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Organochlorine pesticides removal from groundwater by citrus coal and UV/O_3: a hybrid pilot-scale study

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ABSTRACT

In this laboratory-scale study, organochlorine pesticides (OCPs) reduction using citrus coals and O_3 assisted by solar UV as an integrated treatment of groundwater under visible UV to reach sustainable development were traced. The experimental parameters were set up throughout standard methods and analysis protocols. The best performance of citrus coal was observed at a reaction time of 90 min, pH: 6.5, adsorption bed height = 40 cm, initial OCPs concentration, respectively, as 100 µg/L for alachlor (ALC), α (±)-BHC, atrazine (ATZ), and α-chlordane, 150 µg/L for methoxychlor, 50 µg/L for heptachlor, and 90 µg/L for dieldrin. The best performance of citrus coal was observed at a reaction time of 90 min, pH: 6.5, adsorption bed height 40 cm, initial OCPs concentration of 100 µg/L for ALC, α (±)-BHC, ATZ, and α-chlordane, 150 µg/L for methoxychlor, 50 µg/L for heptachlor, and 90 µg/L for dieldrin. Under the above-mentioned operating conditions, the removal rates were estimated at more than 75% for all these compounds. The adsorption outputs were fitted to the Freundlich model with the average $R^2 > 0.97$, while for the Langmuir model this value was >0.86. Thereby, it is concluded that OCPs adsorption occurs on a heterogeneous surface by multilayer sorption. With regard to $K_f(1/n)$ parameter, for the Freundlich adsorption model, the order of OCPs adsorption was appeared to be methoxychlor > dieldrin > heptachlor > α-chlordane > ALC > α (±)-BHC > ATZ. The optimum variables for UV/O_3 were obtained as 0.4 mg/L ozone, pH = 9, and 35 min reaction time, so that, more than 98% of these substances were degraded from the solution under this condition. The reaction kinetics were fitted with R^2 value of more than 0.9 for most OCPs. The kinetic reaction constants (k) in pH values of 7 and 9.5 were higher than other ranges for all OCPs. The progress of pH at the alkaline area improved the pseudo-first-order constants. The kinetic model indicated that the reaction rates will be restricted by the initial pH value and the

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concentration of $OH^{\bullet}$. This evidence was well-established by monitoring dissolved O_2 at the various pH ranges during the experiment runs. Eight intermediates were detected by gas chromatography-tandem mass spectrometry detection with chemical formula as $C_{14}H_{20}ClNO_3$, $C_{13}H_{16}ClNO_3$, $C_{14}H_{18}ClNO_4$, $–NHCH(CH_3)_2$, $–NHCOCH_3$, $–NH_2$, $C_{13}H_9ClO$, and C_7H_5ClO from the samples taken in the non-optimized UV/O_3 effluent. However, all of them disappeared in the final effluent at the optimized condition. Altogether, this integrated strategy helped to remove OCPs more than 86% on average, with residues less than 1 μg/L and even 0.05 μg/L in some cases. Due to the generation of a large amount of citrus wastes (46,000 ton/y) in the north of Iran and the abundance of solar energy especially solar UV in the middle east, this hybrid approach to treat groundwater contaminated with agricultural OCPs as a type of EDCs can be an effective alternative for conventional and current removal strategies to provide safety and treat groundwater by this agricultural compound.

Keywords: Endocrine disrupter chemicals; Organochlorine pesticides; Groundwater; Citrus coal; Ozone

1. Introduction

Owing to the overwhelming use and exploitation in the farmlands and agrarian societies, organochlorine pesticides (OCPs) with chemical stability are known as omnipresent serious micropollutants over recent decades [1]. Generally, OCPs include dichlorodiphenyltrichloroethane, methoxychlor, dieldrin, lindane, chlordane, and benzenhexachloride which are endocrine disrupter chemicals (EDCs) with superior chronic and advanced toxicity. These substances are proved to have poisoning effects on biota and especially on humans by entering the food chain and bioaccumulation. Since the half-life of OCPs is more than 3 y, the existence of these matters in water bodies causes environmental health concern [2,3].

There are disparate oxidation and separation strategies that can serve as potential treatment alternatives for the effective removal of EDCs from water matrices, but unfortunately, the selected treatment options could not permanently satisfy the acceptable removal efficiency standards. A sub-micro concentration and change in chemical properties of EDCs might be the most probable causes [4]. Accordingly, the presence of these matters in untreated waters conducted for drinking purposes ranges from μg/L to ng/L, which allows them to pass through conventional water treatment. Additionally, physicochemical treatment options like coagulation–flocculation process, especially metal salt coagulants have been proved to be unable to remove these low molecular weight compounds in trace concentration ranges [3,4]. In the low-pressure membrane processes, despite high EDCs removal efficiency at high concentration, there are some technical obstacles to treat micro-contaminants such as bigger pore sizes in microfiltration (MF), ultrafiltration (UF), and nanofiltration or reverse osmosis (NF/RO).

Furthermore, other treatment alternatives are not feasible at the field operation from techno-economical point of view [5,6]. However, adsorption with activated carbon (AC) and biocharcoals could be one of the efficient approachs in terms of implementation cost and environmental concerns as well as removal efficiency to remove low concentration EDCs [7–10]. On the other hand, using green adsorbents to disappear EDCs, especially OPCs from the aqueous environment is more popular than before [11]. Thanks to high reduction rates, the reduction achieved in many studies, applying advanced oxidation processes (AOPs) to remove these substances has become more popular [12–15]. Among AOPs, ozonation with top removal efficiency has got significant results to reduce these substances; ozone oxidizes substrates either directly or by producing hydroxyl radicals that react to other entities [3].

However, applying each of adsorption units and oxidation processes separately can have some disadvantages because AC is not able to remove polar compounds. Furthermore, the presence of dissolved organic matters (DOMs), the solubility of substances, their saturation, competitive adsorption, and contact time affect the removal efficiency. These drawbacks for oxidation processes can be considered for all of the treatments that already need UV. Therefore, higher cost, as well as higher dose of UV, are necessary for efficient reduction rates and prevention of formation oxidation by-products [16,17]. Recently many researches have shown that coupling various processes or units can compensate for the deficiencies of using each of them separately and may result in hybrid strategies that aims at improving ultimate removal efficiencies with the lowest cost. For instance, some of the current combined techniques for pesticides or EDCs removals investigated are TiO_2/solar photocatalyst-powder activated carbon (PAC), photo-Fenton followed by PAC in removal rate more than 90% [9], UV/sonication [1], falling film dielectric barrier discharge (DBD) plasma reactor combined with adsorption on activated carbon textile material [18], the coupling of electro-oxidation, and ozonation for the degradation of Thiodan [19]. Moreover, the study of pesticide removal by means of combined ozonation granular activated carbon (GAC) filtration showed that ozone can dramatically improve atrazine (ATZ) removal by GAC filtration [20].

Annually, the agriculture section in the north of Iran, especially Golestan and Mazandaran provinces creates an awful lot of pesticides as EDCs micropollutants that contaminate water bodies whether directly or indirectly. On the other hand, there are a large amount of lemon or orange tree wastes in this domain but the possibility of reusing these wastes has not been taken into account. Therefore, the aim of this investigation was to evaluate OPCs removal and degradation by exploiting citrus coals and O_3 assisted by solar UV as an integrated treatment of groundwater under visible UV to reach sustainable development. Therefore, the sub-goals were characterization of the identified micropollutants and their possible polluting pathways, investigating the effect of some important variables including contact time, the initial concentration of OCPs, pH, ozone dosage on removal rates of the identified pesticides, adsorption isotherm investigation, and kinetic study, and cost analysis.

2. Materials and methods

2.1. Groundwater, sample collection, and preparation

Groundwater resources and wells in five different regions of Gorgan, Aq Qala, Anbar Olum, Aliabad-e-Katul, and Kordkuy were the locations for sampling water-well springs (agriculture season). Next, after fixing the water-well samples, they were conveyed to the laboratory for chemical analysis. In each well, the volume of the captured samples was 20 L with sampling repetition of three times.

2.2. Reagents and materials

A standard solution of mixed OPCs (200 µg/mL each of pesticides) was achieved through Supelco (Bellefonte, USA). Its relevant chemical formulae and other characteristics are listed in Table 1. Analytical grade *n*-hexane, methanol, and acetone for pesticide residue analysis were purchased from Merck Company (Darmstadt, Germany). Ultra-pure water was obtained from Purix CNX-100, while SPE cartridges and C18 sorbents were prepared from SiliCycle (Quebec City, Canada), H_2SO_4, KI, and NaOH solutions were provided from Merck to adjust samples' pH value.

2.3. Adsorbent (lemon charcoal) preparation

In order to prepare citrus coal the following steps were followed:

Firstly a compressed form was put into a sealed aluminum container, moreover, no oxygen was allowed to enter and a chamber was put into the electric furnace for 2 h at 700°C. Then, the aluminum container was removed from the oven. After the cooling process, carbon was obtained after crushing with a porcelain mortar by means of mesh siezes 50 and 12. Finally, coal was ready in the range of 0.5–0.2 mm [21].

2.4. Adsorption and ozonation pilot and experiment procedure

The experiments were conducted in two steps as batch mode: (1) fixed-bed Plexiglas adsorption cylinders which were filled with citrus coal and volume of 1.5 L, (2) Plexiglas photochemical reactor UV (solar)/O_3 with the volume of 5 L which was equipped with pH meter. Additionally, two chambers were placed for feeding adsorption and oxidation units along with fittings and valves, so that, sampling was carried out from three valves from adsorption column, one valve at the bottom of oxidation reactor as in Fig. 1.

Ozone-containing oxygen (O_2/O_3) gas was produced from a pure oxygen feed gas (99.9%) using an ozone generator (OL80F/DST – Ozone Generator's Model, Ozone services, Canada), and then it was continuously injected into the reactor bottom at a constant flow rate of 0.1 L/min (just first experiment run) using a fine bubble diffuser. The ozone concentration in the injected gas could be adjusted by changing the ozone generator power and flow rate. Dissolved ozone was quantified using the Indigo method [22]. The KI solution was regarded and added to the taken samples from the final effluent to control and harness reaction. The UV source was supplied directly from the solar irradiation on sunny days.

Table 1
Physicochemical characteristics and OPCs concentrations of the taken water samples in each sampling location for feeding adsorption unit inlet

Parameter	Unit	Gorgan	Aq Qala	Anbar Olum	Aliabad-e-Katul	Kordkuy	Mixed sample	SD
pH	–	7.9	8.2	8.1	7.9	8.6	8.2	±0.1
$CaCO_3$	mg/L	27	43	32	20	36	30	±1
HCO_3^{1-}	mg/L	35	46	41	32	27	35	±1
PO_4^{3-}	mg/L	4.5	8.9	8.2	5.7	6.3	6.5	±0.15
NO_3^-	mg/L	8.5	10.8	9.8	7.3	4.9	8.5	±0.1
SO_4^{2-}	mg/L	47	63	66	45	47	54	±1
Cl^-	mg/L	200	210	205	190	200	200	±10
Alachlor (ALC)	µg/L	2.9	4.2	5.4	3.7	3.8	4.2	±0.02
α (±)-BHC	µg/L	1.5	2.3	2.4	1.4	0.95	1.8	±0.015
Atrazine (ATZ)	µg/L	2.1	4.8	5.3	3.65	1.86	4.1	±0.01
Methoxychlor	µg/L	7.1	9.65	10.86	6.43	7.88	8.4	±0.01
Heptachlor	µg/L	0.21	0.31	0.35	0.25	0.15	0.25	±0.001
Dieldrin	µg/L	0.34	0.48	0.54	0.28	0.31	0.4	±0.001
α-chlordane	µg/L	1.85	2.25	2.31	1.25	2.43	2	±0.015
DOC	mg/L	0.38	0.43	0.43	0.38	0.52	0.45	±0.05
TOC	mg/L	0.39	0.43	0.44	0.54	0.6	0.49	±0.05
TDS	mg/L	885	936	910	852	896	895	±10
EC	µS/cm	783	820	805	747	798	790	±5
Hardness	mg/L	38	46	51	31	42	41.6	±1

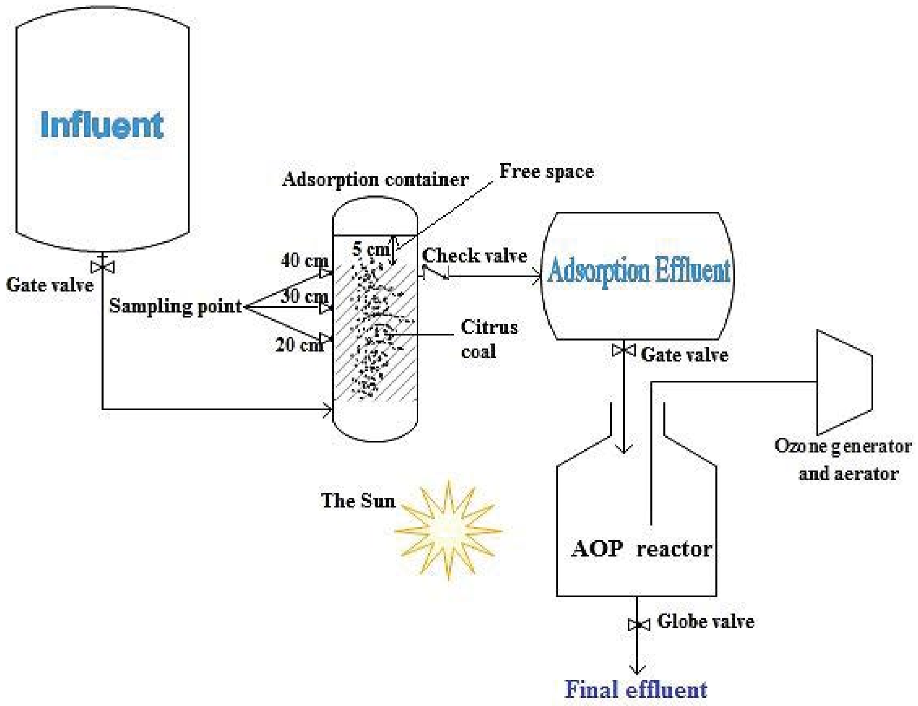


Fig. 1. Scheme of the adsorption-AOP batch-pilot: influent chamber (20 L), fixed-bed tubular adsorption container with citrus coal (1.5 L), adsorption effluent chamber (12 L), Plexiglas AOP reactor (5 L), ozone generator, and aerator device.

2.5. Radiation conditions during experimental survey days

The intensity was metered via a UV radiometer during the experiments. The fixed intensity ranges were varied from 28 to 32 W/m^2 on summer days in the Middle East. The intensity range was fixed from 28 to 32 W/m^2 to fit the intensity of UV radiations which were harvested from sunlight during the experimental days (from July to September).

The method of the experiment was one factor-at-a-time procedure by ranging variables (time, pH, initial concentration of OPCs, ozone dosage, and adsorbent column height) and fixing one variable in each experiment run. The uptake (q_e) values of citrus coal for the substances were estimated by the mass balance [23]:

$$q_e = \frac{\left(C_0 - C_e\right)V}{M} \tag{1}$$

Here, q_e is equilibrium capacity (µg/g), C_0 and C_e represent initial and equilibrium concentration (µg/L), V is the operating volume (L), and M is the weight of adsorbent (g), the quantity used for pH adjustment could be insignificant.

Also, the removal efficiency of OCPs was estimated by Eq. (2):

$$R = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

Adsorption isotherms are applied to explain the relationship between the quantity of adsorbed substance at equilibrium (q_e) and the effluent concentration C_e by a mathematical model. Both Langmuir and Freundlich isotherms were investigated to represent the experimental results of the OCPs. Linear regression was utilized to ascertain the constants of each model.

Langmuir isotherm is characterized in the following linear form [9,24]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m C_e} \tag{3}$$

Here, q_m and b, are the Langmuir constants related to the affinity of the binding sites. q_m (µg/g) is the maximum amount of adsorption per unit mass of adsorbent corresponding to complete coverage of the adsorptive sites while b (L/mg) is the Langmuir constant related to the energy of adsorption. The Langmuir constants were obtained from the plot of q_e vs. C.

Likewise, for Freundlich isotherm, the equation is based on adsorption onto a heterogeneous surface. Considering this point, it is assumed that the concentration of adsorbate on the adsorbent surface will rise as a result of the increase in adsorbate concentration. Accordingly, it is represented by Eq. (4) [23,24]:

$$q_e = K_f C_e^{1/n} \tag{4}$$

The linear form of the Freundlich equation is given as Eq. (5):

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{5}$$

Here, K_f and $1/n$ are the constants. The Freundlich constant K_f indicates the quantity of contaminant adsorbed at an equilibrium concentration of 1 µg/mL. The constant $1/n$ (slope) is the measure of the intensity of sorption and it represents the degree to which sorption is the function of contaminant concentration. The Freundlich constants were achieved from the plot of $\log q_e$ vs. $\log C$.

2.6. Methods of analysis

Measurement of TOC and DOC, SO_4^{2-}, NO^{3-}, $CaCO_3$, HCO_3^{1-}, and PO_4^{3-} were carried out based on standard methods for water and wastewater examinations (latest version) [25]. Total organic carbon (TOC) was measured by a Shimadzu TOC-5000A TOC analyzer (Japan). The dissolved oxygen (DO) concentration and temperature were monitored by Waterproof DO 300 Dissolved Oxygen Meter. The pH adjustment and measurement were done by WTW pH 330i pH messgerät im Koffer. Total dissolved solids (TDS) and electrical conductivity (EC) were obtained by WTW Cond 330i Conductivity Meter.

2.6.1. OCPs analysis

SPE cartridges were activated using 6 mL methanol, followed by 6 mL of ultra-pure water, before loading samples. After the activation, 100 mL aqueous samples were passed through the SPE cartridges. They were then dried in a vacuum for 20 min to remove retained water. The analytes were eluted with 20 mL solutions of *n*-hexane and acetone (9:1, v/v) before samples were made subject to evaporation in a rotary evaporator (Heidolph, Germany). The analytes were then re-dissolved in 1 mL of methanol. Then, the pesticides analysis was performed through a gas chromatography-mass spectrometry (GC-MS) system coupling Trace GC ULTRA with TriPlus to an ITQ 1100 (Thermo Scientific, Waltham, USA). A ZB-5MSplus Zebron Capillary GC column (analytical column) of 30 m × 0.25 mm × 0.25 µm was used. Helium served as the carrier gas. The temperature program was: initial temperature, 100°C was held for 1 min, temperature ramp was increased from 20°C/min to 210°C and then stayed for 1 min, temperature ramp was increased by 5°C/min to 300°C and then stayed for 2 min; the total time was 27.5 min. MS parameters: ion source –230°C, transfer line temperature –280°C, full scan, mass range 50–650. Recoveries for pesticides resulted in values in the range of 78%–124% [1].

3. Results and discussion

By referring to agriculture office of both provinces (Golestan and Mazandaran) and their statistics pertaining pesticides consumption, it was revealed that about 74,500 L OCPs per annum is used in three sections including: livestock and grazing, farmlands, and horticulture. Thus, this volume of OCPs release can contaminate groundwater by disparate emission pathways as Fig. 2a represents and ultimately water treatment plants (WTPs) are regarded as the endpoint. Moreover, both farmland and horticulture sections produce already 46,000 tons of citrus wastes per annum. This amount of waste production can support WTPs by utilizing citrus coals as charcoal.

The characteristics of the water well samples chosen from five regions in Gorgan, Aq Qala, Anbar Olum, Aliabad-e-Katul, and Kordkuy are reported in Table 1. Additionally, seven OCPs such as alachlor (ALC), α-benzenehexachloride, ATZ, methoxychlor, heptachlor, dieldrin, and α-chlordane were detected as predominant micropollutants in trace concentration and their characteristics, as well as the region in which they were detected, are given in Table 2.

By evaluating the data, it was found that the concentration of ALC, ATZ, methoxychlor, and α (±)-BHC were higher than other OCPs. To facilitate the experiments, a mean concentration in a mixed sample was considered to fix the initial concentration.

3.1. Adsorption unit

3.1.1. Surface characterization of citrus coal

The FTIR analysis was carried out to determine the functional groups which are present on the citrus coal surface, and the spectrum result is given in Fig. 2b.

The extensive band at 3,280 cm^{-1} appeared by the stretched bonds of O–H bond in the celluloses and hemicelluloses substances of citrus coal [26,27]. The C–H and C–O bonds stretching could be the leading cause to make the peaks at 1,485 and 1,080 cm^{-1}, respectively [28]. The peak at 1,565 cm^{-1} emerged to be due to C=C stretching in the aromatic ring [29,30]. Additionally, from the spectra, the applied biocharcoal revealed a bond at 765 cm^{-1}, where C–H out-of-plane bending aromatics were the most likely proof [31]. Altogether, a large number of C–OH functional groups found for citrus coal related to aromatics and aliphatics were similar to Zhao et al.'s [32] findings.

3.1.2. Effect of contact/retention time

To determine the retention time effect, the time ranges were chosen in a fixed condition for each run as Fig. 3 shows. Maximum reduction rate for OCPs was obtained at 120 min by average removal rate of 75.7 for all OCPs, and among them, heptachlor by 79.4% and ALC by 66% had the highest and the lowest reduction rates, respectively. Fig. 3 illustrates that the adsorption rose dramatically with arising contact time only within the first 60 min and then it continued steadily until it reached equilibrium. Apart from this, the fast adsorption at early stages maybe because of the fact that a large number of surface sites were accessible for adsorption. Furthermore, the remaining empty surface sites were far from easy to be filled due to the formation of repulsive forces between the OCPs' molecules on the solid surface and in the bulk state. However, since a noticeable difference in residual concentrations and removal rates between contact times of 90 and 120 min was not observed, the first one was chosen as an optimum value [8].

3.1.3. Effect of pH

Since functional groups of adsorbent and chemicals' properties such as the surface charge of an adsorbate, the degree of ionization, and the speciation can be affected by the pH value of the solution, this variable is one of the most

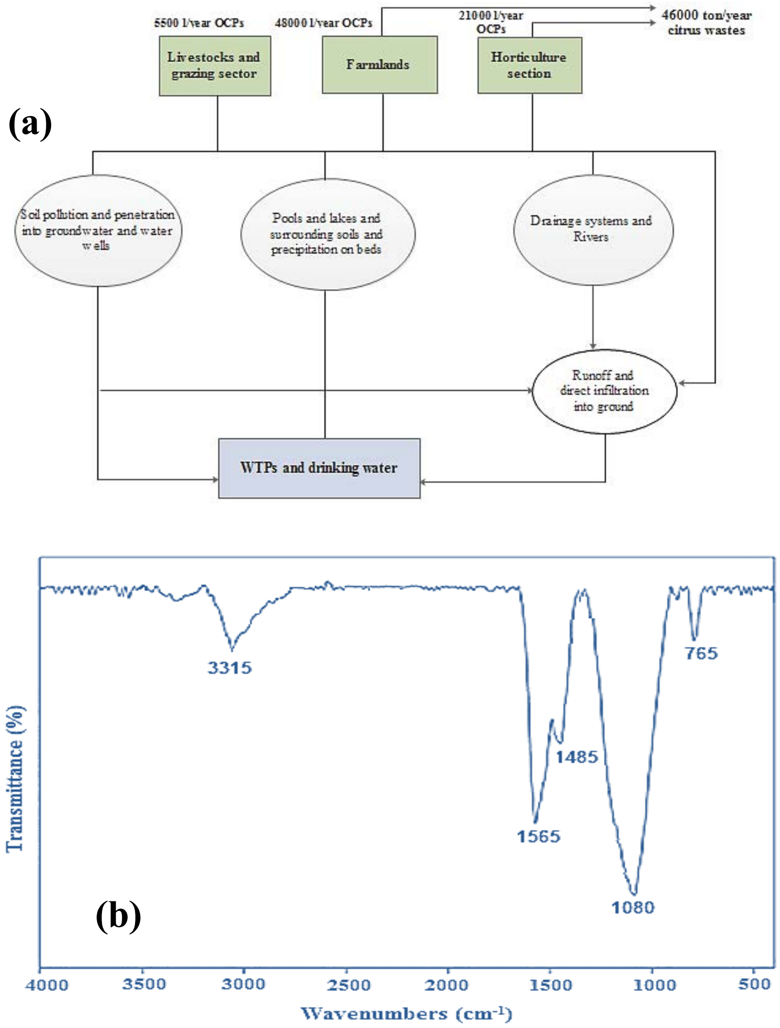


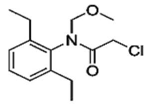
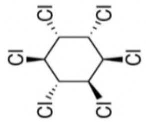
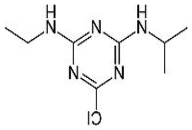
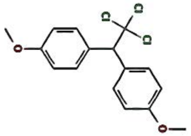
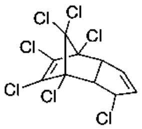
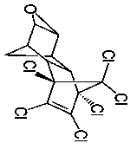
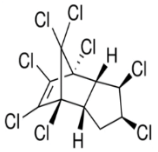
Fig. 2. (a) OPCs emission pathways follow chart, the volume of OCPs used, and citrus wastes produced in three sectors livestock and grazing, farmlands, and horticulture were 74,500 L and 46,000 ton/y, respectively and (b) FTIR spectrum of citrus coal.

crucial factors for adsorption experiments [33]. To evaluate the pH effect, its values were ranged as 2, 3, 4, 5.5, 7, 8, and 9. By doing so, it was disclosed that the sorption capacity of OCPs comparably stabilized at pH 5–8 with the lowest OCPs residual concentrations, dropped considerably at pH 4–5.5 and decreased and slightly went up at the extreme alkaline pH and then leveled off at 9 as Fig. 4a. These phenomena could be attributed to the change of the surface charge of citrus coal and the speciation of OCPs at different pH values [27]. Furthermore, in Jusoh et al.'s [23] study, some OCPs such as ATZ, dieldrin, and heptachlor had the highest adsorption and consequently removal rate at pH 5–7 through various ACs, these results were consistent with the obtained data. However, in pH values more than seven due to the raising of deprotonation of functional groups with the increase of pH and more negative charges on the surface of activated carbon the adsorption capacity and removal rate decreased. Additionally, the negative charges induced electrostatic repulsion forces between the biocharcoal surface and the OCPs, which diminished the possibility of adsorption on the active sites [9].

3.1.4. Effect of bed height

In order to investigate the influence of adsorbent bed height, three adsorbent columns with the height of 20, 30, and 40 cm were considered. After doing the experiments under fixed condition, the results were obtained as Fig. 4b. The residual concentration and adsorption efficiency respectively reduced and increased by rising bed height, so that, maximum OCPs concentration reduction and adsorption rate were observed in the height of 40 cm from adsorbent column bed. Additionally, the findings were in line with the results of the study carried out by Ahmed and Hameed [34]. Therefore, the results suggest that the adsorption performance was considerably influenced by bed height. The total sorption of micropollutant principally depends on the quantity of adsorbent within the column, which will occur by providing suitable adsorption sites for the best uptake operation. The results of many investigations are representative of the same outputs. For example, Kim et al. [35] investigated the impact of various bed heights (5–20 cm) on the adsorption dynamics of trimethoprim (TMP)

Table 2
Characterization of OCPs detected in water samples taken from groundwater in regions of Gorgan, Aq Qala, Anbar Olum, Aliabad-e-Katul, and Kordkuy

Name	Aquifer/region of detection	Chemical formulation	Molecular structure	Guideline limits of WHO and US EPA as MAC* (μg/L)	Water solubility (mg/L)	Molecular weight (g/mol)	Application
Alachlor (ALC)	Gorgan, Aq Qala, Kordkuy, and Aliabad-e-Katul	$C_{14}H_{20}ClNO_2$		20	242	269.767	As herbicide, to control herbs in corn and soybean farms
α (±)-BHC	Aliabad-e-Katul, Anbar Olum, and Aq Qala	$C_6H_6Cl_6$		0.01	100	290.83	As insecticides
Atrazine (ATZ)	Aq Qala, Aliabad-e-Katul, Anbar Olum, and Kordkuy	$C_{14}H_{20}ClNO_2$		2	70	269.767	As herbicide
Methoxychlor	Anbar Olum, Gorgan, and Aq Qala	$C_{16}H_{15}Cl_3O_2$		20	0.04	345.65	To protect crops, pests control, and livestock
Heptachlor	Kordkuy, Anbar Olum, Gorgan, and Aq Qala	$C_{10}H_5Cl_7$		0.03	0.18	373.32	As insecticide
Dieldrin	Aliabad-e-Katul, Anbar Olum, and Aq Qala	$C_{12}H_8C_{16}O$		0.03	0.11	380.91	Used on crops
α-Chlordane	Anbar Olum, Gorgan, Aq Qala, and Aliabad-e-Katul	$C_{10}H_6C_{18}$		0.2	1	409.78	For treatment of termites on crops

*MAC: maximum contaminant level.

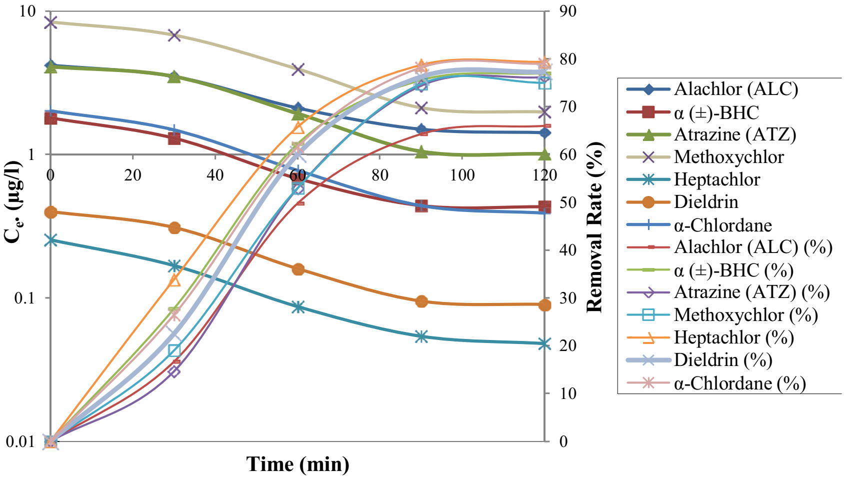


Fig. 3. Effect of contact time on concentration and the removal rate of OCPs. The experiment condition was as pH = 6; column height = 40 cm; DOC = 0.45 mg/L; TOC = 0.49 mg/L; temperature 20°C; initial concentration 4.2, 1.8, 4.1, 8.4, 0.254, 0.4, and 2.018 µg/L, respectively, for alachlor (ALC), α (±)-BHC, atrazine (ATZ), methoxychlor, heptachlor, dieldrin, and α-chlordane.

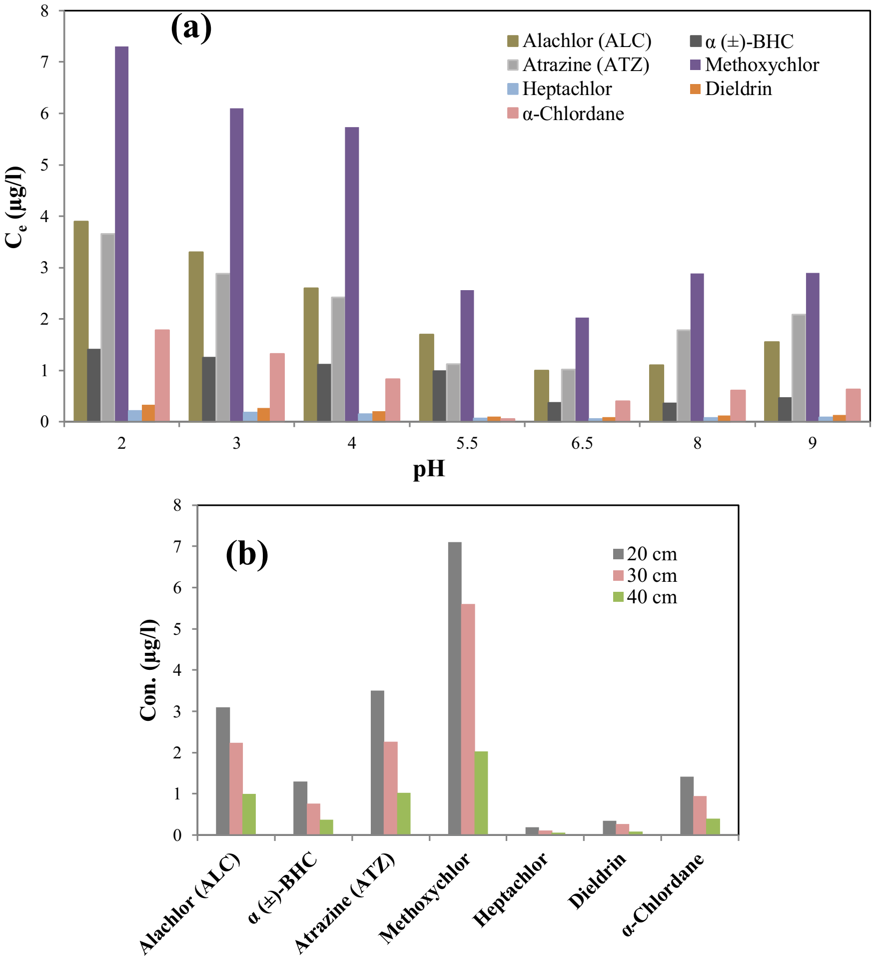


Fig. 4. (a) Effect of initial pH on the residual concentrations of OCPs. Contact time = 90 min; column height = 40 cm; DOC = 0.45 mg/L; TOC = 0.49 mg/L; temperature of 20°C; initial concentration of 4.2, 1.8, 4.1, 8.4, 0.25, 0.4, and 2 µg/L, respectively, for alachlor (ALC), α (±)-BHC, atrazine (ATZ), methoxychlor, heptachlor, dieldrin, α-chlordane and (b) effect of bed height. Experiment condition: pH = 6.5, other conditions were same with section (a).

through a carbon bed. The fixed bed with high depth represented enough contact for TMP molecules onto the adsorbent within the column. Furthermore, Oladipo et al. [36] and Mondal et al. [37] found similar evidence on the pharmaceuticals removal by using activated biochar systems related to the significant function of bed height and providing further adsorption area by arising adsorbent bed height.

3.1.5. Effect of initial concentration and adsorption isotherm

To measure the influence of the initial concentration on OCPs removal, the survey was conducted by varying the initial concentrations of the pilot influent by synthesizing water matrices. For this reason, the initial concentrations were prepared in disparate five levels for each of OCPs given in Table 3. By performing this step of the study, the results were obtained as Fig. 5. It was observed that raising the initial concentration of OCPs led to a significant increase in OCPs sorption. This is likely because of a superior mass transfer driving force as a consequence of the enhancement in the number of molecules rivaling for the binding sites present on the adsorbent when the initial concentration of OCPs is raised [30,38]. In spite of that, the adsorption rate slowly soared after 60 min after the beginning of each experiment run in the concentrations higher than 100 μg/l for ALC, α (±)-BHC, ATZ, and α-chlordane, 150 μg/L for methoxychlor, 50 μg/L for heptachlor, and 90 μg/L dieldrin. Accordingly to the OCPs uptake firmly depends on the initial concentration of OCPs into the solution.

To illustrate how the adsorbates are diffused between the liquid phase and the solid phase when the adsorption mechanism conquers equilibrium state, doing adsorption isotherms is an essential part. For this purpose, two isotherm models of Langmuir and Freundlich have been recently applied in fitting the equilibrium data from a large number of investigations. Langmuir's model is based around the assumption that adsorption energy is constant and independent of surface coverage. The maximum adsorption takes place when the surface is hidden by a monolayer of adsorbate [8,30], while the Freundlich model relies on sorption on a heterogeneous surface of dissipating affinities [8]. Here, both isotherm models, Langmuir and Freundlich were studied based on Eqs. (3)–(5) for each of seven OCPs in the initial concentration represented in Table 3 and the results for isotherm plots are given as Fig. 6. With regard to the plots, the isotherm constants were obtained as Table 4. Overall, adsorption outputs were fitted to the Freundlich model, so that, the values of correlation coefficients with $R^2 > 0.97$ for all OCPs were higher than the Langmuir model with $R^2 > 0.86$, in average.

For this reason, the Freundlich sorption equation was successful to describe the OCPs sorption outputs by citrus coal in accordance with previous studies [24,27,30,39]. This means that OCPs adsorption occurs on a heterogeneous surface by multilayer uptake. However, Chaparadza and Hossenlopp [40], in their study demonstrated that ATZ equilibrium data were well fitted to a nonlinear regression Langmuir model in concentrations higher than 5 mg/L.

To have a meaningful comparison of sorption of various OCPs in citrus coal, the $1/n$ (slope) quantities must be statistically equivalent. Therefore, to have a satisfactory comparison, multiplying Freundlich adsorption constant (K_f) in slope ($1/n$) and considering its result as $K_f(1/n)$ value can be the effective parameter to reach this goal [24]. Accordingly, the $K_f(1/n)$ parameter for ALC, α (±)-BHC, ATZ, methoxychlor, heptachlor, dieldrin, and α-chlordane were estimated respectively as 21.37, 18.87, 5.49, 40.87, 31.68, 34.78, and 22.42. As a result, this adsorption model proposes that the order of OCPs adsorption is methoxychlor > dieldrin > heptachlor > α-chlordane > ALC > α (±)-BHC > ATZ, to reach the research observations.

3.2. Oxidation unit

In the second part, after optimizing adsorption variables as contact time of 90 min, adsorption bed height of 40 cm, pH 5.5–6.5, and initial concentrations respectively as 100 μg/L for ALC, α (±)-BHC, ATZ, and α-chlordane, 150 μg/L for methoxychlor, 50 μg/L for heptachlor, and 90 μg/L dieldrin to feed the adsorption unit, the study was conducted to evaluate the oxidation condition effect made and reinforced by ozone and UV gained from solar energy.

In O_3/UV process the contaminants can be decomposed throughout a set of reaction mechanisms which include direct UV photolysis, direct ozonation, and indirect $OH^\bullet$ oxidation. Also, direct photolysis of the contaminants could occur if it adsorbs the wavelength utilized. The photo-degradation of O_3 results in H_2O_2 generation as *in situ*. Therefore, micropollutant oxidation is reinforced by three components UV, ozone, and hydrogen peroxide, which are omnipresent in the reaction solution. The relative dominance of these components on the degradation reaction relies on UV radiation, and its wavelength and intensity, ozone dosage, and concentration and type of contaminant [41]. In this research, ozone dosage and aeration rate,

Table 3
Synthesized water samples with various concentrations to feed pilot for evaluation of initial concentration's effect on OCPs removal

Sample	Alachlor (ALC) (μg/L)	α (±)-BHC (μg/L)	Atrazine (ATZ) (μg/L)	Methoxychlor (μg/L)	Heptachlor (μg/L)	Dieldrin (μg/L)	α-Chlordane (μg/L)
1	180	180	180	200	100	180	150
2	100	100	100	150	50	90	100
3	50	50	50	60	10	30	50
4	10	10	10	20	1	5	10
5	1	0.6	1	2	0.1	0.5	0.1

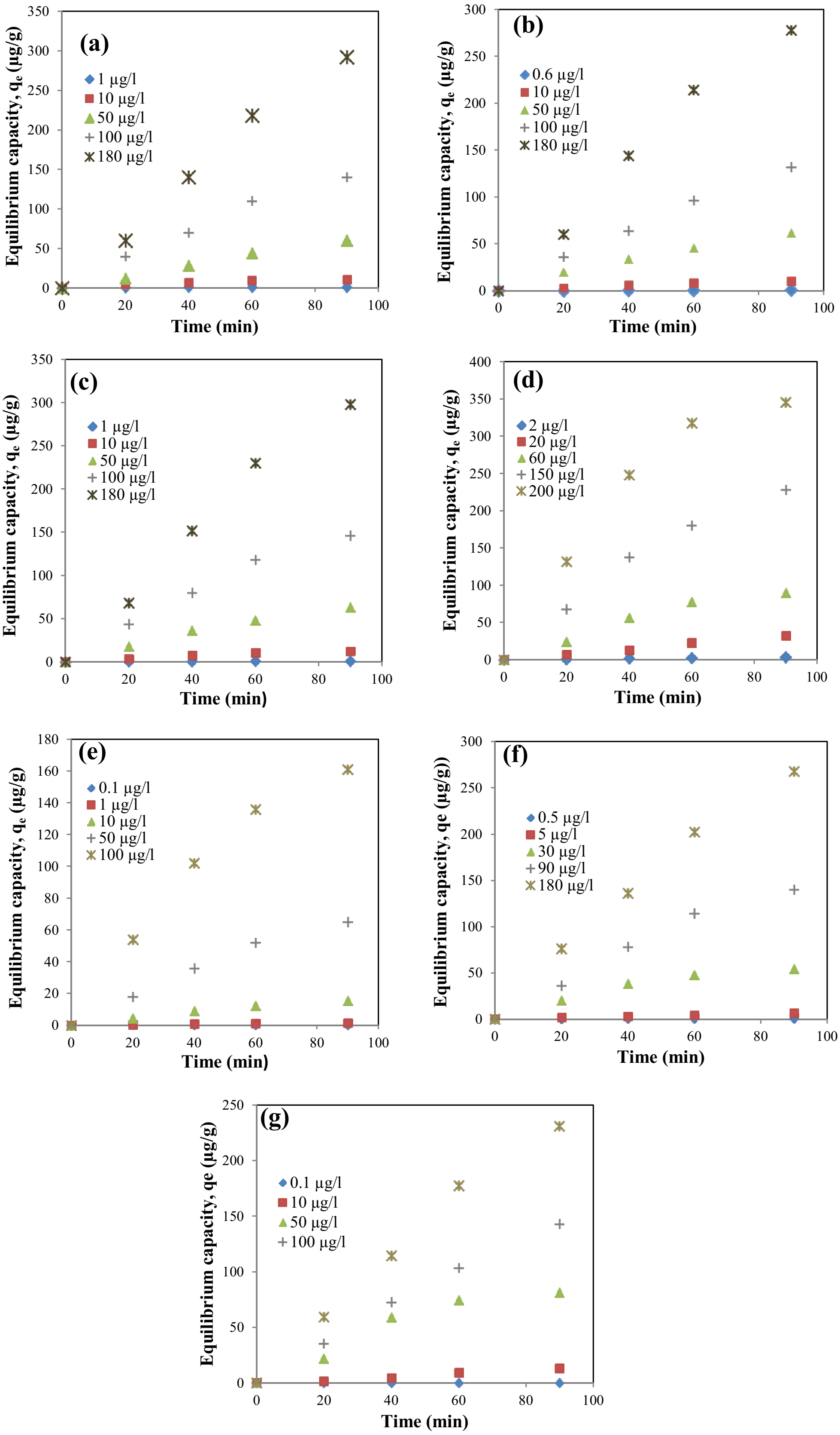


Fig. 5. Effect of initial concentration (µg/L) in samples on equilibrium capacity (µg/g) for (a) alachlor (ALC), (b) α (±)-BHC, (c) atrazine (ATZ), (d) methoxychlor, (e) heptachlor, (f) dieldrin, and (g) α-chlordane; pH = 6.5; temperature = 20°C; contact time = 90 min; column height = 40 cm.

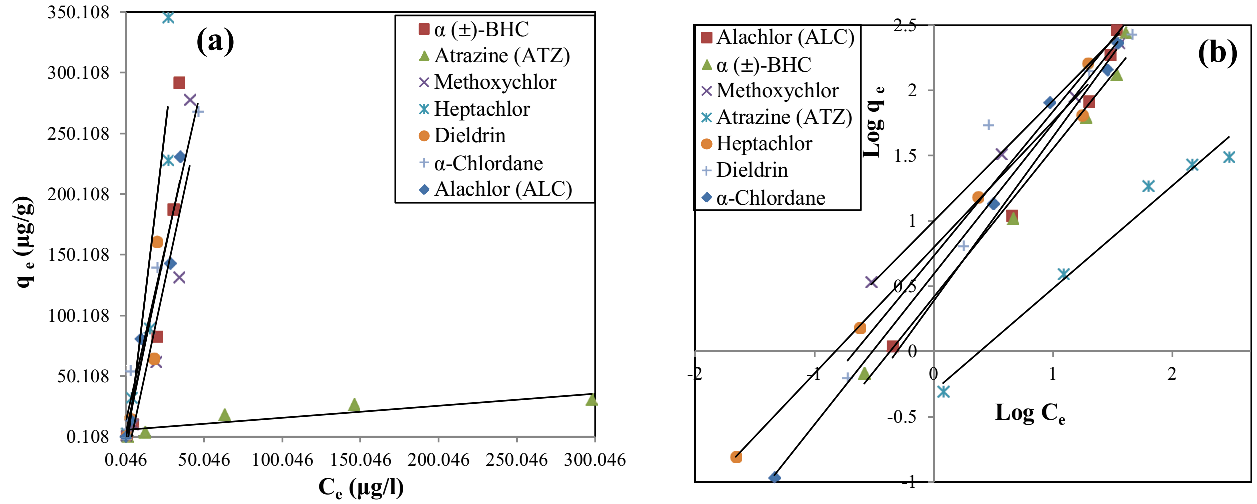


Fig. 6. Langmuir (a) and Freundlich (b) adsorption isotherms of OCPs; pH = 6.5; temperature = 20°C; contact time = 90 min; column height = 40 cm; initial dosage of OCPs were as Table 3.

Table 4
Freundlich and Langmuir adsorption–desorption constants obtained OCPs adsorption on citrus coal. K_f is constant which equals with the amount of contaminant adsorbed at an equilibrium concentration of 1 µg/mL

OCP	Langmuir			Freundlich		
	q_m (µg/g)	B (L/µg)	R^2	k_f	$1/n$	R^2
Alachlor (ALC)	187.7	2.66	0.94	17.1	1.25	0.98
α (±)-BHC	131	25.2	0.9	16.7	1.13	0.98
Atrazine (ATZ)	145.7	5.82	0.88	7.043	0.78	0.97
Methoxychlor	227.3	21.59	0.86	44.43	0.92	0.97
Heptachlor	64.1	5.09	0.85	33	0.96	0.98
Dieldrin	138.9	1.4	0.82	31.62	1.1	0.93
α-Chlordane	142	13.46	0.97	19.5	1.15	0.99

pH, and contact time were chosen as variables for oxidation study in the following adsorption unit.

3.2.1. Effect of ozonation dosage

To determine the influence of ozone dosage on OCPs degradation in aqueous solution, different ozonation dosages as 0.1, 0.2, 0.4, 0.8, and 1 mg/L were injected to the reaction solution. The observed results are provided in Fig. 7a. It is evident that by adding only 0.1 mg/L ozone to the solution, a dramatic drop in the residual concentration of OCPs happens and this reduction was followed by 0.2 mg/L, and since then steadily proceeded to ozonation of 0.4 mg/L where the lowest residues for all seven OCPs were obtained. Finally, this reduction in concentrations nearly leveled off from 0.4 to 1 mg/L ozonation without any tangible progress. The results were similar to the findings of the study conducted by Lester et al. [42] for other EDCs removals in this concentration range of ozonation. By knowing this trend of OCPs residues reduction in the reaction solution, it can be interpreted that OCPs decomposition extremely depends on ozone in the low dosage under UV irradiation through Eqs. (6)–(16) as is the case for the possible OH radical generation pathways. Accordingly, Eqs. (1)–(6) belong to the reaction of ozone with the reaction medium alone, but Eqs. (6)–(16) can happen under UV radiation [43]:

$$O_3 + HO^- \rightarrow O_2 + HO_2^- \tag{6}$$

$$O_3 + HO_2^- \rightarrow HO_2^{\bullet} + O_3^{\bullet -} \tag{7}$$

$$HO_2^{\bullet} \rightleftarrows H^+ + O_2^{\bullet -} \tag{8}$$

$$O_2^{\bullet -} + O_3 \rightarrow O_2 + O_3^{\bullet -} \tag{9}$$

$$O_3^{\bullet -} + H^+ \rightleftarrows HO_3^{\bullet} \tag{10}$$

$$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2 \tag{11}$$

$$O_3 + h\nu \rightarrow O_2 + O^{\bullet} \tag{12}$$

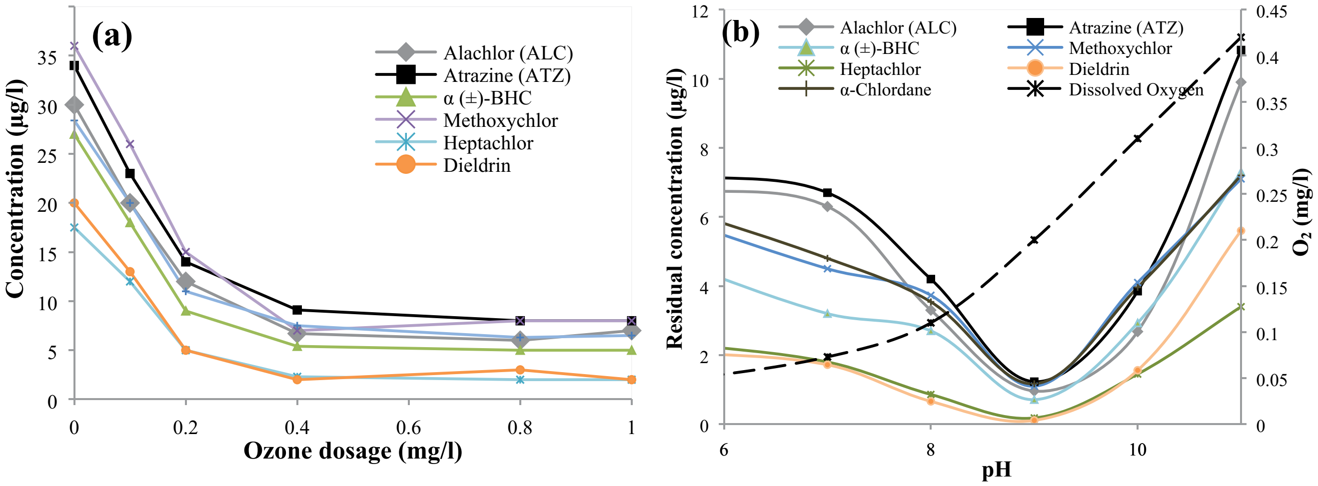


Fig. 7. (a) Effect of ozone dosage on OCPs removal; sunlight UV = 28–32 W/m²; pH = 6.5; temperature = 20°C; TOC = 0.03 mg/L; DOC = 0.025 mg/L; contact time = 20 min; adsorption effluent's OCPs concentrations with regards to the optimized initial concentrations as 30 µg/L alachlor (ALC), 34 µg/L α (±)-BHC, 27 µg/L atrazine (ATZ), 36 µg/L methoxychlor, 17.5 µg/L heptachlor, 20 µg/L dieldrin, 28.4 µg/L α-chlordane. (b) Effect of pH solution on OCPs removal in ozonation reinforced by solar UV. Contact time = 15 min; ozone dosage = 0.4 mg/L; initial concentrations and temperature were the same with section (a).

$$O^{\bullet} + H_2O \rightarrow 2HO^{\bullet} \quad (13)$$

$$O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2 \quad (14)$$

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \quad (15)$$

$$H_2O_2 \rightleftarrows H^+ + HO_2^- \quad (16)$$

Based on Eq. (14) by increasing O_3 concentration in the reaction medium, the amount of hydrogen peroxide begins to rise, so that, it competes with micropollutants to react with hydroxyl radicals as a scavenger in the high dosage of O_3 which reduces OCPs degradation rate. This phenomenon was also referred to in the study conducted by Mustafa at least for ATZ [41]. However, producing $OH^{\bullet}$, $O^{\bullet}$, $O_2^{\bullet-}$, and $O_3^{\bullet-}$ as super oxidizing agents throughout other equations in the low ozonation helps OCPs destruction dramatically. Apart from this, the ozone concentration into the reaction medium slightly dropped during reaction time from the beginning up to the end of the experiments for the levels of 0.1–0.6 which indicates that OCPs are extremely reactive in the scope of ozonation. Additionally, this observation could be due to the acidic fragments generated in intermediates production via H^+ produced in the medium throughout Eqs. (8) and (16). Nevertheless, it is predicted that the Eq. (16) developed toward H_2O_2 generation in the superior concentration of O_3 since it is just a reversible reaction.

3.2.2. *Effect of pH*

To find out the influence of pH on OCPs reduction and residual concentrations in the ozonation reinforced by solar UV, the pH variable was ranged as 5.5, 7, 8, 9, 10, and 11. By doing these experimental runs, the findings were obtained as Fig. 7b shows. It was revealed that pH range of neutral to alkaline was effective to operate ozone for maximum OCPs degradation than acidic and highly alkaline conditions. The findings were in line with the results of the investigation carried out by Grčić et al. [44] and his observations on ATZ removal by UV/O_3.

Overall, ozone can decompose organic pollutants at neutral to acidic pH by a direct electrophilic attack while it happens indirectly at alkaline pH by generating radical agents with higher oxidizing potential than O_3 [45]. For this possible reason, here, neutral to alkaline pH showed further efficiency to degrade OCPs. However, due to some disturbing factors, at the immense alkaline pH, the degradation efficiency loses widely. One probable factor could be the increasing carbonate concentration in this pH domain, since it is a potent $OH^{\bullet}$ scavenger. Furthermore, hydroxyl radicals could recombine into H_2O_2, with an excessive amount of H_2O_2 which acts like radical scavenger [46]. Apart from this, OH^- and HO_2^- ions present in the solution play a harmful and destructive role with Eqs. (6) and (7) to harness O_3 and its influence on OCPs directly. The latest reason was proved by monitoring dissolved oxygen in the reaction medium (Fig. 7 provides a complete description of the pertaining data). Apart from oxygen generation pathway through Eq. (12), Eq. (17) suggested by Beltran states that H_2O_2 and O_2 are two products of ozone decomposition under UV radiation [44]. Thus, it could be deducted that by destructing ozone and its transformation to dissolved oxygen, the OCPs degradation decreases due to the lack of the radicals as a result of ozone diminishing into the solution.

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \quad (17)$$

3.2.3. *Kinetic study*

In the current study, the pseudo-first-order kinetic model was adopted to predict the experimental results and then

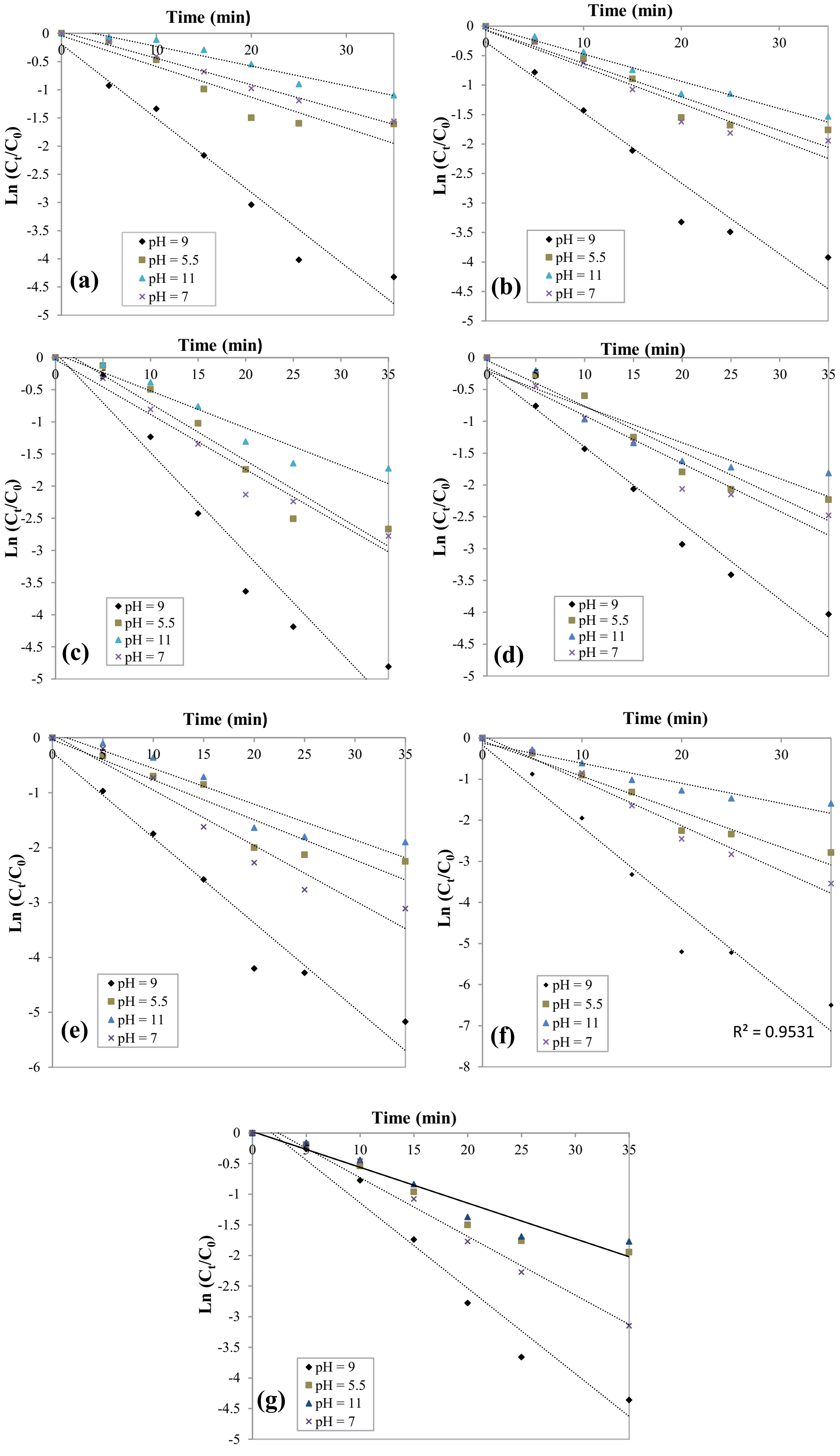


Fig. 8. Kinetic plots and contact time effect on residual amounts of OCPs at miscellaneous pH values throughout UV/O_3; (a) alachlor (ALC) = 30 µg/L, (b) atrazine (ATZ) = 34 µg/L, (c) α (±)-BHC = 27 µg/L, (d) methoxychlor = 36 µg/L, (e) heptachlor = 17.5 µg/L, (f) dieldrin = 20 µg/L, and (g) α-chlordane = 28.4 µg/L; temperature = 20°C; ozone dosage = 0.4 mg/L; TOC = 0.03 mg/L; DOC = 0.025 mg/L.

to implement them throughout a full-scale landscape plant. To this end, Eq. (18) was utilized to draw reaction kinetic plots, as well as the reaction rates constants [15,47,48]:

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \tag{18}$$

where C_0 and C_t are the initial concentration of micropollutant (μg/L) and the concentration of micropollutant at time t (μg/L), respectively, t is reaction time (min), and k is the reaction rate constant (min^{-1}).

The pseudo-first-order reaction kinetic rates were obtained by plotting $\ln(C_t/C_0)$ vs. time (35 min) for various pH values. Eventually, the results of the applied model disclosed that reaction kinetics was fitted well with R^2 more than 0.9 for all OCPs except four cases as Table 5 represents. The reaction kinetic constants (k) in pH values of 7 and 9.5 were more than other ranges for all OCPs. Altogether, based on Fig. 8 and the reaction constants are given in Table 5, it was deducted that the progress of pH at the alkaline area improves the pseudo-first-order constants. Additionally, the kinetic model which was adopted in this study indicates that the reaction rates will be restricted by the initial pH value and the concentration of $OH^{\bullet}$ as a consequence of that [47]. Furthermore, by raising reaction time to 35 min, the residues of OCPs in the reaction medium dropped, but this downward trend was relatively low between 25 and 35 min, therefore, it is anticipated that the reaction times more than this time scope will not be economical and efficient. This finding was also proved by Martinez through an investigation carried out on the removal of herbicides mecoprop for the concentration of 0.1–1 μg/L [13].

After doing the experiments of both pilot-scale units of adsorption and UV/O_3 as a single hybrid treatment, the reduction efficiency for OCPs was calculated and it is represented in Table 6. With this, the applied removal strategy has a yield of more than 85% and even 90% (for ALC, methoxychlor, and dieldrin) in degrading OCPs from real and synthetic solutions.

3.2.4. Intermediates analysis

By analyzing the oxidation effluent, some dominant organic matters were detected by gas chromatography-tandem mass spectrometry (GC-MS/MS) detector qualitatively and the intermediates of the OCPs degraded by oxidation condition and its original pollutant. These compounds are listed in Table 7. ALC's intermediates detected in this study were similar to Qiang's observations and Vanraes' findings [18,49]. Likewise, before the present study, Zaleska et al. [50] found that some chlorobenzaldhyds could be by-products of methoxychlor degradation under an oxidation environment, and the identified compounds in this study were similar to them. However, all of these substances disappeared from the final effluent in the optimized UV/O_3. Therefore, from the risk factor assessment aspects, the potential of these matters to form emerging by-products was minimized in the optimized ozonation under solar UV as were non-detectable in the final effluent. Furthermore, the detected intermediates in the samples could be due to the high initial concentration of its original OCPs.

4. Conclusions and outlook

The removal of seven OCPs from the real samples taken from groundwater wells of Golestan province in the north of Iran was studied through a pilot-scale citrus coal adsorption unit followed by O_3 unit assisted by solar UV.

To sum up, the studied citrus coal adsorption-UV/O_3 revealed that it can remove the OCPs from a water medium higher than 86% with residues less than 1 μg/L and even 0.05 μg/L in some cases. Because of the generation of a large amount of citrus wastes (46,000 ton/y) in the north of Iran and the abundance of solar energy especially solar UV in the Middle East, this hybrid approach to treat groundwater contaminated with agricultural OCPs as a type of EDCs could be a proper alternative for conventional and current removal strategies to provide safety and treat groundwater in this region with regard to the volume of the OCPs consumed by livestock and grazing sector (5,500 L/y), farmlands (4,800 L/y), and horticulture section (21,000 L/y) to reach sustainable development. There is a need for

Table 6
Removal rates percentage of OCPs by citrus coal and UV/O_3

OCPs	Citrus coal (%)	UV/O_3 (%)	Overall (%)
Alachlor (ALC)	76.2	98	91
α (±)-BHC	79.4	99.18	87.7
Atrazine (ATZ)	75.12	98.2	85
Methoxychlor	75.83	98.3	92.7
Heptachlor	79.92	99.37	86.8
Dieldrin	78	99.85	92.5
α-chlordane	95	98.72	82

Table 5
Reaction rate constants for OCPs removal at miscellaneous pH values

pH	Alachlor (ALC)		α (±)-BHC		Atrazine (ATZ)		Methoxychlor		Heptachlor		Dieldrin		α-chlordane	
	K (min^{-1})	R^2	K (min^{-1})	R^2	K (min^{-1})	R^2	K (min^{-1})	R^2	K (min^{-1})	R^2	K (min^{-1})	R^2	K (min^{-1})	R^2
9	0.123	0.96	0.137	0.95	0.112	0.96	0.115	0.97	0.147	0.95	0.1857	0.96	0.124	0.97
5.5	0.046	0.88	0.0762	0.94	0.0502	0.91	0.063	0.93	0.0643	0.89	0.0796	0.95	0.0556	0.95
11	0.0314	0.94	0.0493	0.93	0.0437	0.93	0.052	0.86	0.0543	0.89	0.0454	0.93	0.0505	0.93
7	0.044	0.99	0.0793	0.96	0.0554	0.94	0.070	0.94	0.0888	0.95	0.101	0.97	0.0899	0.98

Table 7
Intermediates detected from non-optimized UV/O_3 effluent and its origin OCPs

	Origin OCP	Intermediate	Molecular formula	RT* (min)	Similarity (%)
1	Alachlor (ALC)	1-(4-methoxyphenyl)-3-(4-morpholinyl)-1-propanone hydrochloride	$C_{14}H_{20}ClNO_3$	36.7	88
		methyl (4R)-5-(4-chlorophenyl)-4-(methylamino)-5-oxopentanoate	$C_{13}H_{16}ClNO_3$	35.8	93
		2-[(3-chloro-4-methoxybenzoyl)amino]-4-methylpentanoic acid	$C_{14}H_{18}ClNO_4$	32.9	76
					91
2	Atrazine (ATZ)	Isopropylamine	$–NHCH(CH_3)_2$	28.38	73
		Acetanilide	$–NHCOCH_3$	18.24	82
		Azanide	$–NH_2$	4.92	75
				12.18	
3	Methoxychlor	4-Chlorobenzophenone	$C_{13}H_9ClO$	10.04	87
		4-Chlorobenzaldehyde	C_7H_5ClO	5.92	71

further research to research on evaluating other natural adsorbents like rice, wheat straws, and husks due to the abundance of these products in this area in the agriculture season. Likewise, investigating the disturbing function of anions and cations in adsorption and oxidation mechanisms bears significance since these ingredients are ubiquitous in each aquifer.

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