

# A review on water pollution by $\gamma$ HCH (lindane) and its removal using nanomaterials

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**ABSTRACT:** Water pollution by the direct discharge of pollutants (fertilizers, pesticides, heavy metals, etc.) into the river without any pretreatment has become a severe environmental/health hazard. Organochlorine pesticides have extensively been used from the 1940s to 1980 as insecticides in agriculture, weedicides, herbicides, etc. Lindane, an organochlorine pesticide, contributes to bioaccumulation in aquatic organisms and biomagnification in the food chain due to its hydrophobic chemical nature and environmentally persistent property with a very slow rate of degradation. Nanotechnology has proven to be very efficient in removing pollutants. Nanomaterials with unique physical and chemical properties have become a tool for toxicant eradication. Some of the properties of nanomaterials, like high reactivity, adhesion, reflectance, surface plasmon resonance to detect toxic materials, quantum effect in which there is no resistance faced by charged particles, small size, and large surface area to volume, enable them to adsorb many toxicants on their surface, thereby assisting in detoxification and removal of pollutants from water. Some examples include the application of nano-zerovalent iron in the oxidation of groundwater, the reusability of photocatalytic membranes, and many more. This review article presents an updated account of some techniques for eradicating lindane from the aqueous medium.

**KEYWORDS:** lindane; nano catalyst; adsorbents; nanofiltration; nanotubes

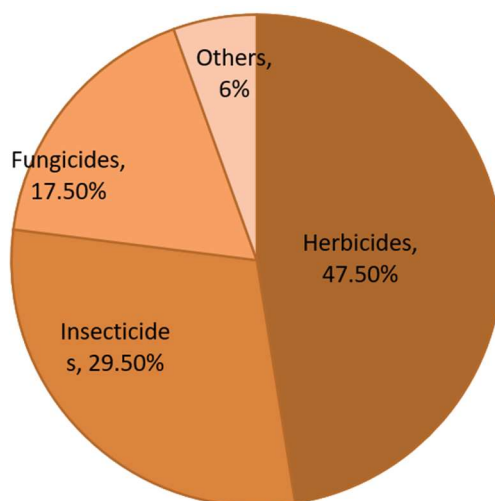
## 1. Introduction

The increased outbursts in population, industrialization, and decreased employment ratio have led to the adaptation of urban life technologies. These technologies, on the one hand, are blossoming for the users, but on the other hand, they are making them diseased in the long run. The fantasy of these technologies is that they never leave users barehanded. In the real sense, everybody is living under the shield of technology.

Water pollution has been a very intriguing subject in all fields of science. The water quality of a river is defined by its physicochemical properties like salt, BOD, pH, suspended solids, speed, colligative (concentration, molarity, molality), and non-colligative (viscosity, solubility, surface tension), which play an important role in the growth of plants and animals. In this review article, a comprehensive study has been made on how nanocatalysts, nanofiltration, and nanoadsorbents can effectively reduce the effects of lindane.

## 2. Water pollution by organochlorine pesticides, especially lindane

The  $\gamma$  isomer of hexachlorocyclohexane (HCH) is the most polar and reactive form of all its isomers,  $\alpha$ ,  $\beta$ ,  $\delta$ ,  $\gamma$ , and  $\epsilon$ . It is a white crystalline solid with a slight musty odour, melting point 112.5 °C, boiling point 323 °C, vapor pressure  $9.4 \times 10^{-6}$  mmHg at 20 °C, density 1.85 g/cm<sup>3</sup>, relative density 1.87, solubility in water (nil), solubility in polar organic solvents 70%–100%, corrosive to aluminum, and non-flammable. Upon heating, it can form toxic fumes of gases such as phosgene, hydrogen chloride, and carbon monoxide. It is slowly metabolized through four possible routes. (i) Dehydrogenation results in gamma-hexachlorocyclohexane; (ii) dehydrochlorination in gamma-pentachlorocyclohexene; (iii) dechlorination to gamma-tetrachlorohexene; and (iv) hydroxylation results in hexachlorocyclohexanol<sup>[1-4]</sup>. Its use has been banned since 2009 under the Stockholm Convention on persistent organochlorine pesticides<sup>[5,6]</sup>. Due to their long half-lives, these chemicals persist in the environment for a long time, adversely affecting the quality of the natural ecosystem<sup>[7]</sup>. The main cause of environmental contamination by lindane is its use in agricultural practices and the intake of foods from treated agricultural commodities. Approximately 12%–30% of lindane volatilizes into the atmosphere, which can again be deposited by rainfall or coming into contact with water bodies ([https://en.wikipedia.org/wiki/Lindane#Pest\\_repellent](https://en.wikipedia.org/wiki/Lindane#Pest_repellent)). So, this cycle is always continued and is known as the grasshopper effect. As a pharmaceutical, it is used for the treatment of lice and scabies; in households as an insecticide; in agriculture as a weedicide or as a fungicide; to treat live stocks, pets, and food crops. Further, their non-hydrophilic and non-biodegradable nature contributes to biomagnification and bioaccumulation in aquatic organisms<sup>[8]</sup>. As an insecticide, it protects crops from insects like locusts, which have put the economy of farmers at risk. The use of fertilizers and pesticides by farmers to grow crops at a faster rate than their growth at optimal conditions results in increased crop turnover. However, this practice has enormously disrupted the natural flora and fauna of soil and water. About 45% of the crops have been destroyed because of pesticide use<sup>[9]</sup>. The nanoparticles of fertilizers, pesticides, etc. endanger the environment. It is difficult to predict when its drift in the air will subside as it is extremely stable in the air<sup>[10]</sup>. **Figure 1** shows the yearly worldwide use of different pesticide formulations<sup>[11]</sup>.



**Figure1.** Worldwide annual pesticide usage.

The human population consuming the fish from any pesticide-contaminated river or pond may be at risk. The residues of lindane have been analyzed in different components like soil, water, air, plants, and even humans. The rhizospheric mycobacterium species p27 can degrade the lindane in soil and help

increase plant growth<sup>[12]</sup>. The safe drinking water directives determine a limit of 0.5 µg/L for all pesticides in water and 0.1 µg/L for individual pesticides<sup>[13]</sup>. Acute health effects from lindane exposure or breathing can cause irritation to the skin, eyes, nose, throat, and lungs. It can also cause headaches, nausea, vomiting, dizziness, seizures, irritability, restlessness, muscle weakness, twitching, convulsions, and a coma. Chronic effects can cause cancer, decreased fertility in females, damage to the developing fetus, blood cells causing anemia, kidney damage, liver damage, and arrhythmia (<https://nj.gov/health/eoh/rtkweb/documents/fs/1117.pdf>). There are numerous studies on lindane toxicity, sublethal exposure of lindane to fish, and changes in enzyme activities that prove its adverse effects on aquatic bodies<sup>[14–17]</sup>. There are several methods for lindane removal from the water, like the non-thermal plasma method, the use of organ zeolites, and the use of microorganisms (gram-negative) as bioremediation. Among all these methods mentioned and many more, no doubt nanotechnology has proved to be very efficient in lindane removal and wastewater treatment.

### 3. Nanotechnology as a tool to eradicate pollutants

The use of nanomaterials has proven to mitigate the levels of pollutants, including pesticides, which can be dangerous, life-threatening, and pose serious threats to aquatic life. The nanoparticles with large surface area, high reactivity for contaminants, magnetic properties, and surface modifiability make them efficient at removing pollutants from water<sup>[18,19]</sup>. They show a quantum effect by decreasing the activation energy for the reaction to occur and diffusing into a contamination zone that microparticles cannot access. Engineered nanomaterials like nano-catalysts capture freely available solar energy to decontaminate water under visible light<sup>[20]</sup>. Nano-metal oxides of titanium and zinc have been used as photocatalysts and adsorbents. Zeolites have been shown to remove heavy metals.

**Nanofiltration** is a technique to remove organic matter and divalent ions from surfaces and groundwater, making it potable and soft. In this process, a membrane (dense/porous) is used that separates solid matter from the aqueous phase. Nanostructured catalytic membranes made of cellulose acetate, polyvinylidene fluoride, polysulphone, etc. are efficient at removing chlorinated toxicants. Properties like molecular weight, membrane pore size, dipole moment, and lipophilicity affect the adsorption of pesticides on membranes. The nanofiltration technique is superior to ultra (0.01 µ) and micro (0.1 µ) filtration, which removes particles in the range of 0.00–0.0001 µ<sup>[21,22]</sup>. This technique works on a diffusion-permeation mechanism. The uncharged pollutants are separated based on the size exclusion limit of the membrane. In contrast, charged contaminants separate based on charge repulsion/electrostatic interaction and require less pressure (7–30 atm) than reverse osmosis (20–100 atm)<sup>[23–27]</sup>. Due to the fixed surface charge of nanomembranes, they possess selective binding specificity to various contaminants in the liquid, apart from physical separation. The 90% retention of toxicants on the membrane depends on the membrane's pore size<sup>[28]</sup>. Hydrogen bonding between organochlorine pesticides and hydrophilic groups on membranes enhances the adsorption of pesticides. The pesticides' polarity/dipole moment helps to retain the toxicants on the membrane; conversely, increased dipole moment leads to lower retention<sup>[29]</sup>. The formation of macromolecular complexes or natural organic matter also intensifies retention<sup>[30]</sup>. Adsorption of toxicants increases with increasing ionic strength and decreasing the pH of feed water<sup>[31]</sup>.

Pesticide adsorption on membranes follows pseudo-second-order kinetics due to oxides of metals such as ferric, manganese, aluminum, titanium, and magnesium. The adsorption process is spontaneous and exothermic. It destroys toxicants, converting them into safer byproducts at different temperatures<sup>[32]</sup>. Oxides of ferric and zinc nanoparticles are potentially useful for the remediation of lindane-polluted

sites because they can reach or penetrate zones that are inaccessible to micro-size solid catalysts<sup>[33]</sup>.

Carbon nanotubes made of graphite and graphene (carbon nanomaterials) have good potential to remove pesticides from water. The small pore size of these tubes allows water to pass at a fast speed while retaining the toxicants<sup>[34,35]</sup>. The adsorption of organic chemicals on carbon nanotubes (multi/single/hybrid) is due to interactions like the hydrophobic effect, covalent bonding,  $\pi$ - $\pi$  interactions, hydrogen bonding, and electrostatic interactions, which make them more hydrophilic and suitable for the sorption of low molecular weight and polar compounds. Graphene can adsorb pesticides ranging from 600–2000 mg/g from water<sup>[36]</sup>. The presence of oxidizing agents tends to increase toxicant retention.

**Nano-catalyst:** Photocatalytic oxidation is a process to degrade non-biodegradable and toxic pollutants into harmless products, carbon dioxide, and water. In this technique, a positively charged semiconductor acts as a catalyst, which absorbs light and generates superoxide/hydroxyl radicals in water, which helps in the oxidative reduction of pollutants<sup>[37]</sup>. The different types of semiconductor materials used as photocatalysts are ZnO (zinc oxide), TiO<sub>2</sub> (titanium dioxide), Fe<sub>2</sub>O<sub>3</sub> (ferric oxide), CdS (cadmium sulfide), and WO<sub>3</sub> (tungsten oxide)<sup>[38]</sup>. WO<sub>2</sub> showed increased adsorption capacity for organic dyes in water, TiO<sub>2</sub> for pesticide degradation<sup>[39,40]</sup>, and non-metallic silica oxide for the removal of organic compounds and heavy metals<sup>[41,42]</sup>. Doping of TiO<sub>2</sub> with nitrogen in a 16:1 M ratio showed 100% photocatalytic oxidation of lindane in visible light, whereas 37.5% under UV light<sup>[43]</sup>. Biopolymers of iron sulfide nanoparticles degraded 94% lindane in 8 h, and 100% degradation of lindane took place under Fe<sub>3</sub> (nano)/H<sub>2</sub>O<sub>2</sub>/UV in 320 min of UV irradiation time<sup>[44,45]</sup>. C18-embedded Fe<sub>3</sub>O<sub>4</sub> are magnetic nanoparticles used for separating non-polar (organochlorines) and polar pesticides (organophosphates). The magnetic nano-iron particles with enzymes decrease their activation energy and increase longevity, durability, and stability by keeping the catalyst in a reduced state and not letting it oxidize<sup>[46]</sup>. The studies on biocatalytic dechlorination of lindane have been done using nanoparticles of Pd (0) coated on *Shewanella oneidensis* and Pd/FeO bimetallic nanoparticles with *Sphingomonas* sp. NM05.

**Nanosorbents:** This is a surface phenomenon. The sorption of pollutants on the sorbent surface depends on the transport of contaminants from water to the sorbent surface, adsorption at the sorbent surface, and lastly, transportation within the sorbent. Magnetic nanoadsorbents with a particular ligand affinity bind to organic contaminants as receptors<sup>[47]</sup>. Iron oxide nanostructures remove organic pollutants and heavy metals from water and can later be regenerated using magnetic separation or catalytic combustion at 300 °C. Granulorous activated carbon has been the best for the removal of organic pollutants as it is a thermally and chemically stable material. The nano-zero-valent ions combined with the reactive nanoscale iron products are best for the dechlorination of organochlorine pesticides. They degrade pollutants effectively with minimal generation of secondary pollutants. The nano-zero-valent iron provides complete reductive degradation of lindane into benzene and chloride within 24 h<sup>[48]</sup>. Some of the biosorbents made from salmon milt DNA hydrogel beads have been used for dioxin eradication<sup>[49]</sup>.

## 4. Conclusion

The unique properties of nanomaterials, like their small size, high reactivity, and eco-friendliness, make them highly efficient for removing toxicants from water. Several studies employing green methods have been done for the eradication of pesticides from the water. Each technique has its own importance, uniqueness, and specificity. Nanozinc oxide with hydrogen peroxide, photo Fenton nanomaterials used as catalysts and adsorption, and many other techniques have been found to be efficient in lindane removal. Though they have proved to be good, their use at the commercial level is also very challenging. Long-term study assessments need to be done to know about different types of risk factors that may arise when

using these technologies.

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## Conflict of interest

The authors declare no conflict of interest.

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## Appendix

**Table A1.** A list of nano technological and bio sorbents to remove pollutants especially lindane.

Author(s)	Year	Title
Ningthoujam, et al.	2023	Green production of zero-valent iron nanoparticles using pomegranate peel extracts and its use in lindane degradation
Kajitvichyanukul et al.	2022	Challenges and effectiveness of nanotechnology-based photocatalysis for pesticides-contaminated water: A review
Yadav and Ahmaruzzaman	2021	Recent advances in the development of nanocomposites for effective removal of pesticides from aqueous stream
Uba and Baba	2021	The use of plants, nanotechnology and surfactants in lindane remediation
Nguyen et al.	2020	Removal of lindane from aqueous solution using aluminum hydroxide nanoparticles with surface modification by anionic surfactant
Fiorenza et al.	2019	Selective photodegradation of 2,4-D pesticide from water by molecularly imprinted TiO <sub>2</sub>
Taghizade et al.	2018	Application of nanotechnology in pesticides removal from aqueous solutions
Golshan et al.	2018	Photocatalytic activation of peroxymonosulfate by TiO <sub>2</sub> anchored on copper ferrite (TiO <sub>2</sub> @CuFe <sub>2</sub> O <sub>4</sub> ) into 2,4-D degradation
Rani et al.	2017	Recent strategies for removal and degradation of persistent & toxic organochlorine pesticides using nanoparticles
Maddah et al.	2017	Fe <sub>3</sub> O <sub>4</sub> /CNT magnetic nanocomposites as adsorbents to remove organophosphorus pesticides from environmental water
Khan et al.	2016	Efficient degradation of lindane in aqueous solution by iron (II) and/or UV activated peroxymonosulfate
Baruah et al.	2016	Perspectives and applications of nanotechnology in water treatment
El-Kady et al.	2016	Evaluation of sorption of lindane on activated carbon derived from rice straw and fungal biomass of phanerochaete chrysosporium
Baruah et al.	2015	Nanotechnology in water treatment
Tanujjal et al.	2014	Applications of nanotechnology in wastewater treatment
Rizwan et al.	2014	Ecofriendly application of nanomaterials: Nanobioremediation
Kaur et al.	2014	Synthesis and surface engineering of magnetic nanoparticles for environmental cleanup and pesticide residue analysis
Jaseetha et al.	2014	Degradation of lindane by a novel embedded bio-nano hybrid system in aqueous environment
Derbalah et al.	2014	Monitoring and remediation of organochlorine residues in water
De et al.	2014	Worldwide pesticide use. In: <i>Targeted Delivery of Pesticides Using Biodegradable Polymeric Nanoparticles</i>
Zhang et al.	2013	Superior adsorption capacity of hierarchical iron oxide @ magnesium silicate magnetic nano rods for fast removal of organic pollutants from aqueous solution
Qu et al.	2013	Applications of nanotechnology in water and wastewater treatment
Singh et al.	2013	An integrated (nano-bio) technique for degradation of $\gamma$ -HCH contaminated soil
Reddy et al.	2013	Emerging green chemical technologies for the conversion of CH <sub>4</sub> to value-added products
Prachi et al.	2013	Nanotechnology in waste water treatment
Musbah et al.	2013	Retention of pesticides and metabolites by nano filtration by effects of size and dipole moment
Danwittayakul et al.	2013	Enhancement of photocatalytic degradation of methyl orange by supported Zinc Oxide nanorods/Zinc Stannate (ZnO/ZTO) on porous substrates



**Table A1.** (Continued).

<b>Author(s)</b>	<b>Year</b>	<b>Title</b>
Coronado et al.	2013	Design of advanced photocatalytic materials for energy and environmental applications
Bhattacharya et al.	2013	Role of nanotechnology in water treatment and purification: Potential applications and implications
Behnam et al.	2013	Destructive adsorption of diazinon pesticide by activated carbon nanofibers containing Al <sub>2</sub> O <sub>3</sub> and MgO nanoparticles
Palakas et al.	2012	Removal of pesticides from water by N.F. and R.O. membranes—A review
Fryxell	2012	Environmental applications of nano materials
El-Safty	2012	Topical developments of nanoporous membrane filters for Ultrafine Noble metal nanoparticles
Anbia et al.	2012	Removal of acid dyes from aqueous media by adsorption onto amino-functionalized nanoporous silica SBA-3
Alvarez et al.	2012	Maize plants ( <i>Zea mays</i> ) root exudates enhance lindane removal by native <i>Streptomyces</i> strains
Wu et al.	2011	Surface plasmon resonance-induced visible light photocatalytic reduction of graphene oxide: Using Ag nanoparticles as a plasmonic
Sarkar et al.	2011	Photoselective excited state dynamics in ZnO-Au nanocomposites and their implications in photocatalysis and dye-sensitized solar cells
Qiu et al.	2011	Controllable corrugation of chemically converted graphene sheets in water and potential application for nanofiltration
Kochuveedu et al.	2011	Surface-plasmon-induced visible light photocatalytic activity
Chan et al.	2011	Recent developments of metal oxide semiconductors as photocatalysts in advanced oxidation processes (AOPs) for treatment of dye waste-water
Cecen et al.	2011	Activated carbon for water and wastewater treatment: Integration of adsorption and biological treatment
Cahill et al.	2011	Semi-automated liquid chromatography-mass spectrometry (LC-MS/MS) method for basic pesticides in wastewater effluents
Zhang et al.	2010	Preparation of carbon coated Fe <sub>3</sub> O <sub>4</sub> nanoparticles and their application for solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples
Senthilnathan et al.	2010	Photocatalytic degradation of lindane under UV and visible light using N-doped TiO <sub>2</sub>
Kowalska et al.	2010	Visible-light-induced photocatalysis through surface plasmon excitation of gold on titania surfaces
Ji et al.	2010	First principles calculations of N:H co-doping effect on energy gap narrowing of ZnO
Jeon et al.	2010	Morphology-controlled synthesis of highly adsorptive tungsten oxide nanostructures and their application to water treatment
Hu et al.	2010	Synthesis of mono disperse Fe <sub>3</sub> O <sub>4</sub> @silica core-shell microspheres and their application for removal of heavy metal ions from water
Fu et al.	2010	Focus on the morphology-dependent nano catalysis papers
Cloete et al.	2010	Nanotechnology in water treatment applications
Baruah et al.	2010	Enhanced visible light photocatalysis through fast crystallization of zinc oxide nanorods
Rehman et al.	2009	Strategies of making TiO <sub>2</sub> and ZnO visible light active
Elliott et al.	2009	Degradation of lindane by zero-valent iron nanoparticles
Baruah et al.	2009	Photoreactivity of ZnO nanoparticles in visible light: Effect of surface states on electron transfer reaction
Baruah et al.	2009	Nanoparticle applications for environmental control and remediation
Ullah et al.	2008	Photocatalytic degradation of organic dyes with manganese-doped ZnO nanoparticles
Tao et al.	2008	Synthesis and optical properties of halogen-doped ZnO phosphor

**Table A1.** (Continued).

Author(s)	Year	Title
Satapanajaru et al.	2008	Remediation of atrazine-contaminated soil and water by nano zero-valent iron
Mauter et al.	2008	Environmental applications of carbon-based nanomaterials
Graciani et al.	2008	Au ↔ N synergy and N-doping of metal oxide-based photocatalysts
Drewes et al.	2008	Comparing nanofiltration and reverse osmosis for treating recycled water
Baruah et al.	2008	Visible light photocatalysis by tailoring crystal defects in zinc oxide nanostructures
Mertens et al.	2007	Biocatalytic dechlorination of lindane by nano-scale particles of Pd(0) deposited on <i>Shewanella oneidensis</i>
Li et al.	2007	Preparation of silica-supported porous sorbent for heavy metal ions removal in wastewater treatment by organic-inorganic hybridization combined with sucrose and polyethylene glycol imprinting
Kanade et al.	2007	Self-assembled aligned Cu doped ZnO nanoparticles for photocatalytic hydrogen production under visible light irradiation
Zhang et al.	2006	Self-assembled 3D flowerlike iron oxide nanostructures and their application in water treatment
Riu et al.	2006	Nanosensors in environmental analysis
Liu et al.	2006	Nanoparticles and their biological and environmental applications
Gorria et al.	2006	Synthesis of magnetically separable adsorbents through the incorporation of protected nickel nanoparticles in an activated carbon
Adak et al.	2006	Fixed bed column study for the removal of crystal violet (C. I. Basic Violet 3) dye from aquatic environment by surfactant-modified alumina. Dyes and Pigments
Zhao et al.	2005	Adsorption properties of mesoporous silicas for organic pollutants in water
Peng et al.	2005	Carbon nanotubes-iron oxides magnetic composites as adsorbent for removal of Pb (II) and Cu (II) from water
Paknikar et al.	2005	Degradation of lindane from aqueous solutions using iron sulfide nanoparticles stabilized by biopolymers
Nurmi et al.	2005	Characterization and properties of metallic iron nanoparticle: Spectroscopy, electrochemistry, and kinetics
Liu et al.	2005	Preparation and characterization of DNA hydrogel bead as selective adsorbent of dioxins
Fitzgerald et al.	2005	Cobalt-doped ZnO—A room temperature dilute magnetic semiconductor
Aksu et al.	2005	Application of biosorption for the removal of organic pollutants: A review
Nghiem et al.	2004	Trace contaminant removal with nanofiltration. In: <i>Nanofiltration—Principles and Applications</i>
Fujihara et al.	2004	Tunable visible photoluminescence from ZnO thin films through Mg-doping and annealing
Zhang	2003	Nano-scale iron particles for environmental remediation: An overview
Chaudhary et al.	2003	Granular activated carbon (GAC) adsorption in tertiary wastewater treatment
Oliveira	2002	Activated carbon/iron oxide magnetic composites for the adsorption of contaminants in water
Košutić and Kunst	2002	Removal of organics from aqueous solutions by commercial RO and NF membranes of characterized porosities
Gupta et al.	2002	Removal of lindane and malathion from wastewater using bagasse fly ash—A sugar industry waste
Bhatkhande et al.	2001	Photocatalytic degradation for environmental applications
Young et al.	1998	The removal of lindane from aqueous solution using a fungal biosorbent
Sayles et al.	1997	DDT, DDD, and DDE dechlorination by zero-valent iron

**Table A1.** (Continued).

<b>Author(s)</b>	<b>Year</b>	<b>Title</b>
Ju et al.	1997	Study on the biosorption of lindane
Šafařík et al.	1997	Adsorption of water-soluble organic dyes on magnetic charcoal
Bowen et al.	1996	Nanofiltration: Principles and applications
Hagfeldt et al.	1995	Light-induced redox reactions in nanocrystalline systems
Mills et al.	1993	Water purification by semiconductor photocatalysis lindane
Cadotte et al.	1988	Nanofiltration membranes broaden the use of membrane separation technology