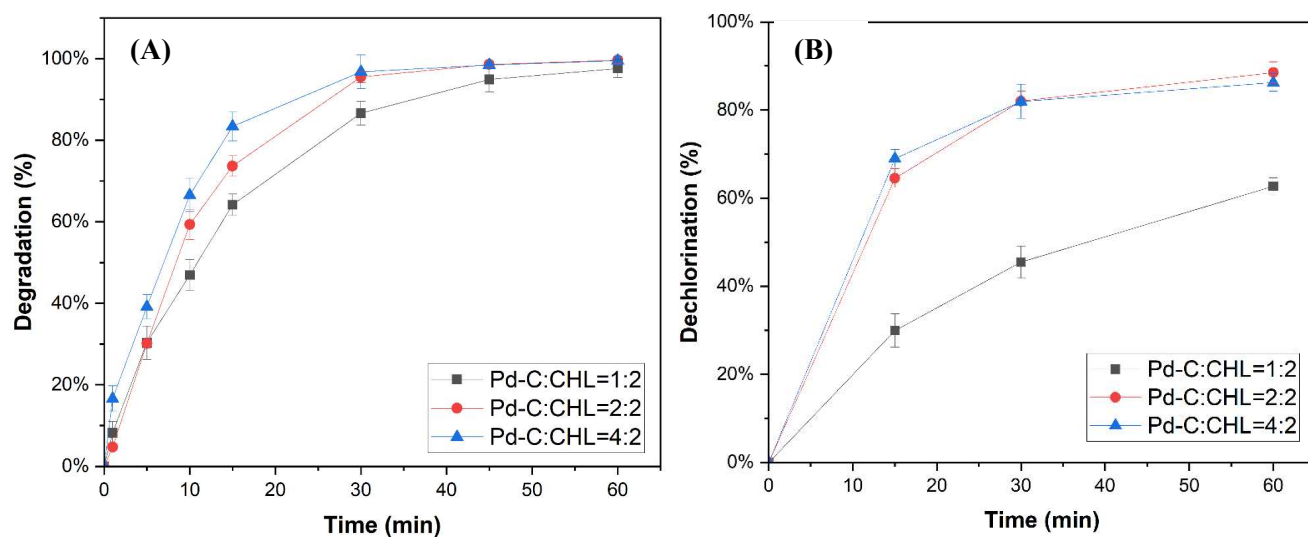


Fig. S6. Effects of Pd-C to CHL pollutant (Pd-C:CHL) = 1:2 to 4:2 mass ratio on (a) degradation and (b) dechlorination through the UV/Pd-C/H₂ process. Conditions of 20 mg/L CHL, H₂ = 2 L/h and pH = 7.

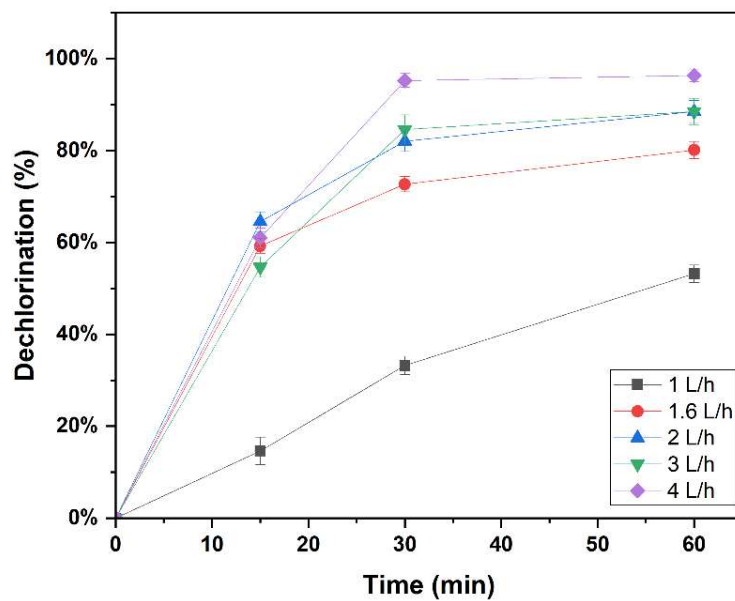


Fig. S7. H₂ gas flow effect on dechlorination. Conditions of 20 mg/L CHL, Pd-C:CHL = 2:2 and pH = 7.

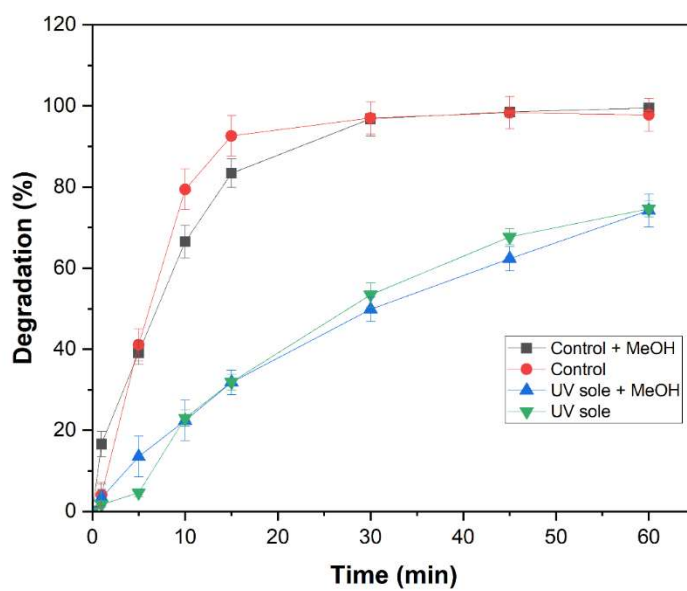


Fig. S8. The effect of methanol (MeOH) (CHL: anions molar ratio = 1:10) on the reduction of 20 mg/L CHL solution.

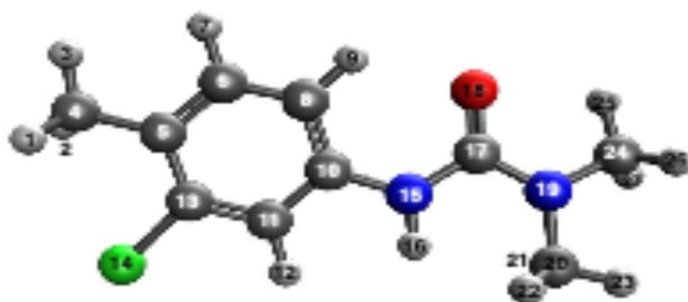


Fig. S9. Chlorotoluron structure with atomic indices indicated. These are the indices used in Table 2S.

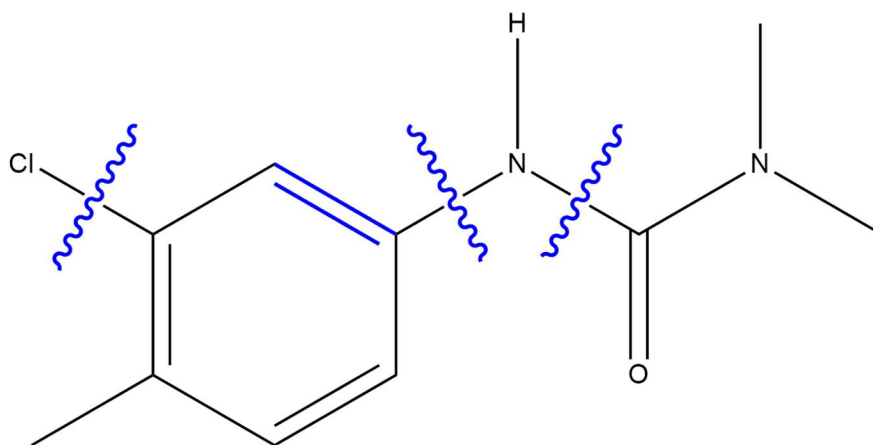


Fig. S10. CHL expected weak positions to get attacked.

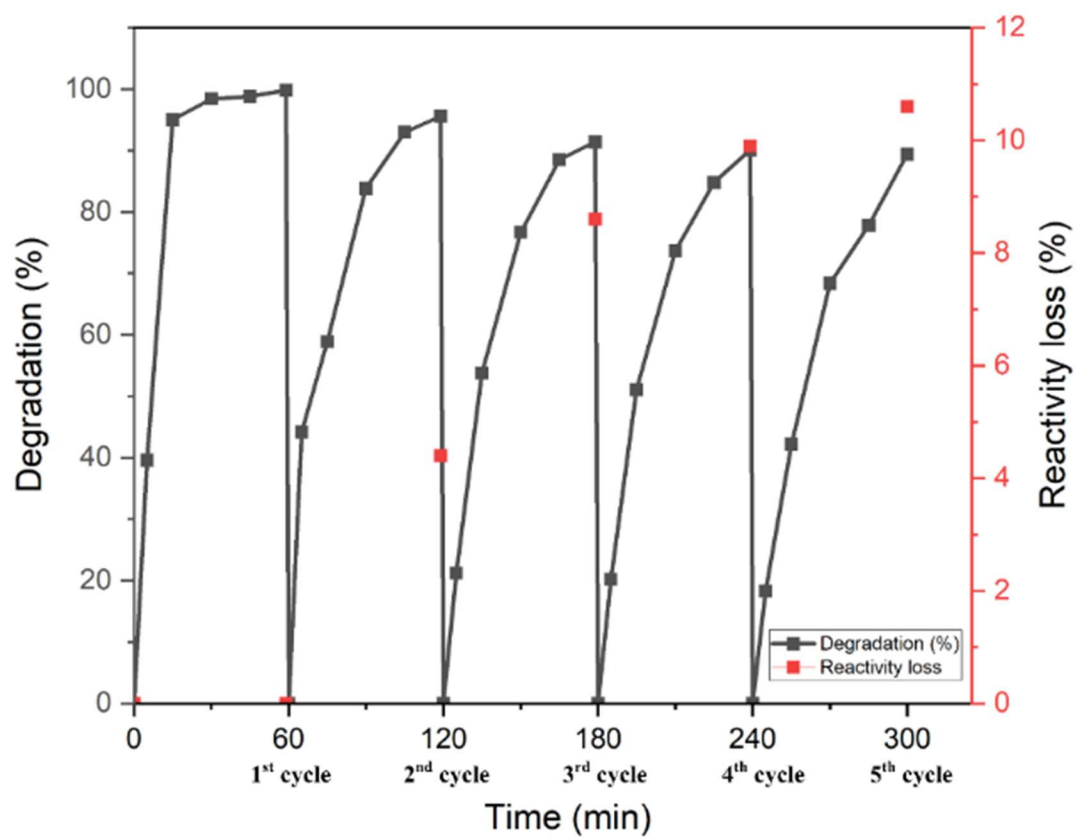


Fig. S11. Activity of Pd-C catalyst (Pd-C:CHL = 4:2 mass ratio) in five consecutive cycles.

References

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