

## Ionic solvent-mediated electrolytic decontamination of pesticide-containing wastewater

John A. O. Oyekunle<sup>a,\*</sup>, Solomon S. Durodola <sup>a</sup>, Oluwakemi O. Tovide<sup>b</sup>, Allen A. Olorunkosebi<sup>c</sup>, Ebuloluwa O. Olufisayo<sup>a</sup>, Abolanle S. Adekunle<sup>a</sup> and Aderemi O. Ogunfowokan<sup>a</sup>

<sup>a</sup> Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

<sup>b</sup> Centre for Environmental Studies and Sustainable Development, Lagos State University, Ojo, Lagos

<sup>c</sup> Department of Physics and Engineering Physics, Obafemi Awolowo University, Ile-Ife, Nigeria

\*Corresponding author. E-mail: oyekunle@oauife.edu.ng

 SSD, 0000-0003-0097-1272

### ABSTRACT

This study investigated the performance of different ionic solvents (NaCl, KNO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub>) in mediating electrolytic decontamination of pesticide-containing wastewaters and established the most suitable ionic solvent that can satisfactorily achieve decontamination of such wastewaters. These were done to find a water-purification technique suitable for the removal of recalcitrant and hazardous trace organic substances from wastewater. Organochlorine pesticide (OCP)-containing wastewaters were constituted according to prescribed modalities. It was observed that complete decontamination of the wastewater was achieved within 2 h of using Na<sub>2</sub>SO<sub>4</sub>. The study concluded that the 1.0 M of Na<sub>2</sub>SO<sub>4</sub> solution-mediated electrolytic process was most efficient in decontaminating OCP-containing wastewater.

**Key words:** decontamination, electrolytic process, ionic solvents, pesticides, wastewater

### HIGHLIGHTS

- Several investigations on wastewater treatment using an electrolytic method for the removal of contaminants have been carried out, but there is paucity of information on the comparative efficiencies of ionic solvents of different strengths to affect decontamination of pesticide-containing wastewater.
- Degradation of organochlorine pesticides (OCPs).
- Effects of ionic solution on decontamination of waste water.

### GRAPHICAL ABSTRACT



This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (<http://creativecommons.org/licenses/by/4.0/>).

## 1. INTRODUCTION

The world population has continuously been on the increase. For example, the world witnessed a population increase from 1.5 to 6.9 billion between 1900 and 2000 (Saleh *et al.* 2020). This increase has led to a corresponding demand for improved crop yields and general healthy living conditions which have come under pressure as a result of a meteoric rise in population figures. Hence, there is widespread use of thousands of tons of pesticides to curb the menace of domestic, industrial, and agricultural pests throughout the world. Without a doubt, such diverse applications of pesticides have generated large volumes of contaminated waste water, whose direct disposal into natural channels causes their accumulation in various environmental compartments (Cabrera 2017; Kim *et al.* 2017; Ouni *et al.* 2021). To a large extent, modern agricultural practices rely on pesticides to increase crop yield to an economically profitable level (Kılıç *et al.* 2020).

Pesticides are chemical substances used for destroying, preventing, mitigating, and repelling any pest; they can also be used as a plant regulator, desiccant, or defoliant (Ouni *et al.* 2021). According to the Food and Agricultural Organization of the United Nations (FAO), more than 500,000 tonnes of obsolete pesticides are stored worldwide (FAO Pesticide Disposal Series 2011). Agriculture can therefore be considered to be the greatest contributor to both surface and groundwater contamination by pesticides.

In addition to pesticides, pharmaceuticals (hormones, antibiotics, and others), cosmetics, and synthetic dyes are also emerging contaminants of concern in many areas around the world (Gomes *et al.* 2018). Pesticides can pose a threat when they leach into groundwater and enter into drinking water supplies. Ingestion through prolonged reliance on a source of drinking water contaminated with pesticides can be a major cause of a myriad of health challenges such as birth defects, respiratory failure, biochemical instability, kidney failure, the onset of diabetes, hepatic problems, and cardiac disorder with symptoms that may include nausea, vomiting, tremors, and hypotension (Jayaraj *et al.* 2016; Bakhsh *et al.* 2021; Masibi *et al.* 2021). The frequency of symptoms has been identified to be higher among planters, weeders, and harvesters (Mergia *et al.* 2021).

Several techniques such as biological processes, filtration, coagulation, adsorption, membrane processes, chemical oxidation, and so on have been employed in the treatment of contaminated wastewater (Rodríguez-Rodríguez *et al.* 2013; Castro-Gutiérrez *et al.* 2019; Saleh *et al.* 2020) but none of these has been found to eliminate the pollutants (Ouni *et al.* 2021). For instance, chemical oxidation is unable to mineralize the persistent organic pollutants (Rodríguez-Rodríguez *et al.* 2013; Saleh *et al.* 2020), coupled with the slow reaction rates and the problem of disposal of sludge, biological treatment lacks efficacy in the presence of non-biodegradable and toxic pollutants (Saleh *et al.* 2020). To overcome these drawbacks, advanced oxidation methods have been developed allowing the destruction of organic pollutants (Moreira *et al.* 2017; Ribeiro *et al.* 2019; Hoang & Holze 2021). Among these methods, electrochemical oxidation has shown a significant efficiency in the destruction of organic pollutants (Moreira *et al.* 2017; Hoang & Holze 2021). Thus, there is a need to develop methods that could satisfactorily decontaminate wastewater to safe levels.

Some investigations on wastewater treatment using an electrolytic method for the removal of contaminants have been carried out (Rodrigo *et al.* 2014; Sirés *et al.* 2014; Martínez-Huitle *et al.* 2015; Min *et al.* 2018; Khan *et al.* 2020; Lourinho & Brito 2021; Santos *et al.* 2022) but there is a need to further investigate the comparative efficiencies of ionic solvents of different strengths to effect decontamination of pesticide-containing wastewater. Thus, the present study aimed to investigate the performance of various ionic solvents in aiding the electrolytic degradation of some organochlorine pesticides (OCPs) in synthetic wastewater to safe levels.

## 2. MATERIALS AND METHODOLOGY

### 2.1. Reagents used and their sources

All chemical reagents used were of analytical grade and they include dichloromethane (DCM) (GFS Chemicals, Coulombus), potassium nitrate (Laboratory Tech Chemicals, Poole England), anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) (GFS Chemicals, Coulombus), n-Hexane (GFS Chemicals, Coulombus), sodium chloride (Aldrich Chemical Company, USA), silica gel (Oxford Laboratory Reagents, Mumbai, India), glass wool (Chemei Laboratory, Mumbai, India), and distilled water (from the preparatory room of Department of Chemistry, Obafemi Awolowo University, Ile-Ife).

### 2.2. Decontamination of apparatus

All glassware used (conical flask, beaker, measuring cylinder, volumetric flask, watch glass, and sample bottles) was washed thoroughly with liquid detergents using a brush and rinsed with tap water until no foam was

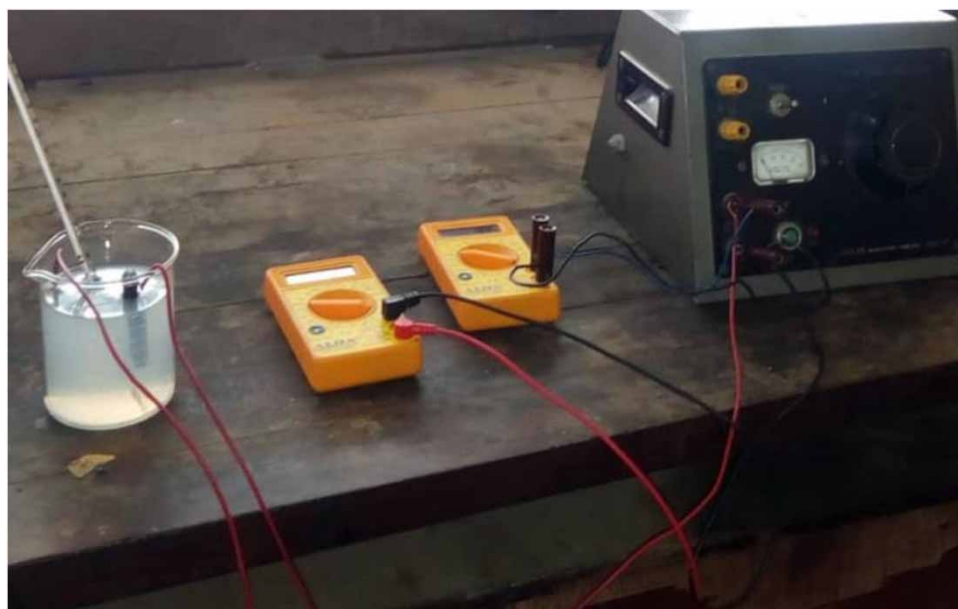
observed. Thereafter, they were rinsed thoroughly first with distilled water followed by analytical grade acetone, and then air dried. The glassware used during the clean-up stage was pre-extracted with DCM to remove organic grits that could interfere with results.

### 2.3. Preparation of solutions and wastewater

Standard solutions (0.3, 0.5, 1.0 M) of NaCl, KNO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub> were prepared by serial dilution of 1.0 M of each of the salt solutions. Also, for the preparation of synthetic wastewaters, three commercially available pesticides, namely: Paraforce (Paraquat dichloride), Weed off (paraquat isopropyl amine), and Perfect Killer (Chlorpyrifos) were mixed in a ratio of 5:5:20 mL, respectively. These pesticides have been reported to contain some levels of OCPs. The mixture was made up to 2.0 L. From this wastewater, 10 mL was collected and poured into a 250-mL volumetric flask. Thereafter, 40 mL of a standard solution of a given ionic solvent was added and made up to the mark with distilled water. The samples were prepared with the intention of being able to retrieve detectable concentrations without approaching the detection limits. As a control, 10 mL of the pesticide solution was also added to an equal volume of distilled water which had been spiked with a corresponding amount of ionic solvent.

### 2.4. Decontamination procedure

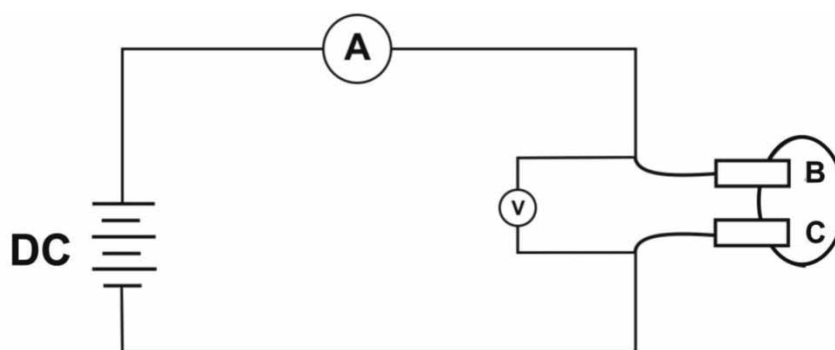
The initial concentration of the pesticides in the uncontaminated wastewater (as contained in the control sample) was determined by liquid–liquid extraction using DCM as the extraction solvent in a separating funnel. The degradation of pesticide metabolites contained in the simulated wastewater was performed in an electrolytic cell. The electrolytic unit, in parallel connection, consisted of an electrolytic cell, a D.C. power source (Analab), Digital multimeter (MASTECH MY 64) for measuring current, graphite electrodes, and pesticide solutions that have been spiked with 40 mL of ionic solutions of various strengths. The graphite electrodes were separated by a space of  $\approx 6$  cm and dipped in the simulated wastewater. The electrolytic decontamination process which lasted 2 h for each process was maintained at an average voltage of  $3.69 \pm 0.44$  V and current of  $0.17 \pm 0.03$  A. The control sample was not subjected to electrolytic decontamination. Set-up of the electrolytic decontamination process is shown in Figure 1, while Figure 2 depicts circuit diagram of the electrolytic set-up.



**Figure 1** | Set-up of the electrolytic decontamination process.

### 2.5. Extraction and clean-up

The wastewater that had been electrolytically decontaminated was subjected to liquid–liquid extraction and the solvent in the extract was allowed to evaporate until the volume remained about 2 mL. The control sample was similarly treated. The clean-up procedure which refers to an extraction in which impurities are extracted from the



A = Ammeter; B = Anode; C = Cathode; DC = Direct current source; V = Voltmeter

**Figure 2** | Circuit diagram of the electrolytic set-up.

solvent containing the desired compound was carried out in solid phase extraction (SPE) columns with adsorbents that have different polarities. For each of the uncontaminated and decontaminated extracts, a silica gel SPE column plugged with glass wool was prepared by packing 10 g of silica gel in a glass column with anhydrous sodium sulfate packed on top of the adsorbent in the glass column. The packed column was conditioned with 20 mL of DCM. The extract was applied to the conditioned column and the flow-through was collected in a 50 mL amber-colored glass vial (Bempah & Donkor 2011). The vial was left open for the cleaned-up sample to fully dry under nitrogen. The air-dried sample was reconstituted with 1 mL of n-hexane in readiness for GC-MS analysis.

## 2.6. Instrumental analysis

The determination of OCPs in the extracts was performed by a gas chromatograph (Agilent Model 7890B) coupled with a Pegasus 4D Mass Spectrometer (GC-MS) at the Nigerian Institute of Oceanography and Marine Research, Victoria Island, Lagos, Nigeria. The features and operating conditions were as follows: a GC column Restek Rtx-CL pesticides; two capillary columns of 30 m  $\times$  0.25 mm id  $\times$  0.25  $\mu$ m film thickness at 340  $^{\circ}$ C. The GC operating conditions were splitless injection, injector temperature of 250  $^{\circ}$ C, helium carrier gas (99.99% purity) at a flow rate of 0.9 mL min<sup>-1</sup> with a column head pressure of 7.4 psi; oven temperature was kept at 70  $^{\circ}$ C for 2 min and then programmed to rise to 130  $^{\circ}$ C at 25  $^{\circ}$ C min<sup>-1</sup>, afterward rise to 220  $^{\circ}$ C at 2  $^{\circ}$ C min<sup>-1</sup>, and then finally set to 280  $^{\circ}$ C at 10  $^{\circ}$ C min<sup>-1</sup>. This temperature was maintained for 4.6 min. The sample (1  $\mu$ L) was injected in splitless modes. The mass spectrometer was set as follows: electron impact ionization mode with 70 eV of electron energy, scan mass range 100–400 at 0.62 s/cycle, ion source temperature of 230  $^{\circ}$ C, MS quad temperature 150  $^{\circ}$ C, EM voltage 1,450, and solvent delay 4 min. The MS system was routinely operated in selective ion monitoring (SIM) mode with electron ionization. The OCP compounds were identified based on a comparison of the retention times of peaks with those of standard OCP compounds. Thereafter, the internal standard method was used for OCP quantification. The chromatogram of the analyzed OCPs can be found in Supplementary material S1.

## 3. RESULTS AND DISCUSSION

### 3.1. Levels ( $\mu$ g/mL) of OCPs in wastewater

The freshly prepared wastewater containing various OCPs indicated that out of the 17 OCPs intended for analysis,  $\alpha$ -BHC, Endosulfan I, p,p'-DDT, and Endosulfan sulfate were below the detection limit (BDL) or absent. On the other hand, the remaining 13 OCP congeners were detected at levels ranging from 1.35  $\mu$ g/mL of  $\delta$ -BHC to 35.92  $\mu$ g/mL of Endrin as shown in Table 1.

### 3.2. Levels ( $\mu$ g/mL) of OCPs remaining in the decontaminated wastewater

Results obtained indicated that out of the 13 OCP congeners in the various solutions, the decontamination process followed the pattern: P (13 OCPs, 100%) > H, J, L (12 OCPs, 92.31%) > I, O (11 OCPs, 84.62%) > K,

**Table 1** | Concentrations ( $\mu\text{g/g}$ ) of the remaining OCPs in wastewater samples

OCP congeners	R	NaCl solutions			KNO <sub>3</sub> solutions			Na <sub>2</sub> SO <sub>4</sub> solutions		
		H 0.3 M	I 0.5 M	J 1.0 M	K 0.3 M	L 0.5 M	M 1.0 M	N 0.3 M	O 0.5 M	P 1.0 M
$\alpha$ -BHC	–	–	–	–	–	–	–	–	–	–
$\beta$ -BHC	6.53	–	–	–	–	–	–	–	–	–
Heptachlor	3.56	–	–	–	–	–	–	–	–	–
Aldrin	4.06	–	–	–	–	–	–	–	–	–
$\gamma$ -BHC	4.07	–	–	–	–	–	1.52	–	3.16	–
$\delta$ -BHC	1.35	–	–	–	1.16	–	–	–	–	–
Heptachlor Epoxide	7.54	–	–	–	–	–	–	–	5.86	–
Endosulfan I	12.35	–	–	–	–	–	3.53	9.50	–	–
p,p'-DDE	9.03	–	–	–	–	–	–	–	–	–
Dieldrin	3.29	–	–	–	–	–	1.43	1.13	–	–
Endrin	35.92	2.60	–	8.06	8.75	9.97	9.23	1.13	–	–
p,p'-DDD	5.31	–	–	–	–	–	2.22	–	–	–
Endosulfan II	–	–	–	–	–	–	–	–	–	–
p,p'-DDT	–	–	–	–	–	–	–	–	–	–
Endrin Aldehyde	6.92	–	4.05	–	–	–	–	–	–	–
Endosulfan sulfate	–	–	–	–	–	–	–	–	–	–
Methoxychlor	7.06	–	1.24	–	4.59	–	1.37	–	–	–
Total remaining	106.99	2.60	5.29	8.06	14.50	9.97	19.30	11.76	9.06	0.00
% Decontamination	–	97.57	95.06	92.47	86.45	90.68	81.96	89.01	91.53	100

R refers to the values of OCPs in untreated wastewater.

N (10 OCPs, 76.92%) > M (7 OCPs, 53.85%). Evaluated in terms of OCPs decontaminated, the percentage efficiency of the solution at effecting decontamination occurred in the order P (100%) > H (97.57%) > I (95.06%) > J (92.47%) > O (91.53%) > L (90.68%) > N (89.01%) > K (86.45%) > M (81.96%). Thus, solution P demonstrated the highest decontamination efficiency and should be considered whenever electrolytic decontamination of OCP-containing wastewater is desirable.

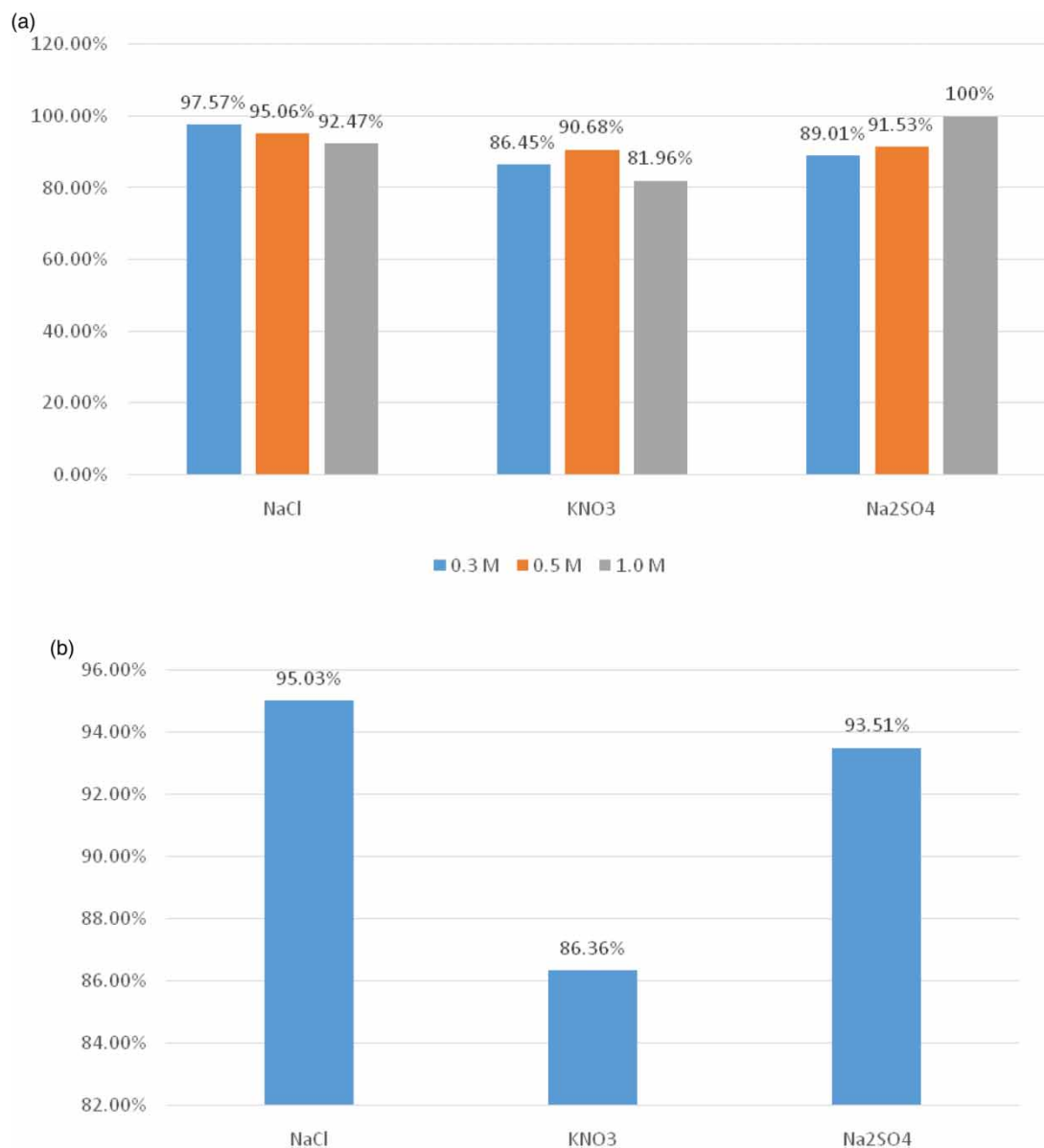
The percentage average performance of the solution (Figure 3(a) and 3(b)) indicated that the pooled efficiency was such that NaCl (95.03%) > Na<sub>2</sub>SO<sub>4</sub> (93.51%) > KNO<sub>3</sub> (86.36%). In addition to the roles played by Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions in achieving the degradation process, Na<sup>+</sup> probably had a more significant role to play as well. This role might be related to making the Cl<sup>-</sup> atoms on the pesticide molecules more amenable to conductivity to the extent that they are readily discharged during electrolysis. This is in agreement with the observation that when chlorides are used as supporting electrolytes, the Cl-mediated oxidation will be favored (Sirés *et al.* 2014; Martínez-Huitle *et al.* 2015), hence NaCl had the highest percentage average performance. The mechanism by which the electrolytic decontamination process occurred could be due to the reduction process of the chlorine atom(s) in the OCP. Ribeiro *et al.* (2013) proposed electrolytic reduction of endosulfan, the mechanism of which is shown in Figure 4. Tefera *et al.* (2021) reported that this reduction of endosulfan is an irreversible process.

### 3.3. Degradation effects on classes of OCPs

The OCP congeners present in the synthetic wastewater are classified into dichlorodiphenylmethane (DDT), cyclodienes, and chlorinated benzenes/cyclohexanes. The degree of their decontamination is discussed in the following.

A total of 14.34  $\mu\text{g/mL}$  of DDTs was present in the synthetic wastewater, both NaCl and Na<sub>2</sub>SO<sub>4</sub> caused a significant degradation process in the decontamination of OCP-containing wastewater except 1.0 M of KNO<sub>3</sub> that had 2.22  $\mu\text{g/mL}$  of DDTs present in the synthetic wastewater.

A total of 80.70  $\mu\text{g/mL}$  of cyclodienes was present in the synthetic wastewater; NaCl with molar concentrations of 0.3, 0.5, and 1.0 caused a significant degradation process in the decontamination of OCP-containing



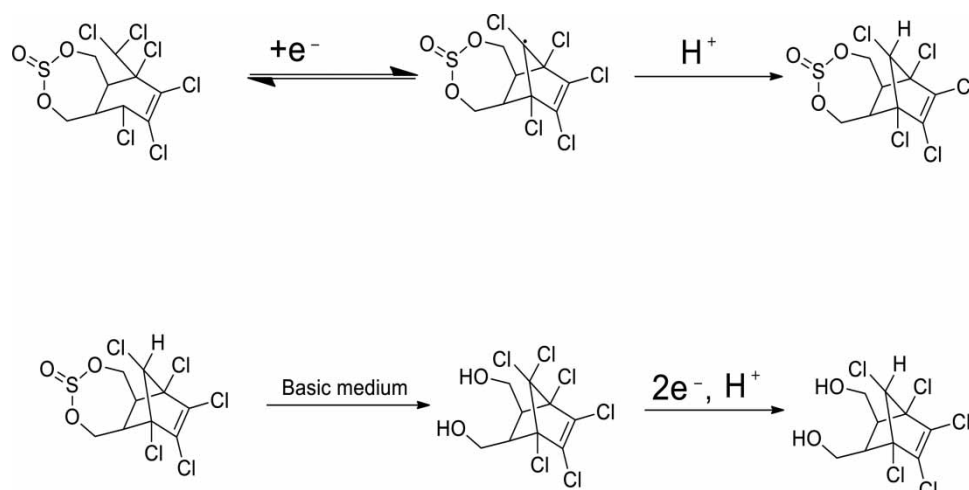
**Figure 3** | (a) Percentage removal efficiency of the OCPs in the ionic solvents. (b) Average percentage removal efficiency of the OCPs in the ionic solvents.

wastewater, reducing it to 2.60, 5.29, and 8.06  $\mu\text{g/mL}$ , respectively. In the case of KNO<sub>3</sub> with molar concentrations of 0.3, 0.5, and 1.0, there was a reduction of the contaminants to 13.34, 9.97, and 15.56  $\mu\text{g/mL}$ , respectively. Furthermore, 0.3 and 0.5 M of Na<sub>2</sub>SO<sub>4</sub> reduced the concentration of the OCPs in the wastewater to 11.76 and 5.86  $\mu\text{g/mL}$ , respectively, while 1.0 M of the Na<sub>2</sub>SO<sub>4</sub> caused a complete reduction of all the OCPs metabolites that were originally present in the wastewater.

For chlorinated benzenes/cyclohexanes, a total of 11.95  $\mu\text{g/mL}$  was present in the synthetic wastewater, all the NaCl solutions, 0.5 M of KNO<sub>3</sub>, 0.3 and 1.0 M of Na<sub>2</sub>SO<sub>4</sub> caused a significant degradation process in the decontamination of OCP-containing wastewater. However, 0.1 and 0.3 M of KNO<sub>3</sub>, and 0.5 M of Na<sub>2</sub>SO<sub>4</sub> left 1.16, 1.52, and 3.16  $\mu\text{g/mL}$ , respectively, of chlorinated benzenes/cyclohexanes undegraded from the synthetic wastewaters as can be seen in Table 2.

### 3.4. Effect of solution strength

From Figure 3(a), it can be deduced that as the concentration of NaCl increased, the decontamination process decreased, whereas for Na<sub>2</sub>SO<sub>4</sub>, as the concentration of the ionic solvent increased, the decontamination process



**Figure 4** | Mechanism of Endosulfan reduction in acidic and basic medium (Ribeiro *et al.* 2013).

**Table 2** | Degradation effects on OCP congeners

OCP congeners	R	NaCl solutions (M)			KNO <sub>3</sub> solutions (M)			Na <sub>2</sub> SO <sub>4</sub> solutions (M)		
		0.3	0.5	1.0	0.3	0.5	1.0	0.3	0.5	1.0
DDTs	p,p'-DDE	9.03	-	-	-	-	-	-	-	-
	p,p'-DDD	5.31	-	-	-	-	2.22	-	-	-
	p,p'-DDE	-	-	-	-	-	-	-	-	-
	<b>Total</b>	<b>14.34</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>2.22</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>
Cyclodienes	Heptachlor	3.56	-	-	-	-	-	-	-	-
	Aldrin	4.06	-	-	-	-	-	-	-	-
	Heptachlor Epoxide	7.54	-	-	-	-	-	-	5.86	-
	Endosulfan I	12.35	-	-	-	-	-	3.53	9.50	-
	Dieldrin	3.29	-	-	-	-	-	1.43	1.13	-
	Endrin	35.92	2.60	-	8.06	8.75	9.97	9.23	1.13	-
	Endosulfan II	-	-	-	-	-	-	-	-	-
	Endrin Aldehyde	6.92	-	4.05	-	-	-	-	-	-
	Endosulfan sulfate	-	-	-	-	-	-	-	-	-
	Methoxychlor	7.06	-	1.24	-	4.59	-	1.37	-	-
	<b>Total</b>	<b>80.70</b>	<b>2.60</b>	<b>5.29</b>	<b>8.06</b>	<b>13.34</b>	<b>9.97</b>	<b>15.56</b>	<b>11.76</b>	<b>5.86</b>
Chlorinated benzenes/ Cyclohexanes	α-BHC	-	-	-	-	-	-	-	-	-
	β-BHC	6.53	-	-	-	-	-	-	-	-
	γ-BHC	4.07	-	-	-	-	-	1.52	-	3.16
	δ-BHC	1.35	-	-	-	1.16	-	-	-	-
	<b>Total</b>	<b>11.95</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>1.16</b>	<b>0.00</b>	<b>1.52</b>	<b>0.00</b>	<b>3.16</b>

R is the amount of pesticides in raw water/synthetic wastewater.

also increased. The concentration of NaCl has an inverse relation with its decontamination process, while that of Na<sub>2</sub>SO<sub>4</sub> has a direct relation with its decontamination process. Nevertheless, there was no regular pattern observed for the KNO<sub>3</sub> solution-mediated decontamination process.

### 3.5. Solution strength efficiency

The three sets of freshly prepared salt solutions (NaCl, KNO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub>) used to mediate the decontamination process of wastewater containing various OCPs were grouped into concentrations of 0.3, 0.5, and 1.0 M, respectively.

#### 3.5.1. Effects of NaCl in electrolytic decontamination of wastewater

It was observed that solution H (0.3 M NaCl) caused the decontamination of 12 out of the 13 OCPs (Supplementary material S2), in which 2.60 µg/mL (7.24%) of Endrin remained uncontaminated. The solution I (0.5 M NaCl)

caused the decontamination of 11 out of the 13 OCPs, in which 4.05  $\mu\text{g}/\text{mL}$  (58.53%) of Endrin Aldehyde and 1.24  $\mu\text{g}/\text{mL}$  (17.56%) of Methoxychlor remained uncontaminated. Solution J (1.0 M NaCl) caused the decontamination of 12 out of 13 OCPs, in which 8.06  $\mu\text{g}/\text{mL}$  (22.45%) of Endrin remained uncontaminated. Therefore, aside from the role played by  $\text{Cl}^-$  atom in effecting the degradation process,  $\text{Na}^+$  probably had a significant role to play in the process.

### 3.5.2. Effects of $\text{KNO}_3$ in electrolytic decontamination of wastewater

It was observed that solution K (0.3 M  $\text{KNO}_3$ ) caused the decontamination of 10 out of the 13 OCPs (Supplementary material S3), in which 1.16  $\mu\text{g}/\text{mL}$  (85.93%) of  $\delta$ -BHC, 8.75  $\mu\text{g}/\text{mL}$  (24.36%) of Endrin, and 4.59  $\mu\text{g}/\text{mL}$  (65.01%) of Methoxychlor remained undecontaminated. Solution L (0.5 M  $\text{KNO}_3$ ) caused the decontamination of 12 out of the 13 OCPs, in which 9.97  $\mu\text{g}/\text{mL}$  (27.76%) of Endrin remained uncontaminated. Solution M (1.0 M  $\text{KNO}_3$ ) caused the decontamination of only 8 out of the 13 OCPs, in which 1.52  $\mu\text{g}/\text{mL}$  (37.35%) of  $\gamma$ -BHC, 3.53  $\mu\text{g}/\text{mL}$  (28.58%) of Endosulfan I, 1.43  $\mu\text{g}/\text{mL}$  (43.47%) of Dieldrin, 9.23  $\mu\text{g}/\text{mL}$  (25.70%) of Endrin, 2.22  $\mu\text{g}/\text{mL}$  (41.81%) of p,p'-DDD, 1.37  $\mu\text{g}/\text{mL}$  (19.41%) of methoxychlor remained undecontaminated. In the previous studies conducted in respect of OCPs removal from wastewater, it was reported that more than 82 and 80% of OCPs were eliminated from the water samples by Sahmarani *et al.* (2021) and Suo *et al.* (2019), respectively. The present study even recorded better performance in the removal of up to 12 out of 13 (92.3%) OCPs from synthetic wastewater.

Therefore, aside from the role played by  $\text{NO}_3^-$  ions in achieving the degradation process,  $\text{K}^+$  probably had little or no significant role to play in the process.

### 3.5.3. Effects of $\text{Na}_2\text{SO}_4$ in electrolytic decontamination of wastewater

It was observed that solution N (0.3 M  $\text{Na}_2\text{SO}_4$ ) caused the decontamination of 10 out of the 13 OCPs (Supplementary material S4), in which 9.50  $\mu\text{g}/\text{mL}$  (76.92%) of Endosulfan I, 1.13  $\mu\text{g}/\text{mL}$  (34.35%) of Dieldrin, and 1.13  $\mu\text{g}/\text{mL}$  (3.15%) of Endrin remained uncontaminated. Solution O (0.5 M  $\text{Na}_2\text{SO}_4$ ) caused the decontamination of 11 out of the 13 OCPs, in which 3.16  $\mu\text{g}/\text{mL}$  (77.64%) of  $\gamma$ -BHC and 5.86  $\mu\text{g}/\text{mL}$  (77.72%) of heptachlor epoxide remained uncontaminated. Solution P (1.0 M  $\text{Na}_2\text{SO}_4$ ) caused the decontamination of all 13 OCPs, in which none remained uncontaminated. Therefore, aside from the role played by  $\text{SO}_4^{2-}$  atom in achieving the degradation process,  $\text{Na}^+$  probably had a significant role to play in the process as well.

## 4. CONCLUSION

This study investigated the effects of various ionic solvents ( $\text{NaCl}$ ,  $\text{KNO}_3$ , and  $\text{Na}_2\text{SO}_4$ ) of different strengths (0.3, 0.5, and 1.0 M) in mediating electrolytic decontamination of pesticide-containing wastewater. It also established the most suitable ionic solvent that could be adopted to affect decontamination of OCP-containing wastewater. The electrolytic decontamination which spanned 2 h in each case indicated that the ranges of decontamination were: 92.47–97.57% OCPs for  $\text{NaCl}$ , 81.96–90.68%  $\text{KNO}_3$ , and 89.01–100%  $\text{Na}_2\text{SO}_4$ . It was also observed that as the concentrations of  $\text{NaCl}$  increased, the decontamination process decreased, whereas for  $\text{Na}_2\text{SO}_4$ , as the concentration increased, the decontamination process also increased. However, no regular pattern was observed for the performance of  $\text{KNO}_3$  to the ionic solvent strength. The study concluded that the  $\text{Na}_2\text{SO}_4$  solution-mediated electrolytic process was the most efficient at the decontamination of OCPs in wastewater. This study has implications in the area of treatment of industrial effluents containing recalcitrant pesticides such as OCPs. It also forms the basis for future researches that bother on wastewater pollutants evaluation and treatment.

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

## REFERENCES

- Bakhsh, H., Buledi, J. A., Khand, N. H., Junejo, B., Solangi, A. R., Mallah, A. & Sherazi, S. T. H. 2021 Nio nanostructures based functional none-enzymatic electrochemical sensor for ultrasensitive determination of endosulfan in vegetables. *Journal of Food Measurement Characterization* **15**, 2695–2704.



- Bempah, C. K. & Donkor, A. K. 2011 Pesticide residues in fruits at the market level in Accra Metropolis, Ghana, a preliminary study. *Environment and Monitoring Assessment* **175**, 551–561.
- Cabrera, L. Y. 2017 Pesticides: a case domain for environmental neuroethics. *Cambridge Quarterly of Healthcare Ethics* **26**(4), 602–615.
- Castro-Gutiérrez, V., Masís-Mora, M., Carazo-Rojas, E., Mora-López, M. & Rodríguez-Rodríguez, C. E. 2019 Fungal and bacterial co-bioaugmentation of a pesticide-degrading biomixture: pesticide removal and community structure variations during different treatments. *Water, Air, & Soil Pollution* **230**(10), 1–13.
- FAO Pesticide Disposal Series 2011 *Environmental Management Tool Kit for Obsolete Pesticides*, Vol. 4. FAO, Rome.
- Gomes, I. B., Simões, L. C. & Simões, M. 2018 The effects of emerging environmental contaminants on *Stenotrophomonas maltophilia* isolated from drinking water in planktonic and sessile states. *Sci. Total Environ.* **643**, 1348–1356.
- Hoang, N. T. & Holze, R. 2021 Degradation of pesticide Cartap in Padan 95SP by combined advanced oxidation and electro-Fenton process. *Journal of Solid State Electrochemistry* **25**(1), 73–84.
- Jayaraj, R., Megha, P. & Sreedev, P. 2016 Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdisciplinary Toxicology* **9**(3–4), 90.
- Khan, S. U., Khan, H., Anwar, S., Khan, S., Zaroni, M. V. B. & Hussain, S. 2020 Computational and statistical modeling for parameters optimization of electrochemical decontamination of synozol red dye wastewater. *Chemosphere* **253**, 126673.
- Kılıç, O., Boz, İ. & Eryılmaz, G. A. 2020 Comparison of conventional and good agricultural practices farms: a socio-economic and technical perspective. *Journal of Cleaner Production* **258**, 120666.
- Kim, K. H., Kabir, E. & Jahan, S. A. 2017 Exposure to pesticides and the associated human health effects. *Science of the Total Environment* **575**, 525–535.
- Lourinho, G. & Brito, P. S. D. 2021 Electrolytic treatment of swine wastewater: recent progress and challenges. *Waste and Biomass Valorization* **12**, 553–576.
- Martínez-Huitle, C. A., Rodrigo, M. A., Sirés, I. & Scialdone, O. 2015 Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: a critical review. *Chemical Reviews* **115**(24), 13362–13407.
- Masibi, K. K., Fayemi, O. E., Adekunle, A. S., Al-Mohaimed, A. M., Fahim, A. M., Mamba, B. B. & Ebenso, E. E. 2021 Electrochemical detection of endosulfan using an AONP-PANI-SWCNT modified glassy carbon electrode. *Materials* **14**, 723.
- Mergia, M. T., Weldemariam, E. D., Eklo, O. M. & Yimer, G. T. 2021 Small-scale farmer pesticide knowledge and practice and impacts on the environment and human health in Ethiopia. *Journal of Health Pollution* **11**(30), 210607.
- Min, X., Luo, X., Deng, F., Shao, P., Wu, X. & Dionysiou, D. D. 2018 Combination of multi-oxidation process and electrolysis for pretreatment of PCB industry wastewater and recovery of highly-purified copper. *Chemical Engineering Journal* **354**, 228–236.
- Moreira, F. C., Boaventura, R. A., Brillas, E. & Vilar, V. J. 2017 Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters. *Applied Catalysis B: Environmental* **202**, 217–261.
- Ouni, A., Rabaoui, N., Mechi, L., Enaceur, N., AlSukaibi, A. K., Azzam, E. M., Alenezi, K. M. & Moussaoui, Y. 2021 Removal of pesticide chlorobenzene by anodic degradation: variable effects and mechanism. *Journal of Saudi Chemical Society* **25**(10), 101326.
- Ribeiro, F., Oliveira, T., da Silva, F., Mendonca, G., Homem-de-Mello, P., Becker, H., Lima-Neto, A., Correia, P. & Freire, V. 2013 Sensitive voltammetric responses and mechanistic insights into the determination of residue levels of endosulfan in fresh foodstuffs and raw natural waters. *Microchemical Journal* **110**, 40–47.
- Ribeiro, A. R. L., Moreira, N. F., Puma, G. L. & Silva, A. M. 2019 Impact of water matrix on the removal of micropollutants by advanced oxidation technologies. *Chemical Engineering Journal* **363**, 155–173.
- Rodrigo, M. A., Oturan, N. & Oturan, M. A. 2014 Electrochemically assisted remediation of pesticides in soils and water: a review. *Chemical Reviews* **114**(17), 8720–8745.
- Rodríguez-Rodríguez, C. E., Castro-Gutiérrez, V., Chin-Pampillo, J. S. & Ruiz-Hidalgo, K. 2013 On-farm biopurification systems: role of white rot fungi in depuration of pesticide-containing wastewaters. *FEMS Microbiology Letters* **345**(1), 1–12.
- Sahmarani, R., Net, S., Chbib, C., Baroudi, M. & Ouddane, B. 2021 Elimination of organochlorine pesticides from water by a new activated carbon prepared from *Phoenix dactylifera* date stones. *Environmental Science and Pollution Research* **28**, 10140–10154.
- Saleh, I. A., Zouari, N. & Al-Ghouti, M. A. 2020 Removal of pesticides from water and wastewater: chemical, physical and biological treatment approaches. *Environmental Technology and Innovation* **19**, 101026.
- Santos, M. C., Antonin, V. S., Souza, F. M., Aveiro, L. R., Pinheiro, V. S., Gentil, T. C., Lima, T. S., Moura, J. P. C., Silva, C. R., Lucchetti, L. E. B., Codognoto, L., Robles, I. & Lanza, M. R. V. 2022 Decontamination of wastewater containing contaminants of emerging concern by electrooxidation and Fenton-based processes—A review on the relevance of materials and methods. *Chemosphere* **307**(Pt 3), 135763.
- Sirés, I., Brillas, E., Oturan, M. A., Rodrigo, M. A. & Panizza, M. 2014 Electrochemical advanced oxidation processes: today and tomorrow. A Review. *Environmental Science and Pollution Research* **21**(14), 8336–8367.
- Suo, F., Liu, X., Li, C., Yuan, M., Zhang, B., Wang, J. & Ji, M. 2019 Mesoporous activated carbon from starch for superior rapid pesticides removal. *International Journal of Biological Macromolecules* **121**, 806–813.
- Tefera, M., Tessema, M., Admassie, S. & Guadie, A. 2021 Electrochemical determination of endosulfan in vegetable samples using mercury film modified glassy carbon electrode. *Sensing and Bio-Sensing Research* **33**, 100431.

First received 28 July 2023; accepted in revised form 9 October 2023. Available online 27 October 2023