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Review

Endosulfan removal through bioremediation, photocatalytic degradation, adsorption and membrane separation processes: A review

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ABSTRACT

Endosulfan is a highly polluting and toxic pesticide which has been used in many areas globally to control pests in view to improve productivity. Concomitantly, endosulfan has also been associated with many cases of environmental pollution and various types of irreversible metabolic dysfunctions in living organisms both on lands and in waters. Subsequently, since over the last three decades, several endosulfan remediation methods have been studied and many are gradually bringing hope towards efficient clean-up. This article specifically reviews endosulfan degradation and endosulfan removal by discussing the recent findings reported and the trends observed in studies reporting bacterial and fungal bioremediation, photocatalytic degradation, adsorption and membrane separation processes. The salient observations from this review are: there are many bacterial species which degrade endosulfan isomers with relatively high efficiencies; many studies indicate the merits of plants in phytoextracting and accumulating endosulfan but the identification of endosulfan hyperaccumulators remains; photocatalytic systems involving one or two metals also bring about significant endosulfan degradation but issues related with variations in rates of reactions, catalyst deactivation due to fouling, intricacy of metal-based nanocatalyst structures and their complex fabrication methods and lack of control of morphology of the nanosized structures have to be addressed; and membrane retention systems specifically treating endosulfan-contaminated aqueous media are scanty and more analysis is also needed to optimize the shear force-membrane structural integrity-membrane stability rapport of the membranes being developed. In the end, a number of research and development avenues which need further attention and probing towards the development of suitable endosulfan-remediation routes are pointed out.

1. Introduction

Pesticides use has increased considerably during the last thirty years in agriculture control the proliferation and ill-effects of pests and thence aiding in improving yields. Subsequently, many pesticides and their degradation metabolites have persisted in different parts of the environment [1–6] and induced risks and impairment to human health, and to both aquatic and terrestrial flora and fauna at large [7]. Endosulfan is a widely used pesticide in agriculture for protecting crops [8] and is one of the most stable pesticides known and has been detected in the environment throughout the world [9,10]. Based on their findings of the atmospheric organochlorine pesticides concentrations along the plain-mountain transect in central China, Qu et al. [11] reported

that atmospheric concentrations of endosulfan had significantly risen by almost thrice in comparison to the concentrations reported for the year 2005. Qu et al. [11] attributed these very high levels of atmospheric endosulfan to the increased use of endosulfan as a pesticide given the use of HCHs and DDTs was gradually closing down. In the assessment of airborne endosulfan (α -endosulfan, β -endosulfan and endosulfan sulfate) levels in the Rural Pampa and Great Buenos Aires Metropolitan Area and amongst the many interesting results obtained, Astoviza et al. [12] reported that the airborne endosulfan levels were extremely elevated and had actually exceeded the worldwide reported maxima at the Great Buenos Aires Metropolitan Area and Rural Pampa. Moreover, Astoviza et al. [12] also reported that the airborne endosulfan concentrations were highly correlated to the yearly soybean crop in Rural Pampa.

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Endosulfan has been considered as an endocrine disruptor [13] and has also been attributed to adversely affecting human health in a number of ways, for example, by impacting on human primary hepatocytes, by inducing seizures, cancer development and reproductive system disorders, gastrointestinal diseases and physiological disorders [14–16], to name but a few. The use of endosulfan has been banned or is strictly restricted in a number of countries. Endosulfan, its isomers and endosulfan sulfate have been added to the Stockholm convention list of persistent organic pollutants to eventually complete elimination of endosulfan use [17,18]. Technically, endosulfan contains two isomers, α -endosulfan and β -endosulfan. In the environment, soil or water, both endosulfan isomers are slowly degraded to endosulfan sulfate and then to other products such as chloride ions [19], endosulfan diol [20,21], endosulfan ether and endosulfan lactone [21–23], endosulfan diol monosulfate [24] and 2 heptanone, dieldrin and methyl propionate [25]. Endosulfan sulfate is considered more toxic than the parent endosulfan and is usually formed by the oxidation pathway, whereas the other metabolites which are produced by the hydrolytic pathway are known to be less toxic [26]. Biodegradation of endosulfan is the primary pathway for endosulfan degradation in natural soil [27] and the degradation time depends on isomer, environmental conditions such as pH, type of soil and water content [28]. Due to its long degradation time and mobility [5,29], endosulfan is leached over long periods of times and therefore is a potential groundwater contaminant [30] which becomes very difficult to remove from polluted strata. Clay, silt and organic matter in the soil immobilize endosulfan and therefore, reduce bioavailability [31]. Excess organic matter slows down bacterial degradation of endosulfan, increasing its persistence in soil [32]. Moreover, endosulfan has a long half-life [33]. Hence, being persistent [34] and highly soluble in lipids [35,36], endosulfan accumulates in the food chain, hence posing a significant risk of exposure to humans [37].

Contaminated food and water appear to be major exposure routes [38]. Varying concentrations of endosulfan and its metabolites have been detected in human tissues [39]. Exposure of children in utero and through breastfeeding is a matter of serious concern [40]. Endosulfan is found to be acutely toxic to the majority of fauna [41–44]. Systemic poisoning of endosulfan causes nervousness, agitation, tremors and convulsions [45]. Also gagging, vomiting [46] and diarrhea [47] are other possible symptoms of endosulfan poisoning. Additionally, several chronic effects in animals have also reported. Directives on the quality of water set maximum limits on the total pesticide concentration in drinking water but unfortunately the permissible limits have been exceeded frequently in the areas where endosulfan is used especially in the agricultural industry [48]. WHO has set a maximum limit at 20 $\mu\text{g/L}$ for endosulfan for drinking water [49] and Harikumar et al. [34] reported that the Bureau of Indian Standards had fixed this same limit at 0.4 $\mu\text{g/L}$ in the year 2012. In their work, Harikumar et al. [34] also stated that a maximum permissible limit of 74 $\mu\text{g/L}$ for endosulfan in lakes, rivers and streams had been set by the United States Environmental Protection Agency (EPA) in the year 2002 (more details in the report 'Reregistration eligibility decision for endosulfan', United States Environmental Protection Agency, Washington DC, 2002). However, in a report based on the monitoring of soil samples in China, it was found that the concentration of endosulfan could vary from 19 mg/kg dry weight to below the detection limit [50]. Thus, robust techniques are needed for endosulfan removal. Extensive reviews about pesticide removal by membranes [51] using different adsorbents [52–55], and the fate of endosulfan in the environment [4] were published recently. There are other studies which have presented other techniques of endosulfan removal and these were methods based on electrocoagulation, advanced oxidation processes, catalytic non-thermal plasma mineralization, ultraviolet light assisted chemical reactions and electrochemical combustion [56–60]. The present article focuses on endosulfan biodegradation and its removal by photocatalysis, adsorption and

membrane separation processes. The recent findings and trends reported in the relevant literature have discussed. Moreover, endosulfan remediation pathways which can be further studied and developed for viable endosulfan removal have been highlighted.

2. Endosulfan removal methods

Various methods for removing endosulfan from the environment have been studied. Even the efficiency of basic household processes, such as peeling, washing and cooking in removal of endosulfan from vegetables has been studied [61]. However, Saraiva Soares et al. [62] have indicated that conventional treatment methods for treating drinking water are not suitable for endosulfan removal. In general, bioremediation is an environmentally friendly approach which is capable of removing a wide range of pesticides (including endosulfan) which cannot be removed by chemicals or other technologies [63,64]. However, bioremediation approaches may be limited by the need for large surface areas for implantation and biomass separation units [65–67], may equally suffer from relatively low digestion rates which occur in the tune of days or weeks, and are dependent on strain selection [68]. Photocatalytic degradation is capable of degrading multiple pesticides and can thus accelerate pesticide removal [69–71]. However, during photocatalytic degradation of organic pollutants, there is also the formation of by-products [72–74]. The energy costs for largescale photocatalytic degradation processes are also apparently high [75,76]. Adsorption is a low cost pollutant remediation approach when natural and waste materials are used as adsorbents. Moreover, adsorption systems are relatively simple to design and easy to operate, and also offer the possibility for regeneration of adsorbents [54,77,78]. However, there is the production of residual toxic sludge [54]. Also, the adsorptive removal of organic pollutants is highly dependent on operational parameters such as adsorbent's surface chemistry, pH, contact time, agitation modes and initial adsorbate concentration [79]. In general, membrane technologies operate without phase changes or chemical conditioning and have relatively low energy consumption and low production costs [80–82]. Yet, the quantum of energy consumption persists in being an economic hurdle to the wide use of pressure driven membrane processes [83]. Moreover, fouling shortens the lifetime of membranes [83].

Therefore, in the series of more advanced methods, biological removal and membranes separations have been studied, but adsorption comes out better in terms of initial cost, simplicity, operability and insensitivity to pollutants. Adsorption also does not result in the formation of harmful by-products. In bioremediation, the main goal lies in the degradation of the endosulfan using microbes, whereas endosulfan removal by membranes or adsorption occurs via separation based on physical and/or chemical properties. Nanofiltration and reverse osmosis are the most common membrane separation technologies [51], but other methods, namely electrodialysis [84] or membrane-coated fiber techniques [85] have also been investigated. Furthermore, over 90% degradation of endosulfan can be achieved by ozone oxidation [86,87] or via photocatalytic oxidation doped titanium dioxide [88]. Some of the important methods used for endosulfan removal and the recent findings of enhanced approaches are discussed below.

2.1. Biological removal of endosulfan

In natural soils, high concentrations of endosulfan have detrimental effect on fungi, but bacteria seem to manage the load better [27]. Certain strains tolerate very high concentrations of endosulfan and might even degrade endosulfan without toxic metabolites [89]. Naturally occurring bacterial degradation of endosulfan in the environment could be exploited in treatment processes. Quite a few studies of these types of bioremediation have been published and the results and interpreta-

tions are diverse in terms of the tolerances exhibited for endosulfan and the extent of decontamination thereof [33,90–99]. These studies have been performed in solid matrices such as soil, sediments and food processing wastes, where the endosulfan degrading microorganisms have solid support and carbon source. For example, Ali et al. [100] studied the degradation of endosulfan using the biochemical process of composting in two modes of composting and reported the peak removals of α -endosulfan and β -endosulfan in the rotary drum composting configuration at 83.3% and 85.3%, respectively. In the second configuration of windrow composting, endosulfan removal efficiencies were lower with 77.7% for α -endosulfan and 67.2% β -endosulfan. Another example is the recent work of Wang et al. [101] who investigated the potential for remediating endosulfan contaminated soil using a co-cultivation of *Pleurotus eryngii* and *Coprinus comatus* in pot experiments and reported that the co-cultivation strategy had been very effective in endosulfan decontamination with removal rates higher than 87% in all treatments.

There are a number of important merits and demerits of the biological remediation technique for pesticide. As per discussions in Niti et al. [102], the main advantages are that bioremediation can be conducted in situ and without the need to disturb the day to day activities around the contaminated zone and therefore cutting down significantly on transportation requirements; bioremediation makes use of natural resources to sustain the remediation process, and finally, in a certain number of cases, bioremediation can be less costly in contrast with other treatment techniques. However, bioremediation has a number of limitations [102], and these are summarized as follows: bioremediation can be labour intensive and time consuming before the targeted levels of decontamination and detoxification are reached; bioremediation methods which have worked well in lab scale milieu are pretty difficult and very challenging to upscale to real field scenarios; and finally the collateral impacts of bioremediation have to be fully understood and assessed for a particular case of pollution. Recently, the combination of bioaugmentation and biostimulation is coming up as a potential approach for the treatment of contaminated soils [102–108]. In the bioaugmentation approach, an efficient set of microorganisms are usually imported at the treatment site for degrading the targeted pollutant species. However, bioaugmentation does not always turn out to be effective and this possibly due to the low survival rate of the new microorganisms introduced into the indigenous microorganism flora of the contaminated soil or aqueous medium [109–112]. Under these circumstances when bioaugmentation fails, the biostimulation approach can then be applied to increase the efficiency of the microbial species because biostimulation brings sufficient amount of nutrients, water and oxygen [113–115] which then assists the microorganisms to better compete and survive within the indigenous microbial populations [116,117].

2.1.1. Bacterial degradation

Recently, some newly isolated bacterial strains have also been assessed and they have shown high endosulfan biodegradation potentials (Table 1) following hydrolytic pathways (Fig. 1). A large number of these bacterial strains were indigenous to the contaminated sites or polluted media. Ozdal et al. [21] have isolated *Stenotrophomonas maltophilia* OG2 and tested it to degrade α -endosulfan. Ozdal et al. [21] reported a number of interesting observations, namely, that biodegradation of α -endosulfan was considerably influenced by endosulfan concentration, temperature and pH with the optimum quantities being 100 mg/L, 30 °C and 8.0, respectively; and under these optimal environmental conditions, *Stenotrophomonas maltophilia* OG2 had degraded 81.53% of the α -endosulfan after ten days via a hydrolysis pathway. Zaffar et al. [118] have isolated *Stenotrophomonas maltophilia* EN-1 and assessed it for its endosulfan degradation performance. Zaffar et al. [118] reported that the endosulfan biodegradation kinetics indi-

cated that *Stenotrophomonas maltophilia* EN-1 was significantly capable in degrading the endosulfan. Mir et al. [25] have identified a new bacterial strain as the *Pseudomonas mendocina* ZAM1 strain degraded endosulfan by more than 64.5% (at a concentration of 50 mg/L after twelve days of incubation. Odukkathil and Vasudevan [119] reported that *Bordetella petrii* I GV 34 and *Bordetella petrii* II GV 36 were able in degrading endosulfan with concurrent production of biosurfactant. Odukkathil and Vasudevan [119] recorded that *Bordetella petrii* I had degraded 89% of α -endosulfan and 84% of β -endosulfan whilst *Bordetella petrii* II was capable in degrading 82% of both endosulfan isomers. Jimenez-Torres et al. [120] reported that *Enterobacter cloacae* strain PM-M16 had degraded 100% of β -endosulfan and 71.32% of α -endosulfan within twenty-four days through non-oxidative pathways on basis of the absence degradation metabolites such as endosulfan lactone, endosulfan sulfate or endosulfan diol.

Biodenitrification with sand filtering was found to be an efficient method with over 70% removal efficiency of the endosulfan [132]. Hydraulic residence time was found to be an important factor when measuring the efficiency on endosulfan removal. Other important factors in aqueous media were supplementary carbon source, pH and inoculum size [94]. Almost 90% removal efficiency was achieved when wheat straw was used as a substrate [133]. It was suggested by these researchers that roughly one third of the removal was due to adsorption onto wheat straw and the rest was due to biological degradation. The performance of biodenitrification method has been proven later with other pollutants [134]. Moreira et al. [135] presented a pilot scale study in which biological and advanced oxidation processes were combined to treat pesticide-polluted wastewater. In an attempt to study innovative methods for endosulfan degradation, Shah et al. [136] demonstrated that endosulfan degradation and removal under the influence of gamma-rays in advanced oxidation and reduction processes was dependent on the absorbed dose of the gamma irradiation and the removal increased considerably when aqueous electrons were the primary reacting component. However, it was also reported that endosulfan removal was inhibited when the reaction milieu contained the following species: nitrate, nitrite, bicarbonate, carbonate, ferric ions and humic acid. The latter species were of particular interest in the analysis of Shah et al. [136] because they are present in natural water and are found in quantities which vary according to geographical positions and the types of anthropogenic activities [57,137–141]. Based on their findings, Shah et al. [136] proposed the degradation pathway of endosulfan and the formation of the metabolites (Fig. 2) which involved an attack of hydroxyl radicals at the S=O bond whereas the aqueous electrons attacked at the chlorine atom bonded to the ring.

2.1.2. Fungal biodegradation

There are also a number of studies which have demonstrated the merits and ability of fungal species to degrade endosulfan. For example, some of these species are *Mortierella* sp. strain W8 [50], *Trametes hirsuta* [142], *Aspergillus niger* [108], *Trametes versicolor* [143], *Pleurotus ostreatus* [143], *Gloeophyllum trabeum* [143], *Bjerkandera adusta* [144] and *Lasiodiplodia* sp. JAS12 [97]. Similarly, Bhalerao and Puranik [145] isolated a fungal strain with promising properties in reference to bioremediation of endosulfan contaminated soils. Goswami et al. [146] achieved over 95% removal of endosulfan using isolated fungal strain. Indeed, According to the discussions provided by Maqbool et al. [147], fungal strains are also capable in degrading endosulfan and many other pesticides following different pathways such as hydroxylation, oxidation dechlorination, esterification, dioxygenation and dehydrochlorination with the involvement of a number of enzymatic species such as laccase, peroxidase, dehydrogenase, esterase, hydrolase, lignin peroxidase and manganese peroxidase. Verma et al. [148,149] isolated an endosulfan degrading bacterial strain from earthworm gut and evaluated its suitability for bioremediation applications. Interestingly, the

Table 1
Bacterial strains degrading endosulfan and highlights of biodegradation performance.

Bacterial strain	Source of bacterial strains	Operating parameters and reaction conditions	Extent of endosulfan degradation	Possible metabolites	References
<i>Alcaligenes faecalis</i> JBW4	Isolated from activated sludge	pH 7.0 Incubation temperature 40 °C Endosulfan concentration: 100 mg/L	87.5% degradation for α -endosulfan 83.9% degradation for β -endosulfan Total days in degradation: 5 days (non-oxidative mechanism)	Endosulfan diol Endosulfan lactone	Kong et al. [122]
<i>Bacillus megaterium</i> KKc7, <i>Pseudomonas aeruginosa</i> strain KKc3, <i>Ochrobactrum</i> sp. strain KKc4 and <i>Achromobacter xylosoxidans</i> strain KKc6	Soil Column	Soil pH 6.5–6.7 (in 5% aqueous solution) Incubation time 30 days, Medium: studied NSM and NCM individually and in mixed culture Endosulfan conc. 100 mg/L	KKc7 degraded endosulfan to endosulfan sulphate KKc3, KKc4 and KKc6 strains converted endosulfan through another pathway to endosulfan diol Mixed culture of KKc3, KKc4 and KKc6 showed 94% removal of total endosulfan with endosulfan as the only sulphur substrate KKc3 was good in NCM and NSM with biotransformation rate of 0.098 and 0.094 mg/l/s with the endosulfan removal % as 80% and 73% respectively.	Endosulfan sulphate Endosulfan diol Endosulfan lactone Endosulfan ether	Seralathan et al. [123]
<i>Streptococcus agalactiae</i>	Isolated from enriched sediments of Vellar estuary	pH 8.0 Temp. 35 °C 15 days incubation 100 ppm endosulfan dextrose as carbon source	Efficiency of endosulfan degradation – 40.77%	Endosulfan diol Endosulfan ether	Neelambari and Annadurai [124]
<i>Alcaligenes faecalis</i> strain JBW4	Brown soil	Incubation temp 37 °C Conc. of endosulfan 50 mg/kg of soil Time 77 days Endosulfan conc. 50 ppm	Degradation of 87.0% and 75.8% of α -endosulfan and 69.5% and 58.5% of β -endosulfan in natural and sterilized soils, respectively non-oxidative pathway	Endosulfan ether Endosulfan Lactone	Kong et al. [125]
<i>Klebsiella</i> sp. M3	Soil	Endosulfan conc. 50 ppm Total days 15 Shaking speed 150 rpm Temperature 30 °C	Degradation rate for α -endosulfan > β -endosulfan (kinetic index, V_{max}/K_s for α -endosulfan = 0.051 day ⁻¹). maximum degradation of α -endosulfan was 74.5 ± 2.26% maximum degradation of β -endosulfan 67.5 ± 1.59%	Endosulfan sulphate Endosulfan diol Endosulfan lactone Endosulfan hydroxyether Endosulfan sulphate	Singh and Singh [126]
Halophilic bacterium JAS4	<i>Gossypium herbaceum</i> rhizosphere soil	Conc. 1000 mg/L Incubation temperature 30 ± 2 °C Shaking speed 120 rpm	JAS4 isolate had considerable potential to degrade endosulfan by catabolism α and β -endosulfan degradation rate constants were 0.017 day ⁻¹ and 0.003 day ⁻¹ , respectively Oxidative pathway	Endosulfan diol, Endosulfan ether, Endosulfan lactone	Silambarasan and Abraham [127]
<i>Pseudomonas fluorescens</i>	Talc based formulation of <i>Pseudomonas fluorescens</i>	pH 7.0 5 g Ca-alginate beads Shaking speed 150 rpm Temperature 30 °C	Biodegradation of endosulfan with an average starting concentration of 350.24 µg/L within twelve days by the freely suspended bacterial cells Bacterial cells immobilised on Ca-alginate beads had achieved full degradation of endosulfan isomers at different starting endosulfan concentrations between nine and eleven days Hydrolytic pathway	Endosulfan diol, Endosulfan ether, Endosulfan lactone	Jesitha et al. [128]
Ca-alginate immobilized <i>Pseudomonas aeruginosa</i>	Agricultural soil	For batch: Temperature 37 °C Shaking speed 150 rpm Incubation time 24 h Endosulfan conc 2% For column: Column flow rate 100 ml/h and 20 ml/h Endosulfan conc. 2–10%	Biodegradation of endosulfan occurred through non-oxidative pathway 60% degradation of Endosulfan at the end of the 35th cycle (repeated batch conditions) 100% degradation for 2% conc of Endosulfan at 100 ml/h	Endosulfan lactone Endosulfan ether	Pradeep and Subbaiah [129]
PRB77 and PRB101 had 99% homology with <i>Bacillus</i> sp. LN849696 and <i>Bacillus</i> sp. KF984414, respectively	Agriculture soil	Max degradation at pH 7 and 8 Incubation temp 30 °C Time 30 days	PRB77 and PRB101 strains degraded 70% and 74% of endosulfan in broth and degraded 63% and 67% endosulfan in soil, respectively	NA	Rani and Kumar [130]

Table 1 (Continued)

Bacterial strain	Source of bacterial strains	Operating parameters and reaction conditions	Extent of endosulfan degradation	Possible metabolites	References
Achromobacter xylosoxidans strain C8B	Soil	Incubation tempe. 28 °C Shaking speed 150 rpm Time 15 days 50 ppm endosulfan Broth medium	94.12% biodegradation of α -endosulfan and 84.52% biodegradation β -endosulfan Biodegradation of endosulfan proceeded plausibly through endosulfan ether formation pathway	NA	Singh and Singh [131]
Pseudomonas sp.	Pesticide contaminated soil	Initial concentrations of endosulfan, i.e. 5, 25, 50, 75 and 100 mg/l Incubation 5 days Incubated temp 28 °C Shaking speed 220 rpm	70–80% of each initial concentration was degraded by the isolated strain, Maximum degradation was observed after 5 days of incubation	Endosulfan lactone	Zaffar et al. [26]

bacterial strain survived in high endosulfan concentrations, and using endosulfan as a carbon source, 97% degradation was observed without producing toxic metabolites, such as endosulfan sulfate. On the other hand, Castillo et al. [150] isolated a strain that degraded over 70% of endosulfan in 6 days by using it as sulfur source rather than carbon source. The recent literature on the use of fungal species to biodegrade and metabolize endosulfan seems scarce. However, the endosulfan degradation performances of the fungal species recently studied are very high and hence bring adequate hope that fungal biodegradation pathways could become promising as bioremediation techniques for this xenobiotic. However, it appears there is an arguably limited diversity of fungal species which can be prioritized and used for developing fungi-based endosulfan degradation schemes at large scales of contamination. Using a very narrow mix of potent endosulfan degrading fungal species will surely do less well in the overall remediation process than would a more diverse cocktail of equally effective fungi. Hence, there is a need to develop more such fungal consortia which can degrade endosulfan fast and with high removal efficiency.

2.1.3. Phytoremediation

Vegetation could also be exploited in biological endosulfan removal. Indeed, the use of plant species for cleaning up endosulfan contaminated media is also gradually getting more research and development interest since almost over a decade. The main merits of such plant-based endosulfan removal methods are proposed to be their relative inexpensiveness, good eco-friendliness and high effectiveness. All the more, the protocol for monitoring also appears pretty easy and there is an added advantage which spans the possible reuse of some valuable products of the phytoremediation process. Thus, phytoremediation may be concisely described as the process during which the capabilities of plant root and shoot systems are harnessed altogether to participate in the uptake, conversion, rhizofiltration and phytovolatilization of a number of noxious chemical species [151,152].

Mersie et al. [153] studied applicability of vegetative filter strips to reduce the endosulfan transport out of fields. By studying two different grass species, they achieved over 98% endosulfan removal from agricultural run-off. According to the study of Ramírez-Sandoval et al. [154], basil proved to be a good candidate in endosulfan contaminated soil phytoremediation. Pesticide removal has also been examined by ponded wetland by Rose et al. [155] which shares similarities with a study of Mersie et al. [153]. Results suggested that pond's sediments function as a sink for endosulfan and algae can reduce the persistence of pesticides in water. Indeed, there are a number of studies which indicate the high potential of phytoremediation as a potential green clean-up approach for removing organic pollutants including endosul-

fan. Such a biological approach will in principle have to be developed and optimized based on the specific plant uptake mechanisms and also with respect to the interactions which can develop amongst the organic pollutants, plants and surrounding microorganisms. With respect to endosulfan, there is also a need to ensure that the plant species being used in the phytoremediation process be robust enough to grow healthily given the toxicity of endosulfan [156,157] and tolerate high endosulfan concentrations. In a way, there is a need to look for such endosulfan-uptaking plants which are endosulfan hyperaccumulators. Mitton et al. [156] have performed an extensive study of the uptake of endosulfan in four plants and based on the results, they reported that sunflower plants appeared to be the best phytoremediation plant for endosulfan residue uptake from contaminated soils. Mitton et al. [156] had based their final inference on the biomass production, endosulfan accumulation potential and the decrease in soil endosulfan concentrations. Furthering the application of plants and phytoremediation in cleaning-up endosulfan contaminated soils and waters, it appears that constructed wetlands could be a possible solution after the economics have been worked out viably. Matamoros et al. [158] have investigated the behaviour of eight priority organic pollutants, including endosulfan, in a pilot subsurface constructed wetland system using *Phragmites australis* plants. Amongst the many observations made, Matamoros et al. [158] reported that the absence of endosulfan (below the Limit of Detection) in the final treated effluent could be set on account of a number of processes namely elimination of the endosulfan by degradation, uptake of the endosulfan by the *Phragmites australis* plants and/or by microbial species present into the system and/or by the mechanism of sorption within the organic matter portions of the system and biofilm built up onto the gravel materials used in the constructed wetland. For normal operating conditions (hydraulic loading rate of 36 mm/day and a hydraulic retention time of five to six days), Matamoros et al. [158] eventually hypothesized that the highly efficient removal of endosulfan exceeding 99% could be due to a reductive dehalogenation pathway.

Zhao et al. [106] have developed vertical-flow constructed wetlands at the lab-scale to assess the bioremediation of endosulfan over a twenty-day experimental run. Amongst the many interesting findings and observations, Zhao et al. [106] reported that endosulfan isomers removal efficiencies had been enhanced to 89.24–97.62% through bioremediation. Based on their field monitoring study findings, Singh et al. [159] reported that *Vetiveria zizanioides* had been capable of accumulating more endosulfan as compared to the other plant species tested. One of the interesting findings of Singh et al. [159] was also that there had been enhanced dehydrogenase activity and microbial biomass carbon which indicated the active degradation of endosulfan

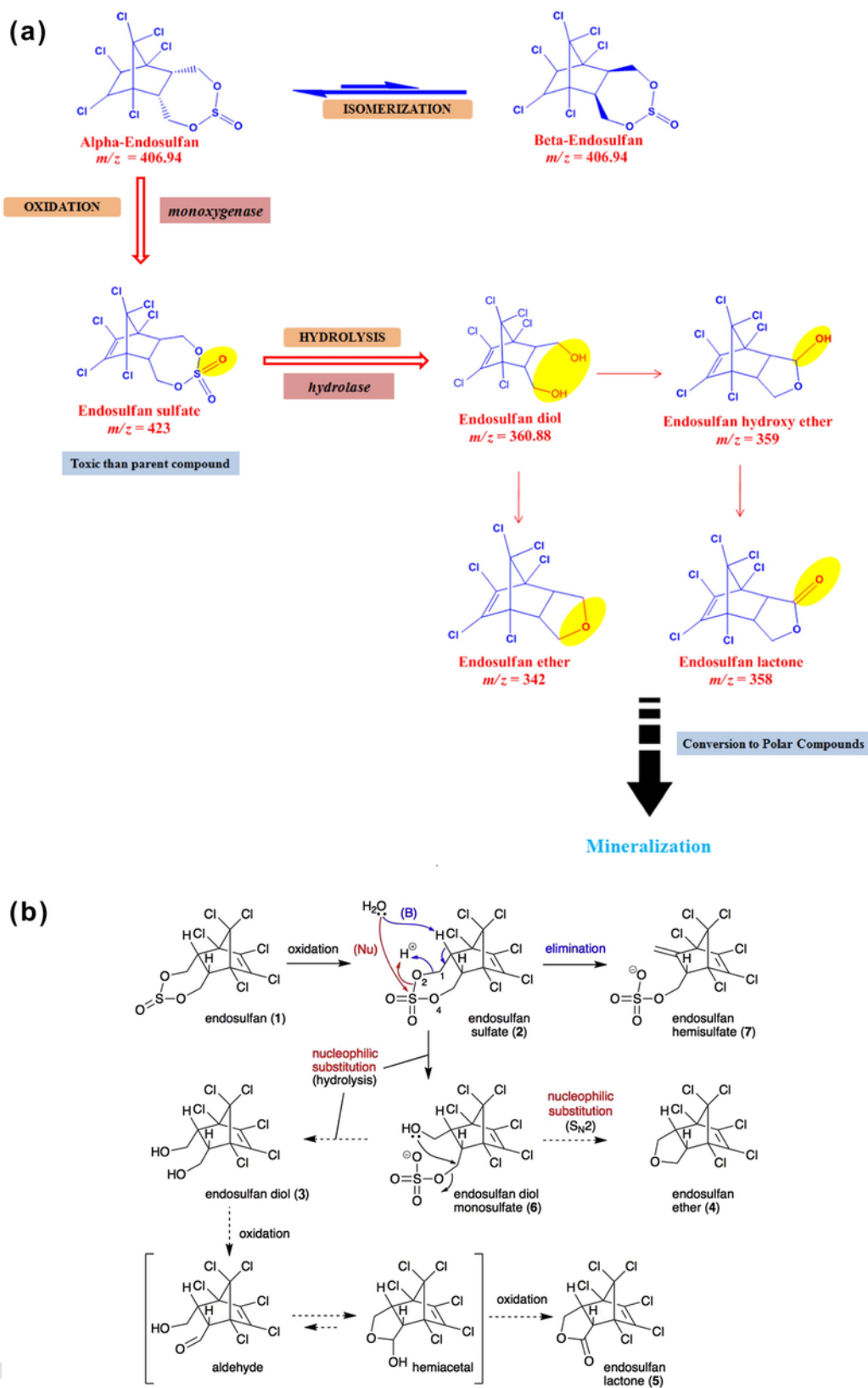


Fig. 1. Mechanisms of microbe-mediated degradation of endosulfan (a) possible conversion pathways for endosulfan degradation by microorganisms proposed by Supreeth and Raju [121]; (b) degradation of endosulfan (1) to endosulfan sulfate (2) and further biodegradation of endosulfan sulfate (2) to endosulfan diol monosulfate (6) by *Rhodococcus koreensis* strain S1-1 proposed by Ito et al. [24]. Figure in part (a) has been reprinted with permission from Supreeth and Raju et al. [121], Copyright © 2017, Springer-Verlag GmbH Germany (for both print and electronic formats) under License number 4474560213779, and figure in part (b) has been reprinted with permission from Ito et al. [24], © 2016 Elsevier Inc. All rights reserved (for both print and electronic formats) under License number 4474560605860.

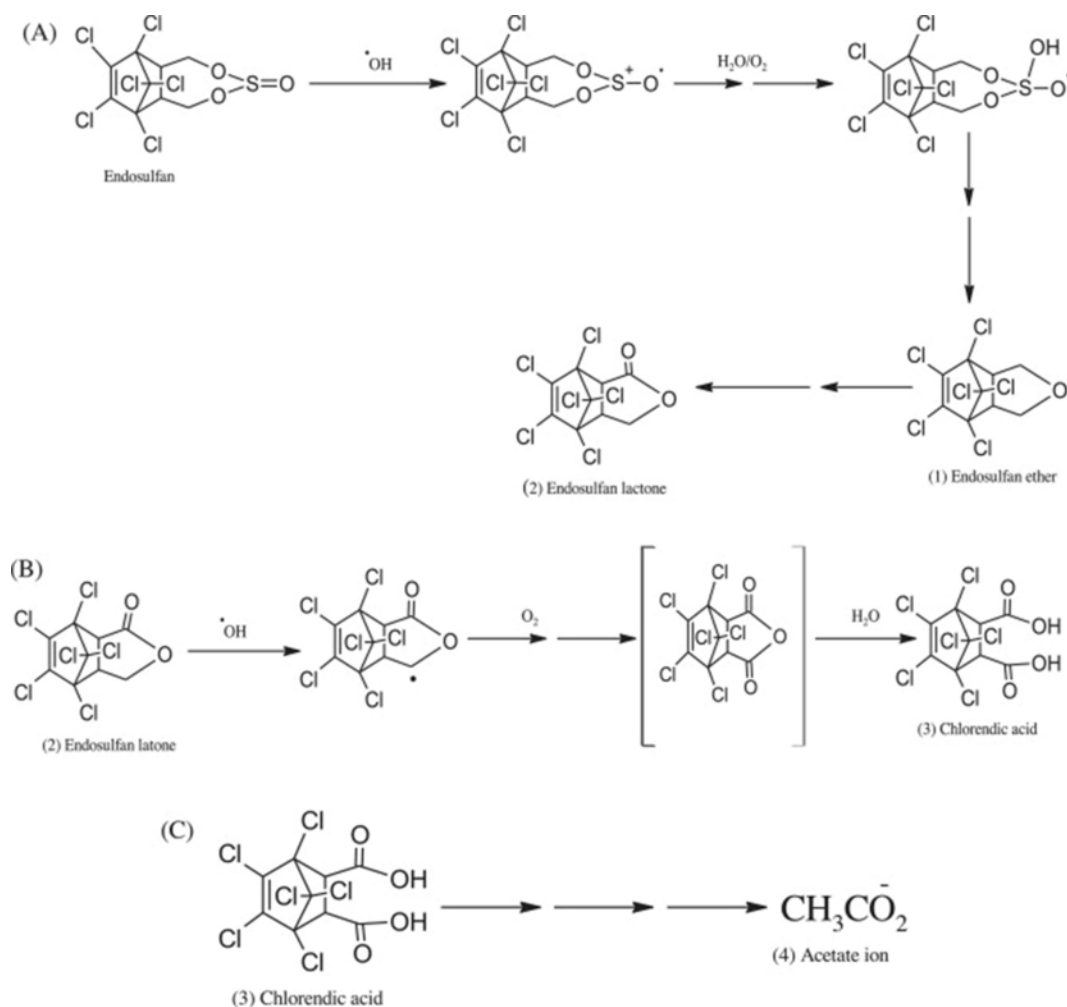


Fig. 2. Endosulfan degradation pathway by hydroxyl radicals under gamma irradiation conditions in advanced oxidation and reduction processes suggested by Shah et al. [136] Reprinted with permission from Shah et al. [136] (for both print and electronic formats), Copyright © 2014 Published by Elsevier B.V. under License number 4474560758141.

by the microbial species which thrived as a result of the secretion of root exudates of the test plants. Furthermore, Singh et al. [159] observed that *Vetiveria zizanioides* had accumulated the highest level of endosulfan in its tissues whilst the lowest concentration of endosulfan had been uptaken in the tissues of *Brassica juncea*. The additional highlight of the study of Singh et al. [159] was that there had been no significant decrease in lipid peroxidation and chlorophyll level in *Vetiveria zizanioides* and these results advocated the appropriateness of the latter plant species for phytoremediation of endosulfan. In another study [160] where *Vetiveria zizanioides* was assessed in its phytoremediation potential for endosulfan in two (lixisol and vertisol) cotton soils using pot experiments for a duration of six months, Abaga et al. [160] reported that endosulfan was not detected in the test soils. Consequently, these workers recommended that the effectiveness of *Vetiveria zizanioides* should be extended and verified at the cotton plot scale. Singh and Singh [161] have analysed the accumulation of the endosulfan isomers and endosulfan sulfate from a contaminated region in Ghaziabad, India, and observed that all the plant species which had been assessed could accumulate these three chemicals in their root and shoot tissues and β -endosulfan was the predominant isomer uptaken (Fig. 3). Singh and Singh [161] also reported the uptake potential in the order *Vetiver zizanioides* > *Digitaria longiflora* > *Chloris virgata* > *Panicum paludosom* > *Sonchus olerceous* > *Sacciolepis interrupta* > *Sphenoclea zeylamica*, and had inferred that both *V. zizanioides* and *D. longiflora* were able to accumulate significant amounts of the endosulfan isomers

and endosulfan sulfate in their root, shoot and leaf systems in comparison with the other five plant species assessed. The variations of the uptake of the endosulfan isomers in the plants' root, shoot and leaf systems can be attributed to the specific properties of the plants such as morphology of the plant, type of root system, number of branches and extent of branching, types and surface area of leaves, tolerance of the plant to the individual chemical.

2.2. Endosulfan removal by photocatalysis

The photocatalysis method has shown high potential in the oxidation of organic compounds using a semiconductor material as catalyst. This process generates holes that can react with water to produce OH radicals. Titanium dioxide (TiO_2) is one of the widely probed catalyst because of its photochemical stability, minimal toxicity and high efficiency in the degradation of pollutants [162–165]. However, there are a few critical limitations to the large scale commercial use of photocatalysts such as TiO_2 and these are related to the (i) inefficient harnessing of visible light available for undertaking the photocatalytic reactions, (ii) low adsorption capacity for hydrophobic environmental pollutants, (iii) homogeneity of photocatalyst particle distribution in aqueous suspensions, and (iv) the potential for recovery of the photocatalyst particles after treatment of the contaminated aqueous media [166]. TiO_2 highly photoactive when exposed to near-UV and the absorption spectrum can be changed by doping. Over 95% removal efficiency of

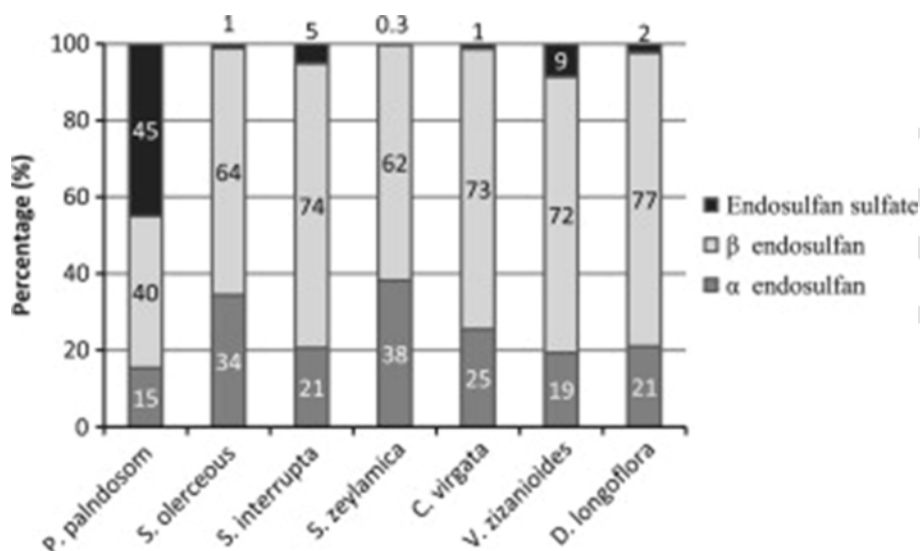


Fig. 3. Distribution of α -endosulfan, β -endosulfan and endosulfan sulfate in the seven plant species analysed by Singh and Singh [161]. Reprinted with permission from Singh and Singh [161], Copyright © 2014 Elsevier Inc. All rights reserved (for both print and electronic formats) under License number 4474590614420.

endosulfan was reported using a photocatalytic reactor coated with TiO_2 [60]. These researchers argued that replacing UV lamps by solar radiation would result in economic savings. Solar photocatalysis has also been studied by different researchers [167,168] and its potential in the degradation of endosulfan has been demonstrated in a few studies [88]. Thomas et al. [88] fabricated Ag doped nano TiO_2 crystals which proved to be significantly efficient solar photocatalysts with better photocatalytic activity than the pure nano TiO_2 and the Degussa P25 commercially available photocatalyst. Thomas et al. [88] then also reported that their highly active solar TiO_2 -based photocatalysts had given quasi complete degradation of endosulfan. Another process was presented by Fallmann et al. [169] wherein they claimed better and faster results with photo-Fenton method than with TiO_2 solar photocatalysis. The efficiency of TiO_2 as a solar photocatalyst could also be increased with doping.

Endosulfan isomers showed a slightly different behavior in ozonation studies [86,87]. Maximum removal of both isomers was found to be over 90%. Decreases in temperature and pH resulted in the increased removal rate. Similar results were reported by Begum and Gautam [170]. Begum and Gautam [170] reported that 57 mg/min of

ozone was an optimal concentration to degrade endosulfan by 89%. Furthermore, Begum and Gautam [170] also observed that alkaline pH (pH 10 as optimum pH) favoured the production of hydroxyl radicals and this optimum pH led to an endosulfan degradation efficiency of 93%. In terms of kinetics of the degradation, the degradation of endosulfan fitted well to a first-order model and based on their analytical results, Begum and Gautam [170] further inferred that the degradation of endosulfan proceeded with the formation of methyl cyclohexane and *o*-xylene (Fig. 4) and these species soon disappeared from the reaction milieu as degradation reaction continued. Comprehensive review articles on the subject were published by Camel and Bermond [171], Burrows et al. [172], Konstantinou & Albanis [173], and more lately by Ikehata and El-Din [174]. Beta-endosulfan solutions were ozonated in a laboratory scale semi-batch reactor under various experimental conditions [87]. Ozonation kinetics of beta-endosulfan and effects of some parameters such as pH, temperature, partial pressure and ozone dosage on oxidation were investigated by Yazgan and Kinaci [87]. In this work, it was found that increasing ozone dosage and decreasing of temperature and pH had increased the oxidation rate of beta-endosulfan and a maximum of 97% of beta-endosulfan could be removed at both

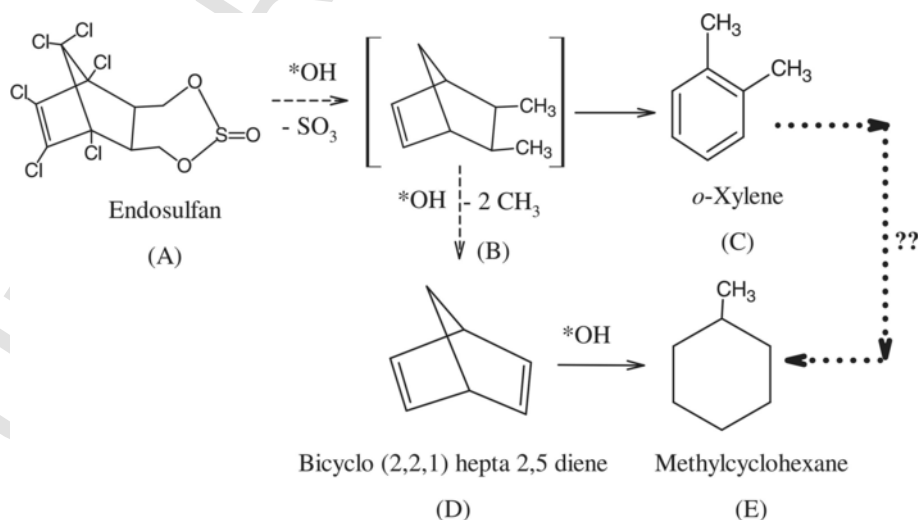


Fig. 4. Endosulfan degradation pathway under reaction conditions of ozonation proposed by Begum and Gautam [170]. Reprinted with permission from Begum and Gautam [170], Rights managed by Taylor & Francis (for both print and electronic formats) under License number 4474560966686.

16-mg/min ozone dosages and at a pH of 4 for 60 min of ozonation [87].

Bimetallic catalysts (Mg/ZnCl_2 , Mg/Pd and $\text{Mg}^0/\text{Pd}^{+4}$) are also able to achieve the degradation of endosulfan to hydrocarbons very efficiently via dechlorination reactions [175–177]. Endosulfan removal efficiencies of 96% were reported by Begum and Gautam [175] and over 99% was observed by Thangadurai and Suresh [176]. Amongst their many findings and observations, Aginhotri et al. [177] reported that in the absence of any acid, a $\text{Mg}^0/\text{Pd}^{+4}$ bimetallic system with a $\text{Mg}^0/\text{Pd}^{+4}$ dose of 10/0.5 mg/mL led to significantly high degradation of endosulfan following dechlorination kinetics. Thangadurai and Suresh [176] proposed the use of immobilized Pd since there are the possibilities of recovery and reuse, which collectively offer the potential to develop economically feasible procedures thereof. Still, in the case of immobilized metal catalyst systems, the issues related to variations in rates of reactions and catalyst deactivation due to fouling have then to be further addressed [178–181].

All the more, the advent and rapid application of nanoscience in environmental pollution abatement and remediation have opened a vast panoply of nanosized bimetallic catalysts which can assist in the degradation of organic environmental pollutants [182]. Indeed, in the detailed review performed by Rani and Shanker [183], it has been highlighted amongst the umpteen interesting aspects that zero-valent iron (Fe^0) and TiO_2 standalone or in combination with oxidizing agents have been much capable in eliminating pollution arising from pesticides and the fabrication of nanosized particles has equally known a gain in research interest accordingly. Hence, the role of nanosized bimetallic catalysts in pesticides degradation for environmental pollution remediation will be crucial towards nurturing a green environment. However, there are some issues which still need to be carefully addressed before an optimal and cost-effective application of the various types of nanosized bimetallic catalysts can be made. To start with, bimetallic nanosized catalysts have very intricate structures and the fabrication methods are equally complicated by reason of the type of specific equipment needed [184], the reactor design and optimization thereof when attempting to upscale the synthesis. Moreover, it is difficult to keep a close control on the morphology of these nanosized structures [184–186] and ensure stability [187–189]. Besides the physical fabrication methods, the chemical procedures used to synthesize bimetallic nanosized catalysts suffer from the need to use toxic reducing agents and toxic solvents [184]. Moreover, further research is still needed to optimize the energy consumption, time of nanostructure synthesis and interphase mass transfers taking through the different mechanisms of catalytic activity mediating the degradation of the pesticide molecule. Annexed with the need to have the best interphase mass transport rates of the pesticide molecules with respect to the active sites, surface porosity and active site fouling [184,190,191] seems to be two more limitations. Accordingly, bimetallic nanosized catalysts have to be synthesized such that they be endowed with enough fouling resistant traits. Furthermore, the propensity for some of the metal species to leach from the bimetallic nanosized catalysts [192,193] also raises concerns of secondary pollution [194,195].

2.3. Endosulfan removal by adsorption

Zeolites and activated carbon are used in environmental applications to remove organic compounds from gases and water [196–200]. Activated carbon, a universal adsorbent, is one the most widely used adsorbent for water and wastewater treatment applications. The demand for activated carbon appears much to keep on increasing [201] and it continues to be one of the most preferred adsorbent for many chemical species by reason of its superior specific surface area, very well developed pore structure and conducive pore size distributions, favorably high adsorption capacities for very many different species and

high variability of surface chemistry and significant degree of surface reactivity because of the presence of many functional groups [202–204]. Zeolites have been gathering much research attention as potent adsorbents of many polluting species such as inorganic anions, xenobiotics and heavy metal ions [205,206]. The main attributes of these porous crystalline structures are in their outstanding separation performance and relatively low cost [207]. Moreover, zeolites have favourable physicochemical properties namely relatively high specific surface areas and high ion-exchange capacities which contribute to their excellent adsorption potentials [205,206].

2.3.1. Organic substrates-derived adsorbents

Activated carbons have been produced from a variety of organic waste materials such as banana stalk [208,209], sewage sludge [210] and industrial waste lignin [211]. The performance of activated carbon can be enhanced by structural and surface modification using different chemicals, for example, by inducing NH_4Cl [212] or by chemical activation with phosphoric acid [213]. However, due to higher cost involved in the process, alternative adsorbents are constantly being studied. An inclusive review about potential low-cost adsorbents was published in 2010 [214]. Promising results for the removal of pesticides with varying adsorbents have been achieved by various researchers such as Ghiaci et al. [215] with cereal ashes, Al-Qodah et al. [216] with oil shale ash and Petrova et al. [217] with apricot stones. In addition to the latter examples, Memon et al. [218] have studied methyl parathion adsorption using watermelon peels. Domingues et al. [219] compared the efficiency of activated carbon and granules of cork in the adsorption of alpha-cypermethrin. Their results indicated that cork might be a better and cheaper alternative to activated carbon. In their work, Thuy et al. [220] have studied the efficiency of low-cost adsorbents for the removal of two pesticides, namely dieldrin and chlorpyrifos. Since this review focuses on endosulfan removal, a detailed discussion is being presented below on the endosulfan removal by various adsorbents.

Activated carbon was found to be the most efficient adsorbent in removal of pesticides in a study by Sen et al. [221], where six pesticides including endosulfan were adsorbed from white wine. No linearity between an increase of the adsorbent dose and the removal rate of the pesticides was observed. The pesticides were affected at different levels from adsorbents except activated carbon. All of the adsorbents had a major effect on the removal of α -endosulfan followed by penconazole, imazalil, and tetradifon, respectively. Vinclozolin and nuarimol were the pesticides that had been the least affected by the adsorbents. Despite of similar adsorption potential ($\log K_{ow}$) of pesticides, the adsorbents removed them to different levels. Meanwhile the adsorbents generally affected the removal of the pesticides. Maldhure and Ekhe [211] prepared activated carbon (AC) from lignin, an industrial waste, using microwave and phosphorous acid. AC obtained by the microwave treatment was found to be more effective for endosulfan adsorption than AC resulting from simple impregnation. An adsorption capacity of 6.24 mg/g for endosulfan was achieved with the microwave treated adsorbent while it was only 3.96 mg/g for AC prepared by simple impregnation. Here, the authors concluded that the use of microwave treatment produced more oxygen surface functional groups. More so, their results indicated that the surface chemistry of the microwave treated sample was more important than the textural properties for the higher adsorption of endosulfan. The microwave treated sample also resulted in less hysteresis and fewer carbonyl surface groups. Palm shell was also found to be a suitable precursor for efficient activated carbon adsorbent [222]. However, rice husk ash did not show any adsorptive properties for endosulfan.

Besides activated carbon, several low-cost adsorbents have also been studied for endosulfan removal. Carbon slurry, for example, is a waste material produced in fuel-oil-based industrial generators [49].

This waste was converted to adsorbent by heat and acid treatment, and the adsorption properties of the product were studied. Here, the adsorption efficiencies of endosulfan were over 30 mg/g in batch and column operations [49]. Changes in environmental conditions, such as temperature or pH, affected negatively the adsorption efficiency. Endosulfan removal rate from real wastewater was only 67% due to competitive adsorption of other contaminants in the water and decreases in particle size did increase adsorption capacity to some extent [49]; and eventually it was concluded that carbon slurry conversion product is effective and selective for endosulfan removal. El Bakouri et al. [223–226] obtained promising results using natural organic substances, such as date and olive stones, bamboo canes, peanut shells and avocado stones. Adsorption capacities varied between 4.53 mg/g with *Eucalyptus gomphocephala* leaves and 13.54 mg/g with date stones. The removal efficiency from a pesticide solution was over 90% with date stones, though the adsorption efficiency was significantly dependent on pH and temperature as reported by Gupta and Ali [49]. A decrease of sorbent particle size increased the adsorption capacity due to the increase in surface area. Chitosan powder and beads from crustaceans have also been proven potential as a low-cost adsorbent material for 17 organochlorine (OCP) pesticides in water samples [227]. In the latter study, the 17 OCPs were significantly removed by chitosan beads and porous crab shell, and their percentages of removal were >99%. These results indicated that the adsorption capacity of chitosan beads is between 6.7 and 10 µg, and that of crab shell powder is between 0.1 and 0.15 µg. Furthermore, Aslan and Türkman [133] examined the simultaneous biological removal of endosulfan ($\alpha + \beta$) and nitrates from drinking waters using wheat straw as substrate and reported that 21.3% of the endosulfan removal was achieved by adsorption onto the wheat straw and 68.2% of the endosulfan removal occurred by biological activity. In another work, Sudhakar and Dikshit [228] reported that activated charcoal showed the best adsorptive capacity for endosulfan with a Q_{\max} of 2.145 mg/g followed by wood charcoal at 1.773 mg/g, soya caju at 1.575 mg/g, kimberlite tailings at 0.8821 mg/g, and silica at 0.3231 mg/g. Later, Yedla and Dikshit [229] examined the performance of a fixed bed adsorber (FBR) column to remove endosulfan from the water environment using wood charcoal. In the latter work, a laboratory column study was performed for 3 successive cycles of operation (adsorption-desorption) and it was found that the column could treat 47.27 bed volumes of endosulfan-contaminated water up to breakthrough and 158.45 bed volumes up to exhaustion and that after the third adsorption/desorption cycle, the removal efficiency for endosulfan was more than 89%. In another study, endosulfan removal efficiency was higher than 90% and regeneration of wood charcoal with methanol was found to be efficient and eventually reaching over 80% efficiency after four cycles [230]. All the more, the adsorption capacity of wood charcoal was 1.77 mg/g with 2–50 mg/L endosulfan concentration [230]. Coexisting pesticides decreased endosulfan adsorption of wood charcoal due to the competitive sorption [231] and this type of behaviour was also observed with the carbon slurry adsorbent in Gupta and Ali [49]. Moreover, Mishra and Patel [232] observed that the efficiency for removal of pesticide was higher in activated charcoal with 94% removal followed by sand at 90% removal. Mishra and Patel [232] pointed out that although the efficiency of sand was better than that of sal wood charcoal, it was not possible to regenerate it. Additionally, these authors indicated that inexpensive acid treatment could increase the surface area of wood charcoal by corroding the pores.

2.3.2. Inorganic materials-derived adsorbents

Besides organic materials, inorganic materials have also been studied for endosulfan removal. Different types of zeolites were studied by Yonli et al. [233] for endosulfan removal. Adsorption data was fitted to the Langmuir isotherm and the maximum adsorption capacity was noted at over 800 mg/g, and a decrease of the adsorption capacities

was also noticed when the acidity of zeolites increased [233]. There was also a linear relation between the adsorption capacities of α -endosulfan and the hydrophobicity of the samples [233]. Noble metal nanoparticles have also been studied as a possible pesticide detection and removal agent [234]. Nair et al. [234] observed that endosulfan adsorbs on gold nanoparticles, and the nanoparticles slowly precipitate from the solution. However, here, adsorption on silver nanoparticles was found to be weaker.

Endosulfan adsorption and desorption on different soil materials have been a persistent subject of research interest, not only for environmental concerns like accumulation, leaching or transport [31,235,236], but also for potential application in water treatment. Clays have been utilized in adsorption since historical times. Kumar and Philip [31] also pointed out the better adsorption capacity of clayey soil over other soil types. According to Iraqi and Iraqi [237] and Tariq et al. [238], the amount of organic matter is one of the crucial factors which affects adsorption capacity. Rauf et al. [239] used bentonite clay as adsorbent for endosulfan removal and reported that adsorption efficiency increased with lengthened contact time and increased amount of adsorbent. Rauf et al. [239] made a number of interesting observations with regards to the efficacy of bentonite clay as an adsorbent for the endosulfan isomers. These observations were: (i) in batch adsorption experiments, endosulfan adsorption was influenced by the initial endosulfan concentration, temperature and bentonite clay dosage, (ii) the adsorption isotherms data at equilibrium for β -endosulfan fitted best with the Temkin model and such data for α -endosulfan fitted with the Freundlich model, (iii) based on the results of activation energy, the adsorption process had occurred most plausibly by chemisorption, (iv) the kinetics of adsorption was pseudo-second-order, and finally the sorption was exothermic and spontaneous. In this work, it was concluded that bentonite clay could be used as a cheap and efficient adsorbent for pesticides removal [239].

Sorption behavior of calix[4]arene based silica resin to remove α and β endosulfan isomers from aqueous solution was studied by Memon et al. [240]. The latter workers found that removal efficiency was dependent on pH, while cation- π interactions played an important role in the removal of endosulfan isomers from the aqueous solutions. Their results of sorption experiment showed that calix[4]arene based silica resin was more efficient than pure silica [240]. Cyclodextrin-functionalized silica nanocomposites were proven to remove pesticides, including endosulfan, from water efficiently, and could be useful for the treatment of pesticides contaminated water [241]. Here, endosulfan, though, had a higher affinity for pristine HMS silica than for cyclodextrin loaded material. In this study, the latter behavior was set on account of the polar attraction of the endosulfan molecule with exposed silica surface. Qian et al. [242] have reported that lateritic red and latosol soils had been very good sorbents for endosulfan which was firmly adsorbed onto the two soils adsorbent materials with the following performance: 0.209 and 0.186 mg/g for α -endosulfan in lateritic red and latosol soil, respectively and 0.148 and 0.140 mg/g for β -endosulfan in lateritic red and latosol soil, respectively.

2.4. Endosulfan removal by membrane separation

In recent years, significant effort has been deployed to develop effective treatment methods based on membrane processes. According to Jhaveri and Murthy [243], pressure-driven membrane-based systems intended for separation have high removal capacity, are flexible in their operation, are cost effective, have less energy requirements and the membrane materials needed are also readily available. Membrane processes are however faced with cake layer formation which eventually leads to the blocking of the membrane pores and fouling of the membrane [244]. Such fouling leads to considerable decreases in the flux of water and thus increases both the energy requirements and as-

sociated costs of treatment [244]. All the more, membrane-based filtration systems only concentrate pollutants into retentates of high concentrations, which thereafter require additional treatment before final discharge [244].

A search in the literature reveals a very sparse number of studies having addressed the removal of endosulfan by membrane-based separation processes. These works, which have been described and discussed below, do provide reasonable evidence of the merits but also of the high variability in the performance of the specific membrane-based separation methods studied for endosulfan sequestration. In point of fact, these merits and variabilities in performance also indicate the relative complexity in the interactions of endosulfan with the membranes under assessment. Banasiak et al. [84] have explained that endosulfan sorption during electrodialysis occurred as a result of membrane catalysed endosulfan degradation, cation- π interactions and hydrogen bonding between the endosulfan molecules and the functional groups present in the membrane. Banasiak et al. [84] also reported that endosulfan sorption onto the ion-exchange membrane at a pH of 7 was more than that occurring at pH 11 due to the alkaline hydrolysed endosulfan and the subsequently lowered bonding ability of this species with the membranes. Banasiak et al. [84] also noticed that due to the presence of humic acid and the subsequent humic acid competitive sorption onto the membrane, the sorption of endosulfan had decreased at the pH of 7 and 11. Later, the work of De Munari et al. [245] has shed more light on the influences of humic acids and their interactions with endosulfan and the separation membrane. In point of fact, De Munari et al. [245] have probed the retention mechanisms of endosulfan in the presence of humic acids two nanofiltration membranes. For the sake of accuracy, the same appellations of the two membrane are used here, namely TFC-SR2 (loose membrane) and TFC-SR3 (tight membrane). The results of De Munari et al. [245] have demonstrated a number of interesting interactions which seem to influence the retention of endosulfan by nanofiltration significantly and could be further studied in view to optimize the operation and performance of such endosulfan removal systems. In a first instance, De Munari et al. [245] reported two mechanisms for endosulfan retention, namely the formation of endosulfan-humic acids complexes leading to increased endosulfan retention, and then a second mechanism wherein there were interactions between the humic acids and the membrane which led to lower endosulfan retention. Furthermore, De Munari et al. [245] also observed that humic acids concentration, pH of the nanofiltration medium and the ratio between the molecular weight of the endosulfan micropollutant and membrane molecular weight cut-off affected the endosulfan retention mechanisms. Moreover, at a pH of 4 and when the humic acids-membrane interactions were not occurring, De Munari et al. [245] observed that endosulfan retention had increased from 60% to 80% in the case of the TFC-SR2 nanofiltration membrane when the humic acids levels were increased, and endosulfan retention was enhanced from 80% to 95% in the case of the TFC-SR3 nanofiltration membrane as a result of endosulfan-humic acids interactions accompanied by complex formation. Conversely, at a pH of 8, De Munari et al. [245] observed that more prominent humic acids-TFC-SR2 nanofiltration membrane interactions induced a decrease from 55% to 30% in endosulfan retention, whereas in the case of the TFC-SR3 nanofiltration membrane endosulfan-humic acids interactions prevailed and endosulfan retention did not decrease.

With a view to promote green chemistry and its application in engineering-related systems formulation intended for environmental pollutant remediation, Pilli et al. [246] have prepared a supported ionic liquid membrane using 1-butyl-2,3-dimethylimidazolium hexafluorophosphate as the ionic liquid and made a number of interesting observation with regards to the permeation of endosulfan. Firstly, they have reported that permeation of endosulfan reached a maximum of 72% after thirty hours of experimentation when using 0.1 mol/L sodium hydrox-

ide as the stripping agent. Pilli et al. [246] also observed that permeation rate of endosulfan decreased from 87% to 55% when pH was varied from 2 to 10. Pilli et al. [246] have also thoroughly explained a plausible endosulfan transport mechanism, the highlights of which read as follows: permeation of endosulfan from the bulk of the feed stream to the stripping phase through supported ionic liquid membrane occurs as a result of concentration diffusion; given endosulfan does not have easily dissociable groups, it is transported via the supported ionic liquid membrane in its molecular form because of a high distribution coefficient between 1-butyl-2,3-dimethylimidazolium hexafluorophosphate which is immobilized on the hydrophilic polyvinylidene fluoride membrane and water; the cationic portion of 1-butyl-2,3-dimethylimidazolium hexafluorophosphate provides protons which then supply the useful energy for endosulfan release; endosulfan which is in its molecular form then diffuses from the feed to the interface following which a complex is formed between the ring system of endosulfan and the cationic part of 1-butyl-2,3-dimethylimidazolium hexafluorophosphate; driven by a concentration gradient, the complex then moves to the stripping phase by permeating through the membrane to eventually form $[\text{Na}]^+[\text{endosulfan}]^-$ after reaction with sodium hydroxide which is the stripping agent. One more interesting observation made by Pilli et al. [246] was that high speed agitation by stirring had induced interfacial shear forces strong enough to cause loss of membrane liquid. As a result, the latter phenomenon rendered the supported ionic liquid membrane instable. At this point, it becomes important to undertake a deeper analysis of the shear force development process and the effects these forces have on the structural integrity and stability of the membrane. It is believed results as those reported by Pilli et al. [246] will assist in optimizing the design of supported ionic liquid membrane and similar structures.

3. Conclusions and research perspectives

Even though endosulfan use is decreasing gradually, highly efficient removal methods are still needed and being actively studied to break the pernicious persistence and long range transport of this compound. The toxicity and persistence of endosulfan pose a serious and severe sets of risks to the population at large and in the environment overall, the various forms of which may not be understated, unfortunately. As behavior of endosulfan is similar to other organochlorine pesticides, research is often focused on real environmental waters containing several pesticides rather than only endosulfan-containing laboratory samples. The majority of presented methods are of excellent academic significance but need further research before largescale, efficient, effective and cost-effective real-scale application could be arranged.

At this point, there are hence a number of critical aspects which are felt to earnestly need immediate research and development attention, and they are:

- Developing such remediation protocols specifically adaptable for in-situ implementation to solid, semi-solid/slurry-type and liquid endosulfan-laden or endosulfan-contaminated media. At this point, the choice of which remediation pathway(s) to select amongst the types discussed above should be based on sound techno-economic feasibility studies. From the above analysis, it appears, from a *prima facie* perspective, that phytoremediation could well be an effective remediation approach for soils and waters contaminated with endosulfan. Once the phytoremediation-based system for endosulfan remediation will have been designed and installed as the core clean-up unit operation, any extension of an additional advanced endosulfan removal unit operation, which can be a standalone or a combination of adsorption, microbe-mediated degradation or photocatalytic degradation, can be made for polishing the final endosulfan levels well down below the permissible safe limits.

- Undertaking further research, and possibly already working out, pursuant to the previous research avenue, on such novel and highly effective degradation methods which will also degrade the endosulfan-degradation metabolites which are themselves harmful. Notwithstanding the different effective techniques which have been able to degrade these metabolites, at this point, further research in developing a new breed of optimal endosulfan-degradation gamma irradiation-based methods have to be probed and optimized. So far the works of Shah et al. [136,247,248] hold some good deal of promise for gamma-irradiation mediated endosulfan degradation.
- From a process engineering perspective, more robust and suitable reactor configurations have to be worked out to enhance the use of supported metal-based catalyst and biocatalyst, supported nanoparticles and supported ionic liquid membrane systems by specifically addressing issues related to poisoning and fouling resistance. Moreover, for endosulfan bioremediation using plants, it appears that constructed wetlands do hold adequate promise to clean up endosulfan contaminated waters, but the implementation of this green technique is still faced with a paucity of field data which could be continually used to plan, design and optimize working conditions in constructed wetland configurations.
- Moreover, there is also the challenge to investigate combinations of endosulfan removal methods in integrated process schemes and work through the relevant process intensification options which will suit best to one contaminated site and/or polluted body. Such integrated endosulfan remediation schemes will also need to be the least intrusive and least destructive as possible, and be hence able to adapt well within the existing environment in the vicinity of the polluted section(s) as smoothly as possible.
- Furthermore, for biological endosulfan remediation methods, the optimized use of genetic engineering and metabolic engineering techniques can be explored to develop such high-performance microbial species and hyperaccumulators which will be as effective in degrading endosulfan isomers in real sites of contaminations as they are in the laboratory-scale microenvironments. Moreover, further work can be done in understanding and thereafter optimizing the plant-endophyte symbiotic relationships [249–252] for more effective phytoremediation of endosulfan in soils and other contaminated media. Thereafter, the harvest and fate of the endosulfan retained in the root and shoot systems of the plants will also have to be elucidated and adapted for minimal secondary pollution.
- It is of utmost importance to make sure there is a minimal translocation of the sequestered endosulfan from the parent polluted medium/media to pristine strata. Hence, the examination of the mobility and fate of endosulfan demand extreme care and objectivity.
- As is the need for the development of any technology, and more so in the current times when green chemistry principles are being implemented to meet the goals of sustainability, lifecycle analysis studies including comprehensive risk assessments and competitive environmental conditions need to be conducted to compare endosulfan clean-up approaches which have scale-up and real-life implementation potentials with excellent endosulfan and endosulfan metabolites efficiencies and chemiselectivities.
- Last but not the least, more intensive awareness and education campaigns and good-practice programs need to be designed and implemented to curb the ill-effects of poor literacy and paucity of technical knowledge which have been attributed to the indiscriminate use of endosulfan.

Notes

The contents of this article were crosschecked in the Turnitin software for similarity and enhanced accordingly.

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