

## **CHAPTER 2**

### **ENVIRONMENTAL APPLICATION OF NANOTECHNOLOGY**

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Nanotechnology is an emerging field that covers a wide range of technologies which are presently under development in nanoscale. It plays a major role in the development of innovative methods to produce new products, to substitute existing production equipment and to reformulate new materials and chemicals with improved performance resulting in less consumption of energy and materials and reduced harm to the environment as well as environmental remediation. Although, reduced consumption of energy and materials benefits the environment, nanotechnology will give possibilities to remediate problems associated with the existing processes in a more sustainable way. Environmental applications of nanotechnology address the development of solutions to the existing environmental problems, preventive measures for future problems resulting from the interactions of energy and materials with the environment, and any possible risks that may be posed by nanotechnology itself.

This article gives a comprehensive review on the ongoing research and development activities on environmental remediation by nanotechnology. First, the essential aspects of environmental problems are reviewed and then the application of nanotechnology to the compounds, which can serve as environmental cleaning, is described. Various environmental treatments and remediations using different types of nanostructured materials from air,

contaminated wastewater, groundwater, surface water and soil are discussed. The categories of nanoparticles studied include those which are based on titanium dioxide, iron, bimetallics, catalytic particles, clays, carbon nanotube, fullerenes, dendrimers and magnetic nanoparticles. Their advantages and limitations in the environmental applications are evaluated and compared with each other and with the existing techniques. The operating conditions such as pH, required doses, initial concentrations, and treatment performances are also presented and compared. The report covers the bulk of the published researches during the period of 1997 to 2007.

## **1. General Introduction**

Nanotechnology is a field of applied science, focused on the design, synthesis, characterization and application of materials and devices on the nanoscale. This branch of knowledge is a sub-classification of technology in colloidal science, biology, physics, chemistry and other scientific fields and involves the study of phenomena and manipulation of materials in the nanoscale [1-3]. This results in materials and systems that often exhibit novel and significantly changing physical, chemical and biological properties due to their size and structure [3]. Also, a unique aspect of nanotechnology is the "vastly increased ratio of surface area to volume", present in many nanoscale materials, which opens new possibilities in surface-based sciences [4].

Similar to nanotechnology's success in consumer products and other sectors, nanoscale materials have the potential to improve the environment, both through direct applications of those materials to detect, prevent, and remove pollutants, as well as indirectly by using nanotechnology to design cleaner industrial processes and create environmentally responsible products. For example, iron nanoparticles can remove contaminants from soil and ground water; and nanosized

sensors hold promise for improved detection and tracking of contaminants.

Behavior of materials at nanoscale is not necessarily predictable from what we know at macroscale. At the nanoscale, often highly desirable, properties are created due to size confinement, dominance of interfacial phenomena, and quantum effects. These new and unique properties of nanostructured materials, nanoparticles, and other related nanotechnologies lead to improved catalysts, tunable photoactivity, increased strength, and many other interesting characteristics [5-7].

As the exciting field of nanotechnology develops, the broader environmental impacts of nanotechnology will also need to be considered. Such considerations might include: the environmental implications of the cost, size and availability of advanced technological devices; models to determine potential benefits of reduction or prevention of pollutants from environmental sources; potential new directions in environmental science due to advanced sensors; effects of rapid advances in health care and health management as related to the environment; impact of artificial nanoparticles in the atmosphere; and impacts from the development of nanomachines [8].

Research is needed using nanoscale science and technology to identify opportunities and applications to environmental problems, and to evaluate the potential environmental impacts of nanotechnology. Also, approaches are needed to offer new capabilities for preventing or treating highly toxic or persistent pollutants, which would result in the more effective monitoring of pollutants or their impact in the ways not currently possible.

Early application of nanotechnology is remediation using nanoscale iron particles. Zero-valent iron nanoparticles are deployed *in situ* to remediate soil and water contaminated with chlorinated compounds and heavy metals.

Among the many applications of nanotechnology that have environmental implications, remediation of contaminated groundwater using nanoparticles containing zero-valent iron is one of the most prominent examples of a rapidly emerging technology with considerable potential benefits. There are, however, many uncertainties regarding the fundamental features of this technology, which have made it difficult to engineer applications for optimal performance or to assess the risk to human or ecological health. This important aspect of nanoparticles needs extensive considerations as well.

One of the main environmental applications of nanotechnology is in the water sector. As freshwater sources become increasingly scarce due to overconsumption and contamination, scientists have begun to consider seawater as another source for drinking water. The majority of the world's water supply has too much salt for human consumption and desalination is an option but expensive method for removing the salt to create new sources of drinking water. Carbon nanotube membranes have the potential to reduce desalination costs. Similarly, nanofilters could be used to remediate or clean up ground water or surface water contaminated with chemicals and hazardous substances. Finally, nanosensors could be developed to detect waterborne contaminants.

Air pollution is another potential area where nanotechnology has great promise. Filtration techniques similar to the water purification methods described above could be used in buildings to purify indoor air volumes. Nanofilters could be applied to automobile tailpipes and factory smokestacks to separate out contaminants and prevent them from entering the atmosphere. Finally, nanosensors could be developed to detect toxic gas leaks at extremely low concentrations. Overall, there is a multitude of promising environmental applications for nanotechnology. Much of the current research is focused on energy and water technologies.

Environmental remediation includes the degradation, sequestration, or other related approaches that result in reduced risks to human and environmental receptors posed by chemical and radiological contaminants. The benefits, which arise from the application of nanomaterials for remediation, would be more rapid or cost-effective cleanup of wastes.

Cost-effective remediation techniques pose a major challenge in the development of adequate remediation methods that protect the environment. Substances of significant concern in remediation of soils, sediment, and groundwater include heavy metals (e.g., mercury, lead, cadmium) and organic compounds (e.g., benzene, chlorinated solvents, creosote, and toluene). Specific control and design of materials at the molecular level may impart increased affinity, capacity, and selectivity for pollutants. Minimizing quantities and exposure of hazardous wastes to the air and water and providing safe drinking water are among the environmental protection agencies' goals. In this regards, nanotechnology could play a key role in pollution prevention technologies [9-11].

In the present article, we have reviewed processes used for the environmental treatment by nanotechnology. It should be mentioned that due to the high variety of techniques and conditions used by different researchers, the results are only summarized in the form of tables and various nanosystems are described in the text.

## **2. Nano-Materials and Their Environmental Applications**

### ***2.1. Titanium Dioxide (TiO<sub>2</sub>) Based Nanoparticles***

Titanium dioxide (TiO<sub>2</sub>) is one of the popular materials used in various applications because of its semiconducting, photocatalytic, energy converting, electronic and gas sensing properties. Titanium dioxide crystals are present in three different polymorphs in nature that

in the order of their abundance, are Rutile, Anatase and Brookite (See Figure.1) [12].

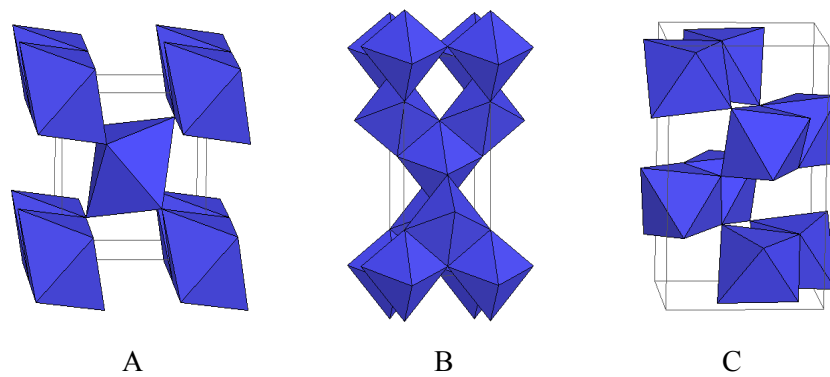


Figure 1. The crystal structures of A) rutile, B) anatase, C) brookite [Ref. 13], <http://ruby.colorado.edu/~smyth/min/tio2.html>.

Many researchers are focused on TiO<sub>2</sub> nanoparticle and its application as a photocatalyst in water treatment. Nanoparticles that are activated by light, such as the large band-gap semiconductors titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO), are frequently studied for their ability to remove organic contaminants from various media. These nanoparticles have the advantages of readily available, inexpensive, and low toxicity. The semiconducting property of TiO<sub>2</sub> is necessary for the removal of different organic pollutants through excitation of TiO<sub>2</sub> semiconductor with a light energy greater than its band gap, which could generate electron hole pairs. These may be exploited in different reduction processes at the semiconductor/solution interface.

A semiconductor can adopt with donor atoms that provide electrons for the conduction band where they can carry a current. These materials

can also adopt with acceptor atoms that take electrons from the valence band and leave behind some positive charges (holes). The energy levels of these donors and acceptors fall into the energy gap.

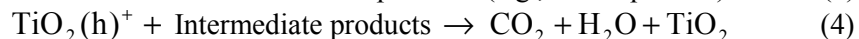
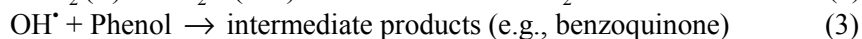
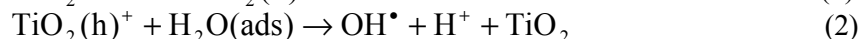
The most affecting properties of semiconducting nanoparticles are distinguished changes in their optical properties compared to those of bulk materials. In addition, there is a significant shift in optical absorption spectra toward the blue shift (shorter wavelengths) as the particle size is reduced [14].

Stathatos *et al.* [15] used reverse micelle technique to produce TiO<sub>2</sub> nanoparticles and deposited them as thin films. They deposited TiO<sub>2</sub> mesoporous films on glass slides by dip-coating in reverse micellar gels containing titanium isopropoxide. The films demonstrated high capacity in adsorption of several dyes from aqueous and alcoholic solutions. It had also a rapid degradation of the adsorbed dyes when the colored films were exposed to the visible light.

It is known that, the semiconducting properties of TiO<sub>2</sub> materials is responsible for the removal of various organic pollutants, but the rapid recombination of photo-generated electron hole pairs and the non-selectivity of the system are the main problems that limit the application of photocatalysis processes [16]. It was suggested that, replacing adsorbed solvent molecules and ions by chelating agents, i.e. surface modification, changes the energetic situation of surface states and considerably alters the chemistry, which is taking place at the surface of titanium dioxide (TiO<sub>2</sub>). The effect of surface modification of nanocrystal TiO<sub>2</sub> with specific chelating agents such as arginine, lauryl sulfate, and salicylic acid on photocatalyst degradation of nitrobenzene (NB) was also investigated and the results are shown in Table 1.

Phenol is one of the toxic materials found in municipal and waste waters. Synthesized titanium dioxide nanoparticles of both Anatase and Rutile forms were used for wet oxidation of phenols by hydrothermal

treatment of microemulsions and their photocatalytic activity [17]. Such treatment has the advantage that the size of particles is affected by the ratio of surfactant to water. Size of water droplets in the reverse microemulsions is found to be almost the same as that of formed particles. The main reactions proposed for phenol degradation are [17]:



In another study, a novel composite reactor with combination of photochemical and electrochemical system was used for the degradation of organic pollutants [18]. In this process, UV excited nanostructure  $\text{TiO}_2$ , was served as the photocatalyst. The reactor performance was evaluated by the degradation process of Rhodamine 6G (R-6G) (See Figure 2).

Fine  $\text{TiO}_2$  particles have shown better efficiency than the immobilized catalysts, but complete separation and recycling of fine particles (less than  $0.5\mu\text{m}$ ) from the treated water, are very expensive. Therefore, from the economics point of view, this method is not suitable for the industrial-scale. This problem was solved by fixing the carbon-black-modified nano- $\text{TiO}_2$  (CB- $\text{TiO}_2$ ) on aluminum sheet as a support [19]. The photocatalytic activity of CB- $\text{TiO}_2$  thin films was observed to be 1.5 times greater than that of  $\text{TiO}_2$  thin films in the degradation of reactive Brilliant Red X-3B. Core  $\text{SrFe}_{12}\text{O}_{19}$  nanoparticles and  $\text{TiO}_2$  nanocrystals were also synthesized as the magnetic photocatalytic particles [20]. This system recovers the photocatalyst particles and protects them from the treated water stream by applying an external magnetic field (See Table1). In the presence of natural organic matters in water, many problems may happen since they can occupy the

catalytically active surface sites and lead to much lower decomposition efficiency. One useful method for overcoming the mentioned problem is the combination of adsorption and oxidative destruction technique.

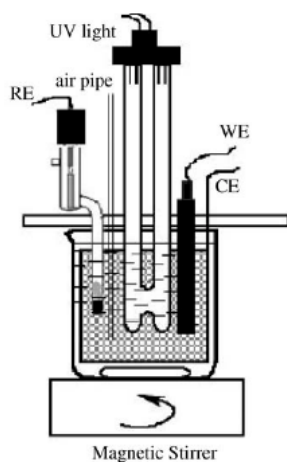


Figure 2. The diagram of the composite reactor with combination of photochemical and electrochemical system used for the degradation of organic pollutants (RE=reference electrode; WE=working electrode; and CE=counter electrode). From [Ref. 18], J. Chen *et al.* Water Research. 37, 3815 (2003).

Ilisz *et al.* [21] used a combination of  $\text{TiO}_2$ -based photocatalysis and adsorption for the decomposition of 2-chlorophenol (2-CP). The three combined systems that they studied and compared were:

- (i)  $\text{TiO}_2$  intercalated into the interlamellar space of a hydrophilic montmorillonite by means of a heterocoagulation method ( $\text{TiO}_2$  pillared montmorillonite, TPM);
- (ii)  $\text{TiO}_2$  hydrothermally crystallized on hexadecylpyridinium chloride-treated montmorillonite (HDPM-T);

- (iii) Hexadecylpyridinium chloride-treated montmorillonite (HDPM) applied as an adsorbent and Degussa P25 TiO<sub>2</sub> as a photocatalyst (HDPM/TiO<sub>2</sub>).

The latter was shown the highest rate for pollutant decomposition compared to the others and it could be re-used without further regeneration. In another application, the work was focused on crystalline Titania with ordered nanodimensional porous structures [22]. In this regard, the mesoporous spherical aggregates of Anatase nanocrystal were first fabricated and then cetyltrimethylammonium bromide was employed as the structure-directing agent. After that, the interaction between cyclohexane micro-droplets and the cetyltrimethylammonium bromide self-assemblies was applied to photo-degrade a variety of organic dye pollutants in aqueous media such as methyl orange (See Table 1).

In addition, in the study of Peng *et al.* [23], the mesoporous titanium dioxide nanosized powder was synthesized using hydrothermal process by applying cetyltrimethylammonium bromide (CTAB) as surfactant-directing and pore-forming agent. They synthesized and applied the nanoparticle products for the oxidation of Rhodamine B (RB) (See Table 1).

The mesoporous structures with high surface area are able to provide simple accessibility and more chances for guest molecules and light to receive by the active sites. In this regard, Paek *et al.* [24] fabricated mesoporous photocatalysts with delaminated structure. The exfoliated layered titanate in aqueous solution was reassembled in the presence of Anatase TiO<sub>2</sub> nanosol particles to make a large number of mesopores and eventually a large surface area TiO<sub>2</sub> photocatalysts (See Table 1).

P-25 TiO<sub>2</sub> is a highly photoactive form of TiO<sub>2</sub> composed of 20-30% Rutile and 70-80% Anatase TiO<sub>2</sub> with particle sizes in the range of

12 to 20 nm. Adams *et al.* [25] synthesized SBA-15 mesoporous silica thin films encapsulating Degussa P-25 TiO<sub>2</sub> particles via a block copolymer templating process. High calcination temperature (above 450°C) is usually required to form a regular crystal structure. However, in the meantime, high temperature treatment would reduce the surface area and loose some hydroxyl or alkoxide group on the surface of TiO<sub>2</sub>, which prevent simple dispersion. This problem was solved by hydrothermal process to produce pure Anatase-TiO<sub>2</sub> nanoparticles at low temperature (200°C, 2 h). These TiO<sub>2</sub> nanoparticles have several advantages, such as fully pure Anatase crystalline form, fine particle size (8 nm) with more uniform distribution and high-dispersion in either polar or non-polar solvents, stronger interfacial adsorption and convenient coating on different supporting materials compared to the other TiO<sub>2</sub> powders.

Asilturk *et al.* [26] examined the behavior of Anatase nano-TiO<sub>2</sub> in catalytic decomposition of Rhodamine B (RB) dye. Rhodamine B was fully decomposed with the catalytic action of nano-TiO<sub>2</sub> in a short time of about 60 min's. It was found that, the nano-TiO<sub>2</sub> could be repeatedly used with increasing the photocatalytic activity.

In recent years, the technology of ultrasonic degradation has been studied and extensively used to treat some organic pollutants. The ultrasound with low power was employed as an irradiation source to make heat-treated TiO<sub>2</sub> powder. This method was used for decomposition of parathion with the nanometer Rutile titanium dioxide (TiO<sub>2</sub>) powder as the sonocatalyst after treatment of high-temperature activation [27]. There is an appropriate method to increase the photocatalytic efficiency of TiO<sub>2</sub>, which consists of adding a co-adsorbent such as activated carbon (AC) to it. The resulting synergy effect can be explained by the formation of a common contact interface between different solid phases. Activated carbon acts as an adsorption

trap for the organic pollutant, and then immediately degraded through mass transfer of organic substances to the photoactivated TiO<sub>2</sub> on the surface. In the study of Li *et al.* [28], carbon grain coated with activated nano-TiO<sub>2</sub> (20-40 nm) (TiO<sub>2</sub>/AC) was prepared and used for the photodegradation of methyl orange (MO) dyestuff in aqueous solution under UV irradiation (See Table1). They have summarized the benefits arise from the applications of these activated carbons as:

- The adsorbent support provides a high concentration environment of target organic substances around the loaded TiO<sub>2</sub> particles by adsorption. Therefore, the rate of photo-oxidation is enhanced.
- The organic substances are oxidized on the photocatalyst surfaces via adsorption states. The resulting toxic intermediates are also adsorbed and oxidized and as a result, they are not released in the air atmosphere to cause secondary pollution.
- Since the adsorbed substances are finally oxidized to give CO<sub>2</sub>, the high adsorbed ability of the hybrid photocatalysts for organic substances is maintained for a long time. The amount of TiO<sub>2</sub> in catalysts play significant role upon the photo-efficiency of hybrid catalysts.

In another investigation, Wu *et al.* [29] studied the dye decomposition kinetics in a batch photocatalytic reactor under various operational conditions including agitation speed, TiO<sub>2</sub> suspension concentration, initial dye concentration, temperature and UV illumination intensity in order to establish reaction kinetic models (See Table 1).

In general, it can be concluded that all the modified and thin film samples prevent rapid recombination, while CB-TiO<sub>2</sub> films and TiO<sub>2</sub>/strontium ferrite samples have the advantage of easy separation because of their fixation on the support.

Mahmoodi *et al.* [30] studied the effect of immobilized titanium dioxide nanoparticles on the removal of Butachlor (N- butoxymethyl-2-chloro-2, 6-diethylacetanilide) which is one of the organic pollutants in agricultural soil and wastewater. Due to high preparation cost and toxicity of nanoparticles in the environment, they used the immobilized form of TiO<sub>2</sub>, because of their easy recovery from aqueous media. The effective parameters investigated in this study were inorganic anions (NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>), H<sub>2</sub>O<sub>2</sub> concentration and PH. In another work, Mahmoodi *et al.* [31] immobilized TiO<sub>2</sub> nanoparticles for the degradation and mineralization of two agricultural pollutants (Diazinon and Imidacloprid as *N*-heterocyclic aromatics). Dai *et al.* [32] examined the removal of methyl orange in aqueous suspension containing titania nanoparticles with meso-structure (m-TiO<sub>2</sub>) under UV-irradiation. As mentioned above, immobilization of nanoparticle was useful for their easy recovery. The photocatalytic efficiency of immobilized TiO<sub>2</sub> nanoparticle with 6 nm diameter (supported by glass substrate) as well as conventional suspended catalysts is investigated recently by Mascolo *et al.* [33] for the degradation of methyl red dye. The results have shown that the conventional suspended TiO<sub>2</sub> degussa P25 is more effective than the supported nanoparticles. Although, they found the mechanism for dye degradation was the same for both cases, but lowering the photodegradation was due to reduction in active surface area for adsorption and subsequent catalyst action.

The effect of thermal treatment on the photodegradation of rhodamine B (RhB) in water with titania nanorod film was investigated by Wu [34]. In addition, Srinivasa and white [35] studied the photodegradation of methylene blue using three-dimensionally ordered macroporous (3DOM) titania. Titania (3DOM) was prepared by colloidal crystal templating against the polystyrene spheres. It was found that the

interconnected framework structure of (3DOM) titania provide more active surface sites for the photodegradation through diffusion.

Sobana *et al.* [36] prepared silver nanoparticles doped TiO<sub>2</sub> and used them for the photodegradation of direct azo dyes (Direct red 23, and Direct blue 53). The noble metals such as Ag (or Pt, Au, and ...) could act as electron traps, since they facilitate electron-hole separation and, as mentioned earlier, prevention of electron-hole recombination is useful and gives higher efficiency of photodegradation. The optimum dosage of Ag, which doped on TiO<sub>2</sub> and enhanced the photodegradation of dyes was 1.5%. Chuang *et al.* [37] investigated the synergy effect of TiO<sub>2</sub> nanoparticle and carbonized bamboo for the enhancement of benzene and toluene removal. They prepared carbonized moso bamboo powder (CB), mixture of TiO<sub>2</sub> nanoparticles and carbonized bamboo powder (CBM), and composite of TiO<sub>2</sub> nanoparticle and carbonized bamboo powder (CBC) with two weight ratios of CB to TiO<sub>2</sub> i.e. 1:1 and 1:2. They also compared their performances for the removal of benzene and toluene and found that at the same ratio of TiO<sub>2</sub> to CB, the efficiency increased as follow: CBC > CBM > CB (See Table 1).

Degradation of nitrobenzene by using nano-TiO<sub>2</sub> and ozone were recently studied by Yang *et al.* [38]. They compared the effect of nano-TiO<sub>2</sub> catalyzed plus ozone and ozone only and found that the catalyzed ozonation was more efficient than ozone alone. Titanate nanotubes / anatase nanocomposite was also synthesized via hydrothermal method for the photocatalytic decolorization of rhodamine B under visible light [39]. Lee *et al.* [40] prepared titanate nanotubes (TNTs) by a hydrothermal process and then washed them by HCl solutions with different concentrations. They used TNT treated samples for the removal of basic dyes. In addition, they modified TNTs with surfactant hexa-decyltrimethyl ammonium chloride (HDTMA) via cation exchange process to remove acid dyes. The adsorption capacities for basic and acid dyes were 380 and 400 mg/g, respectively.

**Table 1.** Removal of pollutants using TiO<sub>2</sub> nanoparticles

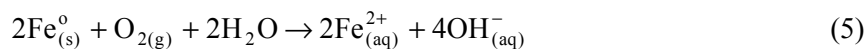
Type of nanoparticle	Removal target	Initial absorbance	Initial concentration	Dose of nanoparticle	Irradiation time (min)	Removal efficiency (%)	Ref.
Arginine- modified TiO <sub>2</sub>	Nitrobenzene	-	50 mg/L	[TiO <sub>2</sub> ]=0.1M <sup>1</sup> [SM] <sup>2</sup> =0.03 M	120	100	16
Anatase TiO <sub>2</sub>	Phenol	0.02 (245nm)	-	1.8 g/L	408	100	17
TiO <sub>2</sub> nanoparticle	Rhodamine 6G	-	125 mmol/L	0.1%(w/w)	12	90	18
TiO <sub>2</sub> /SrFe <sub>12</sub> O <sub>19</sub> composite	Procion Red MX-5B	-	10 mg/L	(2.0mg) 30% TiO <sub>2</sub>	300	98	20
Mesoporous Anatase nanocrystal	Methyl orange	-	30 mg/L	3 g/L	45	100	22
Mesoporous TiO <sub>2</sub> nanopowder <sup>3</sup>	Rhodamine B	-	1.0×10 <sup>-5</sup> M	50 mg/50ml	120	97	23
Mesoporous titania nanohybrid (naohybrid-I) <sup>4</sup>	4-chlorophenol	-	1.0×10 <sup>-5</sup> M	25 mg/100ml	240	99	24
Mesoporous titania nanohybrid (naohybrid-I) <sup>4</sup>	Methyl orange	-	1.0×10 <sup>-5</sup> M	25 mg/100ml	120	100	24
Rutile TiO <sub>2</sub> nanoparticle	Parathion	-	50 mg/L	1000 mg/L	120	>70	27
TiO <sub>2</sub> /AC nanoparticle <sup>5</sup>	Methyl orange	-	1.0×10 <sup>-3</sup> mol <sup>-3</sup>	0.5 g/200ml (47wt% TiO <sub>2</sub> )	100	77	28
TiO <sub>2</sub> /AC nanoparticle <sup>5</sup>	Methyl orange	-	1.0×10 <sup>-3</sup> mol <sup>-3</sup>	0.5 g/200ml (63wt% TiO <sub>2</sub> )	100	66	28
TiO <sub>2</sub> nanoparticle	Basic dye	-	20 mg/L	1.22 g/L	180	>80	29
CBC2 <sup>6</sup>	Benzene	-	45 mg/L	5 g	180	72	37
CBC2 <sup>6</sup>	Toluene	-	45 mg/L	5 g	180	71	37

<sup>1</sup> Molar, <sup>2</sup> Surface modifiers<sup>3</sup> Calcinated at 400°C, <sup>4</sup> [Ti] nanoparticles/[Ti] layered titaaate<sup>5</sup> TiO<sub>2</sub> + activated carbon T=25°C, 150 rpm<sup>6</sup> TiO<sub>2</sub> nanoparticle and carbonized composite (CB:TiO<sub>2</sub>, 1:2)

## 2.2. Iron Based Nanoparticles

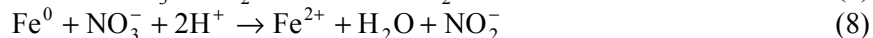
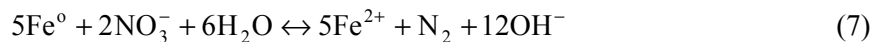
Nanoparticles could provide very high flexibility for both *in situ* and *ex situ* remediations. For example, nanoparticles are easily deployed in *ex situ* slurry reactors for the treatment of contaminated soils, sediments, and solid wastes. Alternatively, they can be anchored onto a solid matrix such as carbon, zeolite, or membrane for enhanced treatment of water, wastewater, or gaseous process streams. Direct subsurface injection of nanoscale iron particles, whether under gravity-feed or pressurized conditions, has already been shown to effectively degrade chlorinated organics such as trichloroethylene, to environmentally benign compounds. The technology also holds great promise for immobilizing heavy metals and radionuclides.

The use of zero-valent iron (ZVI or Fe<sup>0</sup>) for *in situ* remedial treatment has been expanded to include all different kinds of contaminants [41]. Zero-valent iron removes aqueous contaminants by reductive dechlorination, in the case of chlorinated solvents, or by reducing to an insoluble form, in the case of aqueous metal ions. Iron also undergoes “Redox” reactions with dissolved oxygen and water:



Supported zero-valent iron nanoparticles with 10-30 nm in diameter were also prepared [40]. These nanoparticles were used for separation and immobilization of Cr (VI) and Pb (II) from aqueous solution by reduction of chromium to Cr (III) and Pb to Pb (0) [41].

In another research, nanopowder of zero-valent iron (<100nm, with the specific surface area of 35 m<sup>2</sup>/g) was used for the reduction and immobilization of Cr (VI) too (See Table 2) [42]. Nitrogen oxidants also react with Fe<sup>0</sup>, as illustrated by the de-nitrification of nitrate (NO<sub>3</sub><sup>-</sup>).



Nanopowder of zero-valent iron (ZVI or  $\text{Fe}^0$ ) was used for the removal of nitrate in water. These nanoparticles have a large ratio of surface area to mass ( $31.4\text{m}^2/\text{g}$ ) [43] (See Table 2). Nanoscale ZVI was employed by Lowry *et al.* [44] for dechlorination of polychlorinated biphenyl (PCB) to lower-chlorinated products under ambient conditions.

More recently, it was demonstrated that nano-sized zero-valent iron (nZVI) oxidizes organic compounds in the presence of oxygen [45]. The high surface area of nano scale nZVI may allow for more efficient generation of oxidants. A decrease in reactivity is expected with the build-up of iron oxides on the surface, particularly at high pH. Feitz *et al.* [44] investigated the oxidization of herbicide molinate by nano scale zero-valent iron (nZVI), when it is used in the presence of oxygen (See Table 2).

The EZVI (emulsified zero-valent iron) technology with nanoscale or microscale iron was enhanced to address this limitation associated with the conventional use of ZVI [46]. Quinn *et al.* [45] evaluated the performance of nanoscale emulsified zero-valent iron (nEZVI) to improve in-situ dehalogenation of dense, nonaqueous phase liquids (DNAPLs) containing trichloroethene (TCE) from ground water and soil (See Figure 3).

Lindane ( $\gamma$ -hexachlorocyclohexane) is one of the persistent organic pollutants (POP) in the drinking water. FeS nanoparticle could degrade Lindane from water. These nanoparticles were synthesized by the wet chemical method and stabilized using a polymer from basidiomycetous [47]. One of the applications of ZVI is the removal and sorption of Arsenic contamination from water, ground water and soil [48].

Nanopowder of ZVI as a fine powder cannot be used in fixed-bed columns unless they have granular shape [49].

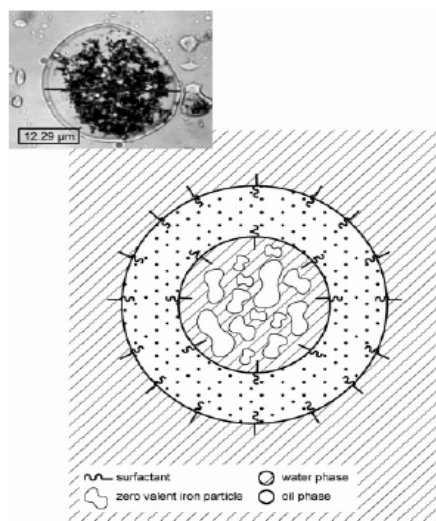


Figure 3. Schematic and photograph of EZVI (emulsified zero-valent iron) droplet showing the oil-liquid membrane surrounding particles of ZVI in water. From [Ref. 46], J. Quinn *et al.* Environ. Sci. Technol. 39, 1309 (2005).

Cellulose beads are a promising adsorbent due to their special characteristics including hydrophilic, porous, high surface area, and excellent mechanical and hydraulic properties. Cellulose and its derivative in the form of beads are widely applied as ion exchangers, adsorbents for heavy metal ions and proteins, and as the carriers for immobilization of biocatalysts. Guo *et al.* [49] prepared and used new adsorbent, bead cellulose loaded with iron oxyhydroxide (BCF), for the adsorption and removal of arsenate and arsenite from aqueous systems (See Figure. 4).

It is recognized that oxides of poly-valent metals such as: Fe (III), Al (III), Ti (IV), and Zr (IV), show ligand sorption properties through formation of inner-sphere complexes. Furthermore, hydrated Fe (III) oxide (HFO) is inexpensive, readily available and chemically stable over a wide pH range. Iron (III) oxides have high sorption affinity toward both As (V) or arsenates and As (III) or arsenites, which are the Lewis bases [50]. In the study of Cumbal and Sengupta [50], sizes of the fresh precipitated amorphous HFO particles were found to vary from 20 to 100 nm. Despite their high arsenic removal capacity, such fine submicron particles and their aggregates are shown to be unusable in fixed beds or any flow through systems due to excessive pressure drops and poor mechanical strength. To overcome these problems, HFO nanoparticles were dispersed within a macro porous polymeric cation exchanger and the resulting hybrid material were then employed for arsenic removal.

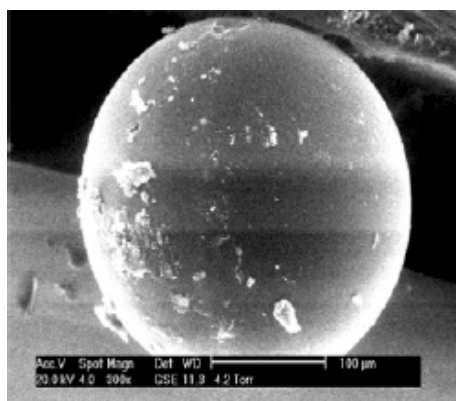


Figure 4. ESEM micrograph of BCF (bead cellulose loaded with iron oxyhydroxide). From [Ref. 49], X. Guo, and F. Chen. *Environ. Sci. Technol.* 39, 6808 (2005).

Cation and anion exchangers were used as host materials for dispersing HFO nanoparticles within the polymer phase. The resulting

polymeric/inorganic hybrid adsorbent, referred to as hybrid ion exchanger or HIX, combines excellent mechanical properties of spherical polymeric beads. HIX was amenable to efficient *in situ* regeneration with caustic soda and could subsequently be brought into service following a short rinse with carbon dioxide spiked water [51].

Xu and Zhao [52] used carboxy methyl cellulose (CMC) stabilized ZVI nanoparticles to reduce Cr (VI) in both aqueous and soil media through batch and continuous flow column study. They found that the stabilized ZVI nanoparticle is more effective than the non-stabilized one for the removal of Cr (VI). In the batch experiments, the reduction of Cr (VI) was improved from 24% to 90% as the dosage of ZVI increased from 0.04 to 0.12 g/L [52].

In another work, Xiong *et al.* [53] studied the degradation of perchlorate ( $\text{ClO}_4^-$ ) in water and ion exchange brine. They used CMC-stabilized ZVI nanoparticles and compared CMC-stabilized Fe(0), non-stabilized Fe(0), and CMC-stabilized Fe-metal catalysts (such as Fe-Pd catalyst), for the reduction of perchlorate. The results showed that the stabilized ZVI nanoparticle is more efficient than the other nanoparticles for perchlorate reduction. The results also illustrated the stabilized ZVI nanoparticles could increase perchlorate reduction rate by 53% in saline water (with concentration of NaCl up to 6% w/w) [53].

Giasuddin *et al.* [54] investigated the removal of humic acid (HA) with ZVI nanoparticles (nZVI) and also their interaction with As (III) and As(V). The effect of competing anion was also studied and the results indicated the complete removal of HA in the presence of 10 mM  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , whereas HA removal were only 0%, 18%, and 22% in the presence of 10 mM  $\text{H}_2\text{PO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{H}_4\text{SiO}_4^0$ , respectively. Li and Zhang [55] used core-shell structure of iron nanoparticle as a sorbent and reductant to remove of Ni(II) from aqueous solution. The results indicated that the sorption capacity for the removal of Ni(II) was 0.13

gNi/gFe or 4.43 meq Ni(II)/g. Cheng *et al.* [56] also applied ZVI-nanoparticle and commercial form of Fe<sup>0</sup> powder with different mesh sizes for the dechlorination of p-chlorophenol from water. Comparison between those particles indicated that the nanoscale Fe<sup>0</sup> was more effective for the reduction process. Celebi *et al.* [57] synthesized nanoparticles of zero-valent iron (nZVI) and used them to remove Ba<sup>2+</sup> ion from aqueous solution. Hristovski *et al.* [58] prepared a hybrid ion-exchange (HIX) for the simultaneous removal of arsenate and perchlorate by impregnation of nano-crystalline iron hydroxide nanoparticle onto strong base ion-exchange (IX) resin.

**Table 2.** Removal of pollutants using iron nanoparticles

Type of nanoparticle	Removal target	Initial concn. (mg/L)	Dose of nanoparticle	Contact time (min)	Removal efficiency (%)	pH	Adsorption capacity	Ref.
Zero-valent powder iron <sup>1</sup>	nitrate	400	4.0 g/L	30	100	-	-	43
Colloidal zero-valent powder iron <sup>2</sup>	Herbicide Molinate	0.10	-	180	>90	8.1	-	45
Iron sulfide nanoparticle <sup>1</sup>	Lindane	5.0	-	480	94	-	-	47
Zero-valent powder iron <sup>1</sup>	Arsenic(V)	1.0	1.0 g/L	60	100	7.0	-	48
BCF <sup>1</sup>	Arsenate	7.5	1.0 mL <sup>3</sup>	120	30	7.0	33.2 (mg/g BCF)	49
BCF <sup>1</sup>	Arsenite	7.5	1.0 mL <sup>3</sup>	120	70	7.0	99.6(mg/g BCF)	49
CMC <sup>4</sup> -stabilized ZVI nanoparticle	perchlorate	10	1.8 g/L	120	100	6.5-6.8	-	53
ZVI	Humic acid	20	1.0 g/L	5	100	6	-	54
Iron nanoparticle	Ni (II)	100	5.0 g/L	< 180	100	-	-	55

<sup>1</sup> Batch<sup>2</sup> Column<sup>3</sup> Fe content of 220 mg/mL<sup>4</sup> CMC= carboxymethyl cellulose (0.9%w/w)

### 2.3. Bimetallic Nanoparticles

Destruction of halogenated organic compound (HOCs) by zero-valent iron represents one of the latest innovative technologies for environmental remediation. Laboratory investigation in the past few years indicated that granular iron could degrade many HOCs, such as chlorinated aliphatics, chlorinated aromatics and polychlorinated biphenyls. Wang and Zhang [59] stated that the implementation of zero-valent iron technique would encounter challenges such as:

- Production and accumulation of chlorinated by-products due to the low reactivity of iron powders toward lightly chlorinated hydrocarbons. For example, reduction of tetrachloroethene (also known industrially as perchloroethylene, PERC or PCE) and trichloroethene (TCE) by zero-valent iron has been observed to produce *cis*-1, 2-dichloromethane (DCE) and vinylchloride (VC), both being of considerable toxicological concern.
- Decrease in iron reactivity over time, probably due to the formation of surface passive layers or the precipitation of metal hydroxides (e.g. Fe (OH)<sub>2</sub>, Fe (OH)<sub>3</sub>) and metal carbonates (e.g., FeCO<sub>3</sub>) on the surface of iron.

Some other metals, especially zinc and tin, can transform HOCs quicker than iron. Palladium, with its superior catalytic ability produced spectacular results as well. For example, recent studies found out that palladized iron can completely dechlorinate many chlorinated aliphatic compounds to hydrocarbons [59]. In some researches, synthesized nanoscale iron and palladized iron particles are used for degradation of chlorinated compounds (See Table 3) [59-61].

Another metal acting as a catalyst is nickel, Ni(II). This metallic catalyst could prevent formation of toxic by-products by dehalogenation of chlorinated compounds via hydrogen reduction rather than electron transfer [63]. Many researchers have focused on the synthesis of Ni/Fe

nanoparticles for the reduction of chlorinated compounds (See Table 3) [62, 63].

One of the major problems associated with ground- and surface-waters is nitrate contamination. The pH value is a means to control the reduction of nitrate by iron and, in effect, the formation of a passive oxide layer. Huang *et al.* [64] reported that iron powder can effectively reduce nitrate only at a  $\text{pH} < 4$ . They also found that the amount of nitrate removal was insignificant except when the pH of the solution was low enough to dissolve the passive oxide layers. {MEANING OF THIS SENTENCE IS NOT CLEAR TO ME. PLEASE CHANGE IT}

The deposition of small amounts of a second metal, such as Pd, Pt, Ag, Ni, and Cu, on iron has been shown to accelerate the reaction rate [65]. Whereas iron is deposited with the second metal, a relative potential difference drives the electron from iron to that metal [65].

Liou *et al.* [66] used uncatalyzed and catalyzed nanoscale  $\text{Fe}^0$  systems for the denitrification of unbuffered 40 mg/L nitrate solutions at initial neutral pH. Compared to microscale  $\text{Fe}^0$  (<100 mesh), the efficiency and rate of nitrate removal using uncatalyzed and catalyzed nano- $\text{Fe}^0$  were highly promoted. The maximum elevated rate was obtained using copper-catalyzed nano- $\text{Fe}^0$  (nano-Cu/Fe). Figure 5 shows the proposed scheme for reaction of nitrate reduction in the Cu/Fe system [66].

Another synthetic bimetallic nanoparticle is Pd/Au, which reduced the chlorinated compounds from water and ground water. Nutt *et al.* [67] synthesized Pd supported on gold nanoparticles (Au NPs). They found that these catalysts were considerably more active than Pd NPs. Joo and Zhao [68] prepared Fe-Pd bimetallic with 0.2% w/w of sodium carboxy methyl cellulose (CMC) as stabilizer and used them for the degradation of lindane and atrazine, the chlorinated herbicides.

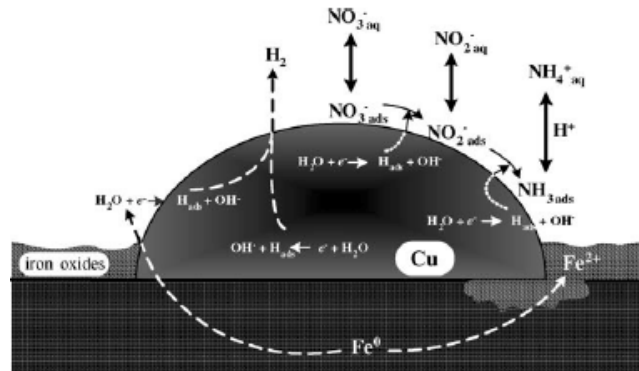


Figure 5. Proposed scheme of the nitrate reduction reaction at Cu/Fe system. From [Ref. 66], Y.H. Liou *et al.* J. Hazardous Materials B, 127, 102, (2005).

**Table 3.** Removal of pollutants using bimetallic nanoparticles

<b>Type of nanoparticle</b>	<b>Removal target</b>	<b>Initial concentration</b>	<b>Dose of nanoparticle</b>	<b>Contact time (min)</b>	<b>Removal efficiency (%)</b>	<b>Ref.</b>
Pd/Fe nanoparticle	Trichloroethene	20 mg/L	2 g /100 ml	15	100	59
Pd/Fe nanoparticle	Tetrachloroethene	20 mg/L	5.0 g /L	90	100	60
Ni/Fe nanoparticle	Trichloroethene	24 mg/L	0.1g /40ml	120	>90	62
Ni/Fe nanoparticle	Carbon tetrachloride	130 $\mu$ M	2.5 g /L	20	>99	63
Cu/Fe nanoparticle	Nitrate	40 mg/L	0.5 g of 0.44% bimetallic particles /65 mL	60	100	65

#### ***2.4. Nanoparticulate photocatalysts and catalysts***

Catalysis involves the modification of a chemical reaction rate, mostly speeding up or accelerating the reaction rate by a substance called catalyst that is not consumed throughout the reaction. Usually, the catalyst participates in the reaction by interacting with one or more of the reactants and at the end of process; it is regenerated without any changes. There are two main kinds of catalysts, homogeneous and heterogeneous. The homogeneous type is dispersed in the same phase as the reactants. The dispersal is ordinarily in a gas or a liquid solution. Heterogeneous catalyst is in a different phase from the reactants and is separated by a phase boundary. Heterogeneous catalytic reactions typically take place on the surface of a solid support, e.g. silica or alumina. These solid materials have very high surface areas that usually arise from their impregnation with acids or coating with catalytically active material e.g. platinum-coated surfaces.

Catalysts usually have two principal roles in nanotechnology areas:

- (1) In macro quantities, they can be involved in some processes for the preparation of a variety of other nanostructures like quantum dots, nanotubes, etc.
- (2) Some nanostructures themselves can serve as catalysts for certain chemical reactions.

The chemical activity of a conventional heterogeneous catalyst is proportional to its overall specific surface area per unit volume, which is customarily reported in the unit of square meters per grams, with typical values for commercial catalysts in the range of 100 to 400 m<sup>2</sup>/g. There are different procedures to enhance the surface area of the catalyst, which result in voids or empty spaces within the material. It is quite common for these materials to have pores with diameters in the nanometer range. The pore surface areas are usually determined by the Brunauer-Emmett-Teller (BET) method.

The active component of a heterogeneous catalyst can be a transition ion. Example of some metallic oxides that serve as catalysts, either by themselves or by distribution on a supporting material, are NiO, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>. For some reactions, the catalytic activity arises from the presence of acid sites on the surface. These sites correspond to either Bronsted acids, which are proton donors, or Lewis acids, which are electron pair acceptors [14].

Pajonk [69] prepared nanoparticles from the sol-gel chemistry combined with the supercritical drying method (aerogels) to enhance the catalyst properties such as textural and thermal qualities. Rare earth metal oxides modification of automotive catalysts (e.g. CeO<sub>2</sub>, ZrO<sub>2</sub>) for exhaust gas treatment has resulted in the structural stability, catalytic functions and resistance to sintering at high temperatures [70]. Owing to the low redox potential of non-stoichiometric CeO<sub>2</sub>, oxygen could release with conversion between 3<sup>+</sup> and 4<sup>+</sup> oxidation states of the Ce ions. This is shown to be essential for effective catalytic functions under the dynamic air-to-fuel ratio cycling [70, 71] (See Figure 6).

Nanocrystal surfaces usually are coated with capping ligands. These ligands manage the surface character (both the chemistry and physical structures) which expressed greatly the photocatalytic properties, such as fluorescence lifetimes, quantum yields, surface charge and particle solubility [72].

The metal complex porphyrins and other biological porphyrin-type molecules like vitamin B<sub>12</sub>, which are referred to as metalloporphyrinogens, have several characteristics that make them very applicable for the treatment of persistent organic pollutants [73]. They act as redox catalysts for many reactions and known to be active over a long range of redox potentials, electrochemically active with almost any metal, function well in aqueous solutions in the groundwater

environment, and highly stable, which enables reactions under severe conditions that prevent other treatment methods (e.g., bioremediation).

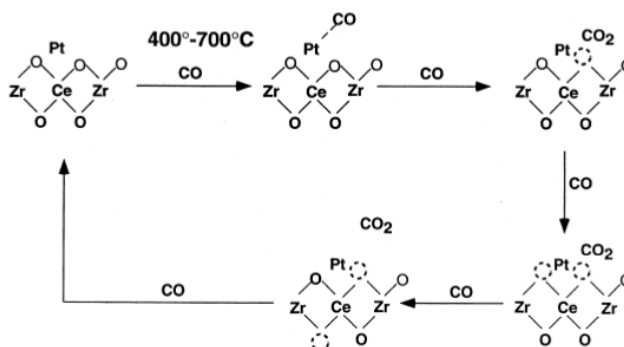


Figure 6. A schematic model for oxidation of CO by a  $\text{CeO}_2.\text{ZrO}_2/\text{Pt}$  catalyst promoted by metal–oxide support interaction. The dashed circles represent oxygen vacancies. A key step is the release of oxygen atoms in conjunction with the  $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$  conversion. Oxygen vacancies are generated initially at the ceria (cerium(IV) oxide)/Pt interface and subsequently migrate into the interior of the lattice. From [Ref. 70], C.K. C.K. Loong, and M. Ozawa. *J. Alloys and Compounds*, 303,60, (2000).

Metalloporphyrinogens are molecules with nanometer size and known to catalyze the decomposition of COC (chloro-organic compounds) by reduction reactions. Dror *et al.* [73] applied these catalysts immobilized in sol-gel matrix, for the reduction of COC. They performed experiments under conditions suitable for ground water systems with titanium citrate and zero-valent iron as electron donors. All the chloro-organic compounds used in these experiments were reduced in the presence of several sol-gel-metalloporphyrinogen hybrids (heterogeneous catalysts).

Wang *et al.* [74] investigated the effect of size, fabrication method, and morphology of ZnO nanoparticles as photocatalysts on the decomposition of methyl orange. They have used ZnO nanoparticles with different diameters of 10, 50, 200, and 1000 nm. ZnO particles were prepared by two methods of chemical deposition and thermal evaporation. It was found that the preparation method was the most important step and ZnO-nanoparticle, with 50 nm diameter synthesized via thermal evaporation method, provided the highest photocatalyst activity [74].

Huang *et al.* [75] used ZnWO<sub>4</sub> nanoparticle as photocatalyst for the degradation of rhodamine B in water and decomposition of formaldehyde in gas phase. The sample had the highest photocatalytic activity when prepared at 450°C for 1h. The temperature and time of annealing was observed to be effective for photoalytic activity. In addition, Lin *et al.* [76] prepared ZnWO<sub>4</sub> nanoparticles and nanorods and used them as photocatalysts for the photodegradation of Rhodamine B and gaseous formaldehyde.

### 2.5. Nanoclays

Clays are layered minerals with space in between the layers where they can adsorb positive and negative ions and water molecules. Clays undergo exchange interactions of adsorbed ions with the outside too. Although clays are very useful for many applications, they have one main disadvantage i.e. lack of permanent porosity. To overcome this problem, researchers have been looking for a way to prop and support the clay layers with molecular pillars. Most of the clays can swell and thus increase the space in between their layers to accommodate the adsorbed water and ionic species. These clays were employed in the pillaring process.

As stated previously, ultra-fine  $\text{TiO}_2$  powders have large specific surface areas, but due to their easy agglomeration, an adverse effect on their catalytic performance has been observed [77]. Ding *et al.* [77] experienced that the recovery of pure  $\text{TiO}_2$  powders from water was very hard when they used them in aqueous systems. They dispersed  $\text{TiO}_2$  particles in layered clays and it appeared to provide a feasible solution to such problems. The composite structures, known as pillared clay, could stabilize  $\text{TiO}_2$  particles and give access of different molecules to the surface of  $\text{TiO}_2$  crystals. In addition, the interlayer surface of pillared clays is generally hydrophobic, and this is an advantage in adsorption and enriching diluted hydrophobic organic compound in water (See Table 4).

Ooka *et al.* [78] prepared four kinds of  $\text{TiO}_2$  pillared clays from different raw clays such as montmorillonite, saponite, fluorine hectorite and fluorine mica. They have tested the surface hydrophobicities and performances of clays in adsorption- photocatalytic decomposition of phthalate esters. It was found that surface hydrophobicity of pillared clays (especially  $\text{TiO}_2$ ) largely varied with the host clay. Since the  $\text{TiO}_2$  particles in the pillared clays are too small to form a crystal phase, they presented a poor photocatalytic activity. To overcome this problem, nanocomposite of titanium dioxide ( $\text{TiO}_2$ ) and silicate nanoparticles were made by reaction between titanium hydrate sol of strong acidity and smectite clays in the presence of polyethylene oxide (PEO) surfactants [79]. It resulted in forming larger precursors of  $\text{TiO}_2$  nanoparticles and condensing them on the fragmented pieces of the silicate. Introducing PEO surfactants into the synthesis process significantly enhanced the porosity and surface area of the composite solid.

In other works, nanocomposite of iron oxide and silicate was also synthesized for degradation of azo-dye orange (II) [80] (See Table 4). To improve the sorption capacity, clays were modified in different ways,

such as treatment by inorganic and organic compounds, acids and bases. Organoclays have recently attracted lots of attention in a number of applications, such as dithiocarbamate-anchored polymer/organosmectite for the removal of heavy metal ions from aqueous media [81] (See Table 4).

A new class of nano-sized large porous titanium silicate (ETAS-10) and aluminum-substituted ETAS-10 with different  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios were successfully synthesized and applied to the removal of heavy metals, in particular  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  (See Table 4). Since tetra-valent Ti is coordinated by octahedral structure, it creates two negative charges that must be normally balanced by two mono-valent cations. This leads to a great interest in ion exchange or adsorption property of this material [82]. Wang and Wang [83] prepared a series of biopolymer chitosan / montmorillonite (CTS/MMT) nanocomposites and used them as sorbents for the adsorption of Congo Red. They investigated the effect of pH and temperature and found that the sorption capacity was increased with increasing the CTS to MMT ratio.

**Table 4.** Removal of pollutants using nanoclays

Type of nanoparticle	Removal target	Initial concentration	Dose of nanoparticle	Contact time	Removal efficiency (%)	Adsorption capacity	Ref.
Fe-nanocomposite	Azo-dye orange(II)	0.1 mM	1.0g Fe nanocomposite/L + 4.8 mM H <sub>2</sub> O <sub>2</sub> +1×8 W UVC <sup>2</sup>	>20 min	75%total organic carbons of 0.1mMOrangeII	-	80
Dithiocarbamate-anchored nanocomposite	Pb(II)	-	-	-	-	170.70 mg/g	81
Dithiocarbamate-anchored nanocomposite	Cd(II)	-	-	-	-	82.20 mg/g	81
Dithiocarbamate-anchored nanocomposite	Cr(III)	-	-	-	-	71.10 mg/g	81
ETAS-10 (A) <sup>3</sup>	Pb(II)	-	-	-	-	1.68 mmol/g	82
ETAS-10(A)	Cd(II)	-	-	-	-	1.26 mmol/g	82
ETAS-10(B) <sup>4</sup>	Pb(II)	-	-	-	-	1.60 mmol/g	82
ETAS-10(B)	Cd(II)	-	-	-	-	1.12 mmol/g	82
CTS/MMT nanocomposite	Congo Red	-	-	-	-	81.23 mg/g	83

<sup>1</sup> Pseudo-second order parameters<sup>2</sup> UV irradiation<sup>3</sup> ETAS-10 (A): ( $Al_2O_3 / TiO_2 = 0.1$ ), T=25°C,<sup>4</sup> ETAS-10(B): ( $Al_2O_3 / TiO_2 = 0.2$ ), T=25°C,

## 2.6. Nanotubes

The discovery of fullerenes and carbon nanotubes has opened a new chapter in carbon chemistry. Superconducting and magnetic fullerenes, atoms trapped inside the fullerene cage, chemically bonded fullerene complexes, and nanometer-scale helical carbon nanotubes are some of the leading areas that have generated much excitement. The creation of the hollow carbon buckminsterfullerene molecule as well as methods to produce and purify bulk quantities of it has triggered an explosive growth of research in the field [84-89].

Carbon nanotubes, in particular, hold tremendous potential for applications because of their unique properties, such as high thermal and electrical conductivities, high strength, high stiffness, and special adsorption properties [90] (See Figures 7 and 8).

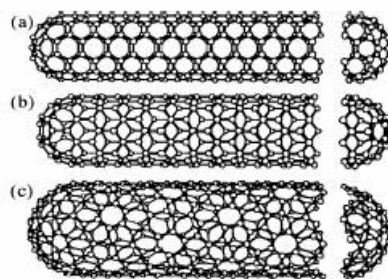


Figure 7. Some SWNTs (single-walled carbon nanotubes) with different chiralities. The difference in structure is easily shown at the open end of the tubes. a) armchair structure b) zigzag structure c) chiral structure. From [Ref. 91], [students.chem.tue.nl/ifp03/default.htm](http://students.chem.tue.nl/ifp03/default.htm)

Carbon nanotubes have cylindrical pores and adsorbent molecules interact with their carbon atoms on the surrounding walls. This interaction between molecules and solid surface depends on the pore size

and geometry of pores. When a molecule is placed in between two flat surfaces, i.e., in a slit-shaped pore, it interacts with both surfaces, and the potentials on the two surfaces overlap. The extent of the overlap depends on the pore size. However, for cylindrical and spherical pores, the potentials are greater because more surface atoms interact with the adsorbed molecule [90]. In addition, carbon nanotubes are highly graphitic (much more than the activated carbons). Hence, the carbon nanotubes can adsorb molecules much stronger than activated carbons, which have slit-shaped or wedge-shaped pores [90].

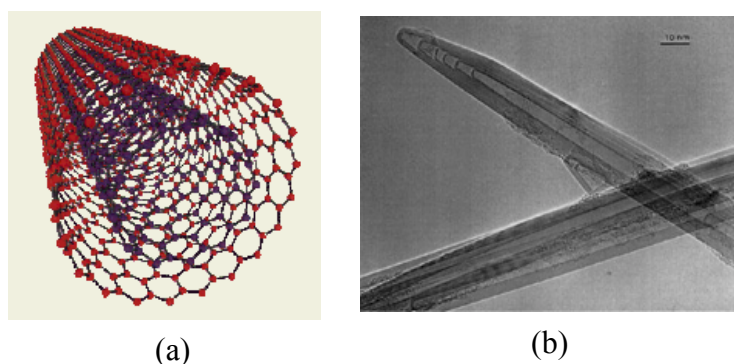


Figure 8. a) Structure model of Multiwall Carbon Nanotube (2-layer) and b) TEM Image of MWNTs. From [Ref. 92], <http://www.noritake-elec.com/itron/english/nano>.

Carbon nanotubes (CNTs) show adsorption capability and high adsorption efficiency for removal of heavy metals such as lead (See Table 5) [93, 94]. Li *et al.* [95] oxidized carbon nanotube (CNTs) with  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ , and  $\text{HNO}_3$ , and found that cadmium (II) adsorption capacities enhanced for three types of oxidized CNTs, due to the functional groups introduced by oxidation compared with the as-grown CNTs (See Table 5).

Lu *et al.* [96] purified commercial single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) by sodium hypochlorite solutions and used them as adsorbent for the removal of zinc from water. Likewise, fluoride is one of the pollutants in the drinking water and it has been adsorbed from water by amorphous  $\text{Al}_2\text{O}_3$  supported on carbon nanotubes ( $\text{Al}_2\text{O}_3/\text{CNTs}$ ) [97]. Also, Aligned carbon nanotubes (ACNTs), a new kind of carbon material, were prepared by catalytic degradation of xylene via ferrocene as catalyst and used for the adsorption of fluoride from drinking water [98].

Carbon nanotube shows the adsorption capability for the removal of organic pollutants like 1, 2-dichlorobenzene, trihalomethanes, n-nonane, and  $\text{CCl}_4$  with different modification and purification from water [99-101]. Agnihotri *et al.* [102] used gravimetric techniques to determine the adsorption capacities of commercially carbon nanotubes for organic compounds (toluene, methyl-ethyl-ketone, hexane and cyclo-hexane).

Stafiej and Pyrzynska [103] prepared purified carbon nanotubes via soaking them in  $\text{HNO}_3$  for 12 h at room temperature and then washed them with deionized water until natural pH. They used the treated CNTs for the removal of heavy metals such as Cu, Co, Cd, Zn, Mn, and Pb. It was found that the affinity of heavy metals toward CNTs at pH of 9 were in the order of  $\text{Cu (II)} > \text{Pb(II)} > \text{Co(II)} > \text{Zn(II)} > \text{Mn(II)}$ . Wang *et al.* [104] employed pristine MWCNTs, acidified MWCNTs (with different durations of soaking in nitric acid solution), and annealed MWCNTs for the removal of Pb (II). The results indicated that the maximum adsorption capacity of acidified MWCNTs and pristine MWCNTs for Pb(II) were 91 and 7.2 mg/g, respectively. In addition, Wang *et al.* [105] prepared manganese oxide-coated carbon nanotubes ( $\text{MnO}_2/\text{CNTs}$ ) as an adsorbent for the removal of lead (II) from aqueous solution. They found that the adsorption capacity of Pb(II) was 78.74 mg/g from the Langmuir isotherm model. Xu *et al.* [106] applied oxidized (MWCNTs) as

adsorbent to remove Pb(II) from aqueous solution. Similar studies done by Kandeh and Menuier [107] revealed that the oxidized MWCNTs has higher affinity for Ni(II) removal than the non-oxidized {IS THIS CORRECT?} sample. The results showed maximum Ni(II) adsorption capacity of 18.083 mg/g for oxidized MWCNTs and 49.261 mg/g for as prepared MWCNTs from Langmuir isotherm {I AM NOT SURE IF THIS IS CORRECT}. In addition, Lu and Su [108] used thermally treated MWCNTs as sorbent for the adsorption of NOM (natural organic matters) from aqueous solution.

**Table 5.** Removal of pollutants using carbon nanotubes (CNTs)

Type of nanoparticle	Removal target	Initial concentration	Dose of nanoparticle	Equilibrium concn. ( $C_e$ )	Adsorption capacity (mg/g)	pH	Ref.
CNTs	Pb(II)	10 mg /L	0.05 g / L	-	11.2	5.1	93
CNTs	Pb(II)	-	-	-	34	5.0	94
CNTs KMnO <sub>4</sub> oxidized	Cd(II)	-	0.05g/100ml	-	11	5.5	95
SWCNTs	Zn(II)	10–80mg /L	-	-	437	-	96
MWCNTs	Zn(II)	10–80mg /L	-	-	32.7	-	96
Al <sub>2</sub> O <sub>3</sub> /CNTs	Fluoride	-	-	12 mg/L	14.9	-	97
ACNTs	Fluoride	-	-	15 mg/L	4.5	7.0	98
CNTs(graphitized)	1,2-dichlorobenzene	20 mg/L	-	-	160	5.5	99
CNTs	Trihalomethanes (CHCl <sub>3</sub> )	-	-	-	2.7	3.0-7.0	100

### 2.7. Dendrimer & nanosponges

Another example of environmental treatment and remediation-related application of nanomaterials includes dendritic nanoscale chelating agents for polymer-supported ultrafiltration (PSUF). Dendrimers are highly branched polymers with controlled composition and an architecture that consists of nanoscale features. In other words, dendrimers or cascade molecules have branching construction similar to a tree, in which one trunk forms several large branches; each forming smaller branches, and so on. The roots of the tree also have the same branching mode of growth. This kind of architecture characterized by fractal geometry in which dimensions are not just integers such as 2 or 3, but also fractions (See Figure. 9).

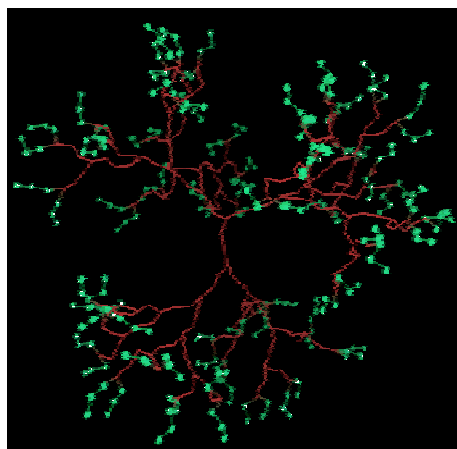


Figure 9. Schematic representation of a dendrimer. From [Ref. 109], [rati.pse.umass.edu/usim/gallery.html](http://rati.pse.umass.edu/usim/gallery.html)

These nanostructures can be designed to encapsulate metal ions and zero-valent metals, enabling them to dissolve in suitable media or bind to appropriate surfaces.

Modification of any compound in these branched polymeric structures give variety of means for controlling critical macromolecular parameters such as internal and external rigidity, hydrophilicity and hydrophobicity, degrees of void, excluded volumes, and response to stimuli such as changes in solvent polarity and temperature [110]. {THIS SENTENCE-PARAGRAPH IS NOT CLEAR}

The ability of synthesize water soluble dendrimers with metal ion chelating functional groups and also surface groups with weak binding affinity, provided opportunities for developing the treatment efficiency [110]. Some dendrimers can trap molecules such as radicals, charged moieties (part of molecules) and dyes. When molecules with different sizes are trapped inside the dendrimer, they can be selectively released by gradual hydrolysis (reaction with water) of the outer and middle layers.

Poly amidoamine (PAMAM) dendrimers are a new class of nanoscale materials that can be carried as water-soluble chelators. Usually, PAMAM macromolecules are synthesized by repeatedly attaching amidoamine monomers in their radial branched layers, termed “generations”, to a starting ammonia core [111].

The environmental applications of dendrimers were first explored by Diallo *et al.* [110]. They have reported the effective removal of copper from water via different generations of PAMAM dendrimers (See Table 6). Later, Diallo *et al.* [111] studied the feasibility of using dendrimer-improved ultrafiltration to recover Cu (II) from aqueous solution. The dendrimer-Cu (II) complexes can be efficiently separated from aqueous solutions by ultrafiltration. The metal ion laden dendrimers can be

regenerated by decreasing the solution pH to 4.0, thus enabling the recovery of the bound Cu (II) ions and recycling of the dendrimers

The soil treatment of PAMAM dendrimers was also tested. Different generation and terminal functional groups for removal of copper (II) and lead from a sandy soil were investigated [112, 113].

Rether and Schuster [114] made a water-soluble benzoylthiourea modified ethylenediamine core-polyamidoamine dendrimer for the selective removal and enrichment of toxicologically relevant heavy metal ions. They studied complexation of Co(II), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II) by the dendrimer ligand and using the polymer-supported ultrafiltration process. The interactions of the different heavy metal ions with the dendritic ligands were determined by measuring the metal ion retention, which was dependent upon the pH of the solution. The results indicate that all metal ions can be retained almost quantitatively at pH=9. Cu(II) as well as Hg(II) formed the most stable complexes with the benzoylthiourea modified PAMAM derivatives and can be separated selectively from the other investigated heavy metal ions. The bound metal ions can typically be recovered by decreasing the pH of the solution.

Diaminobutane poly (propylene imine) dendrimers functionalized with long aliphatic chains were employed to remove organic impurities such as polycyclic aromatic hydrocarbons from water and produce ultra pure water. These types of dendrimers are completely insoluble in water. The encapsulating properties of these new dendrimeric derivatives for lipophilic molecules should not be hindered by the introduction of the alkyl chains [115].

One of the novel systems for encapsulating organic pollutants is cross linked dendritic derivatives. In the research carried out by Arkas *et al.* [116] for the preparation of ultra pure water, the amino groups of poly propyleneimine dendrimer and hyper branched polyethylene imine were

interacted under extremely mild conditions with 3-(triethoxysilyl) propyl isocyanate. They produced porous ceramic filters and employed these dendritic systems for water purification. In this experimental work, the concentration of polycyclic aromatic compounds in water was reduced to few ppb's by continuous filtration of contaminated water through these filters. Then, the filters loaded with pollutants were effectively regenerated by treatment with acetonitrile.

In another work, Arkas *et al.* [117] developed a method that permits removal of organic pollutants with employing a simple filtration step, which can be easily scaled-up. They used the long-alkyl chain functionalized polypropylene imine dendrimers, polyethylene imine hyper branched polymers and  $\beta$ -cyclodextrin derivatives which are completely insoluble in water.

**Table 6.** Removal of pollutants using dendrimers

Type of nanoparticle	Removal target	Metal ion/dendrimer molecule	Loading capacity	Metal/dendrimer loading <sup>1</sup>	Ref.
Poly(amidoamine)dendrimer PAMAM(G3)	Cu(II)	$8 \pm 1$ mol/mol	-	11 mol/mol	110
Poly(amidoamine)dendrimer PAMAM(G5)	Cu(II)	$29 \pm 3$ mol/mol	-	41 mol/mol	110
Poly(amidoamine)dendrimer PAMAM(G8)	Cu(II)	$153 \pm 20$ mol/mol	-	306 mol/mol	110
Octylurea DAB-32	Pyrene	-	34 mg/g	-	115
Octylurea DAB-64	Pyrene	-	38 mg/g	-	115

<sup>1</sup> Extent of Binding

**2.8. Micelles (Self-assembled surfactants)** {WE HAVE PUBLISHED TWO PAPERS ON MICELLIZATION WHICH NEED TO BE ADDED TO THE REFERENCES SECTION. THE ARE: **1.** "Measurement of property relationships of nano-structure micelles and coacervates of asphaltene in a pure solvent" S. Priyanto, G.A. Mansoori and A. Suwono, Chem. Eng. Science, Vol.56, pp.6933 –6939, 2001. <<http://tigger.uic.edu/labs/trl/CES.PriantoMansooriSuono.pdf>> **2.** "Prediction of the Phase Behavior of Asphaltne Micelle / Aromatic Hydrocarbon Systems" Juan Horacio Pacheco-Sanchez and G.A. Mansoori, Petrol. Sci. & Technology, Vol. 16, No's 3&4, pp. 377-394 (1998).}

Micelles are self-assembled surfactant materials in a bulk solution. Surfactants or "Surface active agents" are usually organic compounds that are amphipathic, meaning they contain both hydrophobic groups (tails) and hydrophilic groups (heads). Therefore, they are typically soluble in both organic solvents and water.

There are hundreds of compounds that can be used as surfactants and are usually classified by their ionic behavior in solutions; anionic, cationic, non-ionic or amphoteric (zwitterionic). Each surfactant class has its own specific properties. A surfactant can be classified by the presence of formally charged groups in its head. There are no charge groups in a head of nonionic surfactant. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic and if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic.

The concentration at which surfactants begin to self-assemble and form micelles is known as critical micelle concentration or CMC. When micelles appear in the water, their tails form a core that is like an oil droplet, and their (ionic) heads form an outer shell that maintains favorable contact with water. The self-assembled surfactant is referred to as "reverse micelle" when surfactants assemble in the oil. In this case,

the heads are in the core and the tails have favorable contact with oil [14].

Surfactant-enhanced remediation techniques have shown significant potential in their application for the removal of polycyclic aromatic hydrocarbon (PAHs) pollutants in the soil. Increasing surfactant concentration in the solution has shown higher effectiveness in the extraction of NAPLs (non-aqueous phase liquids) and PAHs. At high concentrations, surfactant solutions improve the formation of pollutant emulsions that are hard to extract from the sample [118].

On the other hand, surfactant solutions with low concentrations are not very effective in solubilizing the pollutants. As a result, recent research has been directed towards the design of a surfactant that minimizes their losses and the development of surfactant recovery and recycling techniques [118-120]. To overcome these problems, Kim *et al.* [118] tested amphiphilic polyurethane (APU) nano-network polymer particles. They examined the APU efficiency to remove a model hydrophobic pollutant (phenanthrene) from a contaminated sandy aquifer material. One of the advantages of the APU particle emulsion is the wide range of concentration that can be used in soil remediation. APU nano-network suspensions extracted up to 98% of the phenanthrene adsorbed on the aquifer material with extremely low loss of particles [120].

### **2.9. Self-assemblies (In general)** {SINCE MICELLES ARE A CATEGORY OF SELF-ASSEMBLY IT WILL BE BETTER TO DISCUSS THIS SECTION BEFORE MICELLES}

Self-assembly is defined as a reversible process in which pre-existing parts, or disordered components of a pre-existing system, form structures of patterns. In other words, a self-assembly process is the spontaneous organization of small molecules into larger well-defined stable, ordered molecular complexes or aggregates, and spontaneous adsorption of atoms or molecules onto a substrate in a systematic ordered manner [14].

The most well-studied subfield of self-assembly is molecular self-assembly, but in recent years it has been demonstrated that self-assembly is possible with micro and millimeter scale structures lying in the interface between two liquids like micelles as discussed before.

Molecular self-assembly is gathering of molecules without guidance or management from an outside source. There are two types of self-assembly i.e. intramolecular and intermolecular, although the term self-assembly itself usually refers to intermolecular one. Intramolecular self-assembling molecules are complex polymers with the ability to assemble from the random coil conformation into a well-defined stable structure (secondary and tertiary structure). An example of this type of self-assembly is protein folding. Intermolecular self-assembly is the ability of molecules to form supramolecular assemblies (quaternary structure). A simple example is the formation of a micelle by surfactant molecules in solution as discussed before.

Attaching a monolayer of molecules to mesoporous ceramic supports gives materials known as Self-Assembled Monolayers on Mesoporous Supports (SAMMS). The highly ordered nanostructure of SAMMS is the result of three molecular-self-assembly stages. The first stage is the aggregation of the surfactant molecules to make the micelle template. The second generation is the aggregation of the silicate-coated micelles into the mesostructured body, and the third is the self assembly of the silane molecules into an ordered monolayer structure across the pore interface (see Figure. 10).

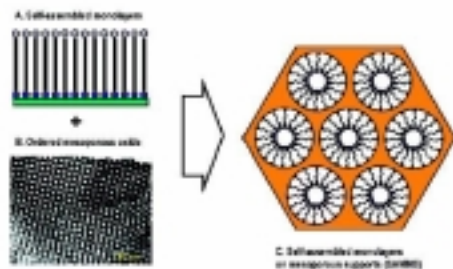


Figure 10. Schematic representation of SAMMS (Self-Assembled Monolayers on Mesoporous Supports). From [Ref. 121], G.E. Fryxell *et al.* Environ. Sci. Technol, 39, 1324 (2005).

The resulted functionalized hexagonal structure is a base to build an environmental sorbent material [121]. The rigid, open pore structure of the supports makes all of the interfacial binding sites accessible to solution species, and results in fast sorption kinetics. All the above advantages of SAMMS make it ready for various chemical bindings.

SAMMS of silica-based materials are highly efficient sorbents for target species, such as heavy metals, tetrahedral oxometalate anions, and radionuclides. The self-assembly technique is also used for preparation of catalysts in the form of thin films on a support material. Some of these thin film catalysts have great uniformities and high photocatalytic activities, but their thicknesses can hardly be controlled. Thus, preparing them in large areas is rather difficult.

A suitable technique of preparing ultra-thin films with precise thickness adjustment is the layer-by-layer self-assembly procedure [122]. The principle of multilayer assembly is quite simple; colloidal particles will self-assemble on the surface of a suitable solid substrate because of its surface forces. In most cases, electrostatic interaction provides the stability for the films.

Szabo *et al.* [122] provided a new process for synthesizing  $\text{Zn}(\text{OH})_2$  and ZnO nanoparticles. For this purpose, multilayer films of  $\text{Zn}(\text{OH})_2$  and ZnO nanoparticles were prepared by the layer-by-layer self-assembly technique on glass surface (See Figure 11). Photocatalytic measurements were made with model organic materials  $\beta$ -naphthol and industrial kerosene in a loop-type batch reactor.

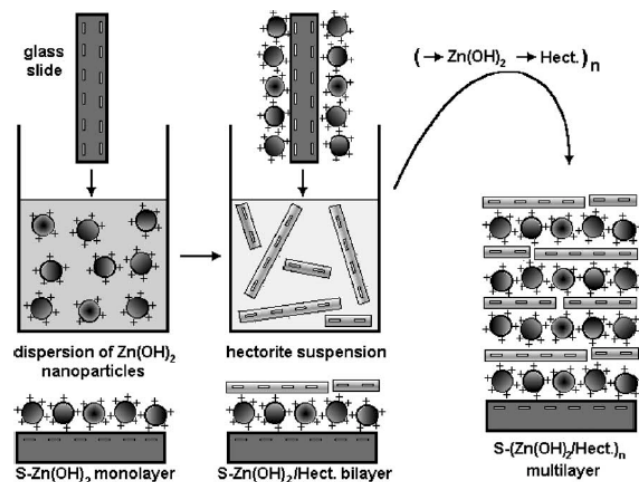


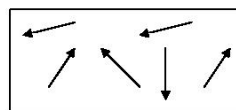
Figure 11. Side view schematics depicting of the self-assembly preparation procedure for the  $\text{S-(Zn(OH)}_2/\text{Hect})_{10}$  multilayer films. From [Ref. 122], T. Szabó *et al.* Colloids and Surfaces A: Physicochem. Eng. Aspects, 230, 23, (2004).

### 2.10. Magnetic Nanoparticles

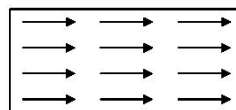
When a material is placed within a magnetic field, the magnetic forces of the material's electrons will be affected. However, materials can react quite differently to the presence of an external magnetic field. Their reaction is dependent on a number of factors, such as the atomic and molecular structure of the material, and the net magnetic field associated with the atoms. The magnetic moments associated with atoms have three origins. These are the electron orbital motion, the change in orbital motion caused by an external magnetic field, and the spin of the electrons. In most atoms, electrons occur in pairs and they spin in opposite directions. So, their

opposite spins cause their magnetic fields to cancel each other. Therefore, no net magnetic field exists. Alternately, materials with some unpaired electrons will have a net magnetic field and will react more to an external field. Most materials can be classified as diamagnetic, paramagnetic or ferromagnetic. Diamagnetic metals have a very weak and negative susceptibility to magnetic fields, while paramagnetic metals have small positive susceptibility to magnetic fields.

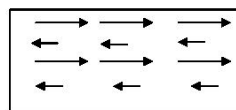
Ferromagnetic materials exhibit a strong attraction to magnetic fields and are able to retain their magnetic properties after the external field has been removed. These materials get their magnetic properties due to the presence of magnetic domains. In these domains, large numbers of atom's moments ( $10^{12}$  to  $10^{15}$ ) are aligned parallel so that the magnetic force within the domain is strong. Some transition ion atoms such as iron, manganese, nickel, and cobalt are examples of ferromagnetic materials (See Figure 12).



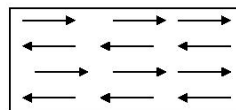
(a) Paramagnetic



(b) Ferromagnetic



(c) Ferrimagnetic



(d) Antiferromagnetic

Figure 12. Illustration of various arrangements of individual atomic magnetic moments that constitute paramagnetic (a), ferromagnetic (b), ferrimagnetic (c), and antiferromagnetic (d), material. From [Ref. 14] C.P. Poole Jr., and F.J. Owens, Introduction to nanotechnology, 2003, John Wiley & Sons Inc.

Depending on the size and subsequent change in magnetic property, the magnetic nanoparticles are used in different applications. Since the relaxation time of magnetic nanoparticles can be changed by changing the size of the nanoparticles or using different kinds of materials, magnetic nanoparticles have been a very useful tool in different kind of applications, from biomedical to data storage systems.

One of the major applications of magnetic particles is in the area of magnetic separation. In this case, it is possible to separate a specific substance from a mixture of different other substances. The separation time is one of the important parameters in the magnetic separation method. Separations using magnetic gradients, such as “High Magnetic Gradient Separation” (HGMS), are now widely used in the fields of medicine, diagnostics and catalysis to name a few. In HGMS, a liquid phase containing magnetic particles is passed through a matrix of wires that are magnetized by applying a magnetic field [123]. The particles are held onto the wires and at the conditions that the field is cut off, they can be released. If these particles are used in order to be fixed to specific molecules, the latter can be isolated from waste water or slurries. For such applications, the materials can be recycled and does not generate secondary waste. These processes sometime called “magnetically assisted chemical separation (MACS)”.

In MACS processes, particles are typically micrometric and are made of magnetite nanoparticles embedded into a polymer microsphere with a diameter ranging between 0.1 and 25  $\mu\text{m}$ . However, the magnetic particles have the disadvantage of small adsorption capacity and slow adsorption rates due to their small surface area or their porous properties [123].

Application of nanoparticles, with diameters ranging between 4 and 15 nm, either dispersed in an extracting solvent, and/or specifically coated by complex species has also been described for MACS [123]. The

magnetic component of the micro and nanoparticles employed for MACS process is typically magnetite ( $\text{Fe}_3\text{O}_4$ ) or its products of oxidation  $\gamma\text{-Fe}_2\text{O}_3$ .

Various studies by different research groups have been employed for treating contaminated water by magnetic nanoparticles some of which will be discussed here.

Takafuj *et al.* [124] prepared polymer poly (1-vinylimidazole)-grafted nanosized magnetic particles as an organic-inorganic hybrid magnetic materials for expanding the sorbent-based separation technology to a multiphase complex system (See Figure 13).

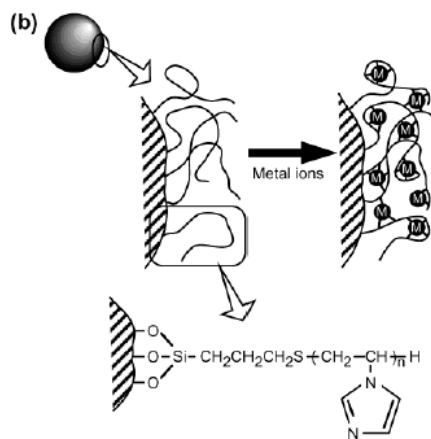


Figure 13. Schematic illustration of polymer-grafted magnetic particles (b). {WHY b IS USED HERE?} From [Ref. 124], Takafuji *et al.* Environ. Sci. Technol, Langmuir, 21, 11173 (2005).

It is well known that Cr(VI) is toxic to animals and plants, while Cr(III) is considered to be less harmful. Hu *et al.* [125] developed an innovative process combining nanoparticle adsorption and magnetic separation for the removal and recovery of Cr(VI) from wastewater. They produced ten nanometer modified  $\text{MnFe}_2\text{O}_4$  nanoparticles as a new adsorbent using a co-precipitation way followed by a surface redox reaction. The results exhibited that surface-modified  $\text{MnFe}_2\text{O}_4$  nanoparticles were efficient adsorbents for the rapid removal of Cr(VI) from aqueous solutions.

In another study, the nanoscale maghemite was synthesized, characterized, and evaluated as adsorbent of Cr(VI) [126]. It is found that some coexisting ions, such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  had no significant effect on the process which illustrated the selective adsorption of Cr(VI) from wastewater.

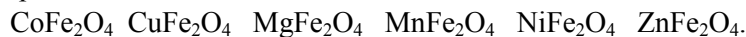
Magnetic nano-carriers can be easily manipulated by an external magnetic field and therefore should be appropriate as the support for adsorbents. Chang *et al.* [127] prepared the magnetic chitosan nanoparticles with an average diameter of 13.5 nm as a magnetic nano-adsorbent. They have done this by the carboxymethylation of chitosan and followed with binding on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles via carbodiimide activation. Magnetic chitosan nano-adsorbent was shown to be quite efficient for the fast removal of Co(II) ions at the pH range of 3–7 and the temperature range of 20–45°C.

Ngomsik *et al.* [128] have studied the removal of nickel ions from the aqueous solution using magnetic alginate microcapsules. They have found that the sorption capacity for nickel removal were increased by increasing the pH of the solution and the maximum uptake capacity was found to be around 0.42 mmol/g at the pH of 8. Also, magnetic particles in the microcapsules allowed easy isolation of the microcapsule beads from aqueous solutions after the sorption process.

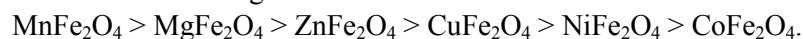
Different kinds of magnetic nanoparticles were also employed for the removal of organic pollutants, such as sorption of methylene blue on polycyclic acid-bound iron oxide from an aqueous solution [129]. In this work, novel magnetic nanoparticle made up of iron oxide nanoparticles as cores and polycyclic acid as ion exchange coating {?}, were applied for the removal of basic dye methylene blue. The results indicated that, these magnetic nanoparticles are efficient for the separation of bromelain [130] (See Table 7).

Cumbal and Sengupta [131] prepared a new class of hybrid (dual-zone) magnetic sorbents as shown in Figure 14 with the characteristics of magnetically active, selective for inorganic and organic environmental contaminants and involving efficient regeneration and reuse. Experimental results showed that the imparted magnetic activity, in terms of magnetic susceptibility within polymer beads, was dependent on the chemical nature of the functional group [131].

Recently, Hu *et al.* [132] synthesized several kinds of magnetic nanoparticles listed below:



They compared their performances in the removal of Cr(VI). They investigated many parameters such as contact time, pH, shaking rate, and magnetic properties. The results indicated their adsorption capacities were in the following order:



Mayo *et al.* [133] also studied the effect of particle sizes in the adsorption and desorption of AS(III) and AS(VI). They found that as the particle size decreases from 300 to 12 nm, the adsorption capacity increases nearly 200 times.

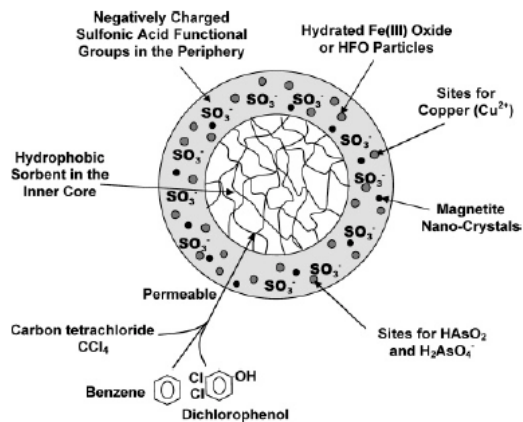


Figure 14. Illustration of a dual-zone magnetic sorbent allowing sorption of a wide array of target contaminants. From [Ref. 131], L.H. Cumbal and A.K. Sengupta, *Ind. Eng. Chem. Res.*, 44, 600 (2005).

Banerjee and Chen [134] study removal of copper ions from aqueous solution with modified magnetic nanoparticles. They treated Fe<sub>3</sub>O<sub>4</sub> with gum Arabic. Gum was attached to Fe<sub>3</sub>O<sub>4</sub> via the interaction between carboxylic groups of gum Arabic and the surface hydroxyl groups of Fe<sub>3</sub>O<sub>4</sub>. The maximum capacity obtained were 17.6 and 38.5 mg/g for MNP and GA-MNP (gum Arabic- magnetic nanoparticle), respectively.

**Table 7.** Removal of pollutants using magnetic nanoparticles

Type of nanoparticle	Removal target	Initial concn.	Removal efficiency (%)	Adsorption Capacity	Dose of nanoparticle	pH	Contact time	Ref.
Mag-Im <sub>18</sub>	Cu (II)	-	95.0	0.11 mmol/g	10 mg/ml	5.3		124
Modified jacobsite (MnFe <sub>2</sub> O <sub>4</sub> )	Cr (VI)	-	-	31.55 mg/g	-	2.0	0.08 h	125
Maghemite nanoparticle	Cr (VI)	50 mg/L	97.3	-	5 g/L	2.5	15.0 min	126
Magnetic chitosan nanoparticle	Co (II)	-	-	27.50 mg/g	-	5.5	1.0 h	127
Magnetic alginate microcapsules	Ni (II)	-	-	0.52 mmol/g	-	5.3	-	128
PAA-bound iron oxide	Methylene blue	-	-	0.199 mg/mg	-	9.0	2.0 min	129
PAA-bound iron oxide	Bromelain	-	87.4	0.476 mg/mg	-	-	-	130

### **2.11. Nanomembrane and Nanosieve**

A membrane is a semi-permeable and selective barrier between two phases (retentive and permeate) through which only selected chemical species may diffuse. Membrane filtration is frequently employed for the separation of dissolved solutes in a fluid or the separation of a gas mixture [135].

Historically, membrane technology has had wide application in wastewater treatment and desalination via reverse osmosis. In this method, a pressure difference across a membrane is employed to overcome the osmotic pressure gradient. The smaller water molecules are literally pushed through the membrane while the large solute species are retained behind [136].

Among different classes of membranes, reverse osmosis (RO) filtration is a well known process in the desalination of seawater and ultrafiltration (UF) is a well established process in the fractionation of Natural Organic Matter (NOM). Nanofiltration (NF) is a process with membrane permeability between RO and UF. Another membrane design is emulsion liquid membrane (ELM). An ELM is formed by first encapsulating an aqueous “receiving” or strip phase within a hydrophobic membrane liquid. This emulsion is then further dispersed within the continuous aqueous feed phase. This technology was used for the extraction of phenols, removal of heavy metal cations such as zinc, cadmium, chromium, copper, lead, palladium and mercury from wastewater and also removal of alkali metal cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$  and  $\text{Cs}^+$ , radioactive fission products, such as Cs-137, Sr-90, Ce-139 and Eu-152 and anions, such as chlorides, sulfate, phosphate and chromate [136].

The efficiency of nitrate removal by three commercial nanofiltration membranes, NF90, NF270 (Dow-FilmTec) and ESNA1-LF (Hydranautics) was studied by Santafe-Moros [137]. The results

indicated that NF270 gave very high flux but very low nitrate rejection, even at the lowest concentrations of the feed.

Natural organic matters (NOM) such as humic acid and fulvic acid are widely distributed in soil, natural water and sediments. These materials include mixture of the degradation products of plant and animal residues [138]. Membrane  $\text{TiO}_2$ -modified photocatalytic oxidation (PCO) has been focused on the NOM removal and/or destruction processes.

Fu *et al.* [138] designed a submerged membrane photocatalysis reactor (SMPR) for degradation of fulvic acid via novel nano-structured  $\text{TiO}_2$ /silica gel photocatalyst. The possibility of using novel  $\text{TiO}_2$  for the prevention of microfiltration membrane fouling for water purification was tested as well.

Ultrafiltration has been applied in most membrane separation processes. The hydrophilicity of the membrane and its porous structure play important roles in these processes. An appropriate porous membrane must have high permeability, good hydrophilicity and excellent chemical resistance to the feed streams. In order to obtain high permeability, membranes should have high surface porosity, and good pore structure. Polyvinylidene fluoride (PVDF) is a material that can form such asymmetric membranes, since it is thermally stable and resistant to corrosion by most chemicals and organic compounds. PVDF-based membranes exhibit outstanding anti-oxidation activities, strong thermal and hydrolytic stabilities and good mechanical properties [139]. Yan *et al.* [139] studied the modification of polyvinylidene fluoride (PVDF) ultrafiltration membrane by dispersing nano-sized alumina ( $\text{Al}_2\text{O}_3$ ) particles uniformly in a PVDF solution (19% polymer weight).

Using selective polymeric membranes for gas separation is also a promising process. Efficient gas separation membranes are required to have both high permeability and selectivity. Compared with flat

membranes, hollow fiber membranes are more favored due to a larger membrane area per volume, good flexibility and easy handling in the module fabrication [140]. Mixed matrix composite membranes that are fabricated by encapsulating the molecular sieves into the polymer matrix have also been recognized. The hollow fibers are developed with a thin zeolite beta-polysulfone mixed matrix selective layer and improved selectivity for He/N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> separation [141].

### **3. Conclusions**

With developing different aspects of nanotechnology, the broader environmental impacts of that will also need to be considered. Such considerations might include models to determine potential benefits of reduction or prevention of pollutants from industrial sources.

Nanoscience technology holds great potential for the continued improvement of technologies regarding environmental protection. The present review has given further evidence to this issue and it has tried to address what all the potential environmental impacts of the technology might be. For a quick review, the summary of practical aspects of nanotechnology applications for efficient removal of pollutants in the environment is briefly presented in Table 8.

**Table 8.** Summary of environmental treatments using nanoparticles

Type of nanoparticle	Type of treatment	Removal target	advantage	Disadvantage
Nanoparticles based TiO <sub>2</sub>	Photocatalyst oxidation	Organic pollutants	Non toxicity, Water insolubility under most conditions, photo-stability	High operation cost, Hard to recovery, sludge generation
Nanoparticles based iron	Reduction, adsorption	Heavy metals, anions, organic pollutants (dechlorination)	In situ remediation, soil & water treatment, Low cost, safe to handle	Hard to recovery, sludge generation, cost for sludge disposal, Health risk
Nanoparticles based Bimetallic	Reduction, adsorption	Dechlorination, denitrification	Higher reactivity than the iron nanoparticle	Hard to recovery, sludge generation,
Nanoclay	Adsorption	Heavy metals, organic pollutants	Low cost, Unique structures, Long-term stability, reuse, High sorption capacity, Easy recovery, large surface and pore volume	sludge generation
Nanotube & fullerene	Adsorption	Heavy metals, anions, organic pollutants	Treatment of pollution from air & water, exceptional mechanical properties, unique electrical properties, Highly chemical stability	High capital cost, low adsorption capacity, Hard to recovery, sludge generation, Health risk
Dendrimers	Encapsulation	Heavy metals, organic pollutants	Simple separation, renewable, large binding capacity, cost-effective, no sludge generation, reduce pollutant to the level of a few ppb, Treatment of pollution from soil & water	Costly
Micelles	Adsorption	Organic pollutants from soil	In situ treatment, high affinity for hydrophobic organic pollutant	Costly
Metal-sorbing vesicles	Adsorption	Heavy metals	Re-use, high selective uptake profile, high metal affinity	
Magnetite nanoparticles	Adsorption	Heavy metals, organic pollutants	Simple separation, no sludge generation	External magnetically field are required for separation, Costly
Nanofiltration & nanosieve membranes	Nanofiltration	Organic and inorganic compound	Low pressure than RO	Costly, prone to membrane fouling

**Glossary**

**Adsorbate:** Any substance that is or can be adsorbed [142].

**Adsorbent:** Any solid having the ability to concentrate significant quantities of other substance of other surface [142].

**Adsorption:** A process in which fluid molecules are concentrated on a surface by chemical or physical forces, or both [142].

**Breakthrough:** The first appearance in the effluent of an adsorbate of interest under specified condition [142].

**Cavitation:** Normally, cavitation is a nucleated process; that is, it occurs at pre-existing weak points in the liquid, such as gas-filled crevices in suspended particulate matter or transient microbubbles from prior cavitation events [143].

**Desorption:** The separation of an adsorbate as such from a sorbent [142].

**Dosage:** The quantity of substance applied per unit weight or volume of the fluid being treated [142].

**Encapsulation:** Encapsulation is the confinement of a guest molecule inside the cavity of a supramolecular host molecule (molecular capsule, molecular container or cage compounds) [144].

**Equilibrium adsorption capacity:** The quantity of a given component adsorbed per unit of adsorbent from a fluid or fluid mixture at equilibrium temperature and concentration, or pressure [142].

**Expanded bed:** A bed of granular particles through which a fluid flows upward at a rate sufficient to slightly elevate and separate the particles without changing their relative positions [142].

**Ex situ:** *Ex situ* means the contaminants are removed from the ground, either by digging up contaminated soil or pumping contaminated ground water and treating the contamination in treatment facilities built at the site. The remediated soils or ground water are then either placed back into the ground or disposed off-site [145].

**Fines:** Particles smaller than the smallest nominal specification conditions [142].

**Fixed bed:** A bed of granular particles through which the fluid flows without causing substantial movement of the bed [142].

**Fluidized bed:** A bed of granular particles in which the fluid flows upward at a rate sufficient to suspend the particles completely and randomly in the fluid phase [142].

**Freundlich isotherm:** A logarithmic plot of quantity of component adsorbed per unit of adsorbent versus concentration of that component at equilibrium and at constant temperature, which approximates the straight line postulate by Freundlich adsorption equation:

$$\frac{X}{M} = kC^n$$

X= quantity adsorbed, M= quantity of adsorbent, C= concentration, k and n= constant [142].

**In situ:** In situ means the technology is delivered directly to the subsurface soils or ground water to treat the contaminants where they are located [145].

**Isotherm:** A plot of quantity adsorbed per unit of adsorbent against equilibrium concentration, or pressure, when temperature is held constant [142].

**Langmuir isotherm:** A plot of isotherm adsorption data which to a reasonable degree fit the Langmuir adsorption equation [142].

**Macropore:** Pores with width exceeding 50 nanometers (500 angstrom units) [142].

**Mesopore:** Pores of width between 2 and 50 nanometers (20 and 500 angstrom units) [142].

**Micropore:** Pores of width between no exceeding 2 nanometers (20 angstrom units) [142].

**Nanocrystal:** Most solids are crystalline with their atoms arranged in a regular manner. They have what is called long-range order because the regularity can extend throughout the crystal. When the size of the crystal approaches the order of the de Broglie wavelength of the conduction electrons, the metal clusters may exhibit novel electronic properties [14].

**Nanoparticles:** Nanoparticles are generally considered to be a number of atoms or molecules bonded together with a radius of  $< 200$  nm [14].

**Nanotechnology:** Nanotechnology means a billionth ( $1 \times 10^{-9}$ ) [14].

**Pollution prevention:** Pollution prevention refers to “source reduction” and other practices that efficiently use raw materials, energy, water, or other resources to reduce or eliminate creation of waste. This strategy also includes using less toxic and renewable reagents and processing materials, where possible, and the production of more environmentally benign manufactured products [146].

**Pores:** The complex network of channels in the interior of a particle of a sorbent [142].

**Pore diameters:** The diameter of a pore in a model in which the pores in a sorbent are assumed to be cylindrical in shape and which calculated from data obtained by a specified procedure [143].

**Pore volume:** volume of the pores in a unit weight of a sorbent [142].

**Quantum yield:** The number of defined events which occur per *photon* absorbed by the system. The integral quantum yield is:

$$\phi = (\text{number of events})/(\text{number of photons absorbed})$$

For a photochemical reaction:

$$\phi = (\text{amount of reactant consumed or product formed})/ (\text{amount of photons absorbed})$$

The differential quantum yield is:  $\phi = \{(d[x]/dt)/n\}$

where  $d[x]/dt$  is the rate of change of a measurable quantity, and  $n$  the amount of photons (mol or its equivalent Einstein) absorbed per unit time.

$\phi$  can be used for photophysical processes or photochemical reactions [147].

**Regeneration:** Distillation or elution –type process for restoring the adsorptive properties of a spent sorbent [142].

**Sorption:** A process in which fluid molecules are taken up by absorption and adsorption [142].

**Sonochemistry:** The chemical applications of ultrasound, "sonochemistry" [143].

**Surface area (B.E.T):** The total surface area of a solid calculated by the B.E.T. (Brunauer, Emmett, Teller) equation, from nitrogen adsorption or desorption data obtained under specified conditions [142].

**Surfactant:** The name "surfactant" refers to molecules that are surface active, usually in aqueous solutions [148].

**Surface oxide:** Oxygen containing compounds and complexes formed at the surface of an adsorbent [142].

**Ultrasound:** Sound is nothing more than waves of compression and expansion passing through gases, liquids or solids. We can sense these waves directly through our ears if they have frequencies from about Hertz to 16 kHz (the Hertz unit is cycles of compression or expansion per second; kiloHertz, abbreviated kHz, is thousands of cycles per second). Ultrasound has frequencies pitched above human hearing (above roughly 16 kHz) [143].

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