Reductive Remediation of Pollutants Using Metals

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Abstract: Metal systems have been extensively used for the abiotic remediation of recalcitrant pollutants. Zero-valent metals such as iron (Fe^0), zinc (Zn^0), magnesium (Mg^0) have been used for the reductive dechlorination of organic compounds Nanoscale zero-valent iron particles have been reported to be very effective for the transformation and detoxification of a wide variety of contaminants, such as arsenic, hexavalent chromium, chlorinated organic solvents, nitroaromatic compounds and azo dyes. Zero-valent metals often result in the production of partially dechlorinated products which are sometimes more toxic than the parent compounds. Also the rate of reactions slow down due to passivation of metals and remediation process may take several days. In this context bimetallic systems offer advantages. Bimetallic systems combine the thermodynamic driving force associated with the corrosion of the reactive metals (like Mg^0 and Fe^0) with the catalytic hydrogenation characteristics of the second metal such as zero valent palladium or silver. Dechlorination of pollutants by bimetallic systems is presumed to occur *via* nucleophilic substitution reactions. The overall rate of the reaction is strongly influenced by the type of substituent groups on the aromatic ring. Commercial application of hydrogenating catalyst such as palladium is limited due to the fact that it is expensive and its recovery after the reduction reaction is very poor. Moreover the presence of trace concentrations of palladium in treated water may exert toxic effects on biological systems. Such problems can be overcome by immobilizing palladium onto suitable support matrices which would enhance its reuse and recovery. Important factors which should be taken into consideration while selecting a support is its stability to by-products, the ease and simplicity with which the catalyst can be immobilized.

Keywords: Bimetallic system, chlorinated compound, palladium, reductive transformation, zero-valent metal.

1. INTRODUCTION

An emerging abiotic technology for the remediation of recalcitrant pollutants such as chlorinated aliphatic and aromatic compounds is the application of metal systems. The focus of this review article is to provide an overview of the available literature on the application of zero-valent metals, bimetallic systems and immobilized metal (palladium) catalysts for the reductive remediation of pollutants with emphasis on chlorinated compounds.
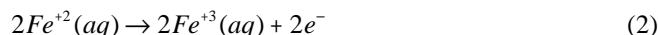
2. ZERO VALENT METALS FOR REMEDIATION OF CHLORINATED POLLUTANTS

Zero-valent metals such as palladium (Pd^0), iron (Fe^0), zinc (Zn^0), magnesium (Mg^0) have been used for the reductive dechlorination of chlorinated organic compounds. Zero-valent palladium is expensive and requires the presence of hydrogen (or a hydrogen donor) for mediating reductive reactions. The redox couples, namely Fe^{2+}/Fe^0, Zn^{2+}/Zn^0 and Mg^{+2}/Mg^0 have standard reduction potentials of -0.44 V, -0.76 V and -2.37 V respectively, with corresponding increase in reactivity towards organic halides. Among the other three metals, iron has been extensively used for dechlorination mainly due its low cost. Table **1** gives a partial list of applications of zero-valent metals for reductive transformation of various categories of pollutants.

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General Pathways of Dechlorination by Zero-Valent Metals

The electrochemical reaction is initiated by the corrosion of a base metal with a stronger reducing power (negative reduction potential). Two pathways may contribute to dehalogenation by zero-valent metals as described by Matheson and Tratnyek [1].

The first pathway involves reduction by direct electron transfer from the zero-valent metal such as Fe^0 surface to the adsorbed halogenated compound. This process is represented in Fig. (**1**). In the presence of water and oxygen, the following half reactions (1-3) also occur.

$$Fe(s) \rightarrow Fe^{+2}(aq) + 2e^- \qquad (1)$$

$$2Fe^{+2}(aq) \rightarrow 2Fe^{+3}(aq) + 2e^- \qquad (2)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (3)$$

Ferric and hydroxide ions form stable complex (rust) according to reaction 4 and deposit on the corroding metal surface.

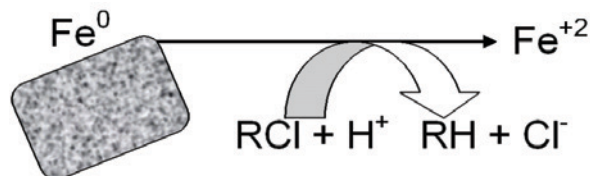**Fig. (1).** Reductive dechlorination using Fe^0 by direct electron transfer (adapted from [1]).

Table 1.   Application of Zero-Valent Metals in the Degradation of Various Types of Pollutants

Type of Pollutant	Author(s) and Reference Number	Compound(s) Removed	Reaction System Used	Reaction Mechanism	Remarks
Chlorinated aromatic	Eykholt and Davenport 1998 [2]	Herbicides Alachlor and Metolachlor	Fe^0	Hydrogenolysis at the chloroacetyl group (followed by N-dealkylation in case of alachlor) to chloride and dechlorinated acetanilides	First-order rate constants 0.12 and 0.1 per hour for Alachlor and Metolachlor
	Ukizu and Miyadera 2005 [3]	Lindane	Pd^0 and alkaline 2-propanol, aerobic condition	Complete dechlorination to benzene	2-propanol acted as H_2 source; Stoichiometric reaction with NaOH followed by catalytic dechlorination
	Sayles *et al.* 1997 [4]	DDT, DDD and DDE	Fe^0 (with and without surfactant) in anaerobic aqueous system	Reductive dechlorination to DDD, DDOH and DDMU observed	Transformation rate independent of specific iron surface area; limited by mass transfer of DDT
	Schuth and Reinhard 1998 [5]	Chlorobenzenes, 4-Chlorobi phenyl, Naphthalene and Phenanthrene	Pd^0 over alumina in hydrogen-saturated water	Hydrodechlorination dehydrochlorination and (partial) hydrogenation to benzene	Dechlorination reactions faster than hydrogenation
Chlorinated aliphatic and alicyclic	Matheson and Tratnyek 1994 [1]	Chlorinated methanes	Fe^0	Dechlorination by anaerobic corrosion of iron	
	Arnold *et al.* 1999 [6]	Polychlorinated ethanes	Zn^0	Reductive elimination of halogen atoms	
	Volpe *et al.* 2004 [7]	Herbicide Triallate	Fe^0, anaerobic conditions	Predominantly reductive β-elimination; to a lesser extent by hydrogenolysis	Complete dechlorination to S-allyl-diisopropylthiocarbamate
	Orth and Gilham 1996 [8]	Trichloro ethylene	Fe^0	Reductive dechlorination by oxidation of Fe by water	Ethene and ethane are the end products
	Mori *et al.* 2004 [9]	Trichloro ethylene	Pd^0/silica	Hydrodechlorination	Ethane is the end product
	Schlimm and Heitz 1996 [10]	Lindane Chloroform Trichloroethylene	Mg^0	Reductive dechlorination	Products obtained: benzene and chlorobenzene; methane; ethane & ethene
	Fennelly *et al.* 1998 [11]	Trichloroethylene	Fe^0	Reductive α-elimination and radical/carbenoid coupling to 1,1-DCA and small amounts of ethane, *cis*-2-butene, ethylene, and a trace of 2-butyne.	
	Fennelly *et al.* 1998 [11]	Trichloroethylene	Zn^0	Reductive α-elimination and radical/carbenoid coupling to ethane and 1,1-DCA	
Inorganic	Dries *et al.* 2005 [12]	Zn, Ni and Cr	Fe^0	Adsorption followed by removal	
	Cantrell *et al.* 1995 [13]	CrO_4^{2-}, TcO_4^-, UO_2^{2+} and MoO_4^{2-}	Fe^0	Reductive precipitation	
	Lee *et al.* 2003 [14]	Cr^{6+}	Fe^0	Reduction to Cr^{3+}	Removal rates faster for waste iron than with commercial iron

(Table 1) contd…..

Type of Pol-lutant	Author(s) and Reference Number	Compound(s) Removed	Reaction System Used	Reaction Mechanism	Remarks
Textile dye	Hou *et al.* 2007 [15]	Azo dyes (Orange I and II & Methyl Orange	Fe^0, anaerobic condition	Reductive cleavage of azo bond to sulfanilic acid & another by-product depending on the substituent group	Fe^0 dosage and pH affected the degradation kinetics
	Nam and Tratnyek 2000 [16]	Azo dyes	Fe^0, anaerobic condition	Reductive cleavage of azo bond to sulfanilic acid and aminonaphthol	Decolorization followed first-order kinetics
	Cao *et al.* 1999 [17]	Azo dyes (Acid orange II, Acid orange IV, Acid orange GG, Acid red 3B and Orange I)	Fe^0, anaerobic condition	Reductive cleavage of azo bond to sulfanilic acid and aminonaphthol	Degradation rates influenced by pH and Fe surface area
Nitroaromatic	Hundal *et al.* 1997 [18]	TNT and RDX	Fe^0	Reduction to amines	

$$2Fe^{+3} + 6OH^- \rightarrow Fe_2O_3(s) + 3H_2O[2Fe(OH)_3] \qquad (4)$$
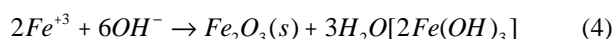
In the second pathway, an immediate corrosion product of metal such as Fe^{+2} in aqueous systems, acts as a reductant for dechlorination (Fig. **2**). However the metal hydroxide (ferric hydroxide in the case of iron, Equation 4) produced during corrosion leads to the rapid passivation of the zero-valent iron (deactivation of the metal) and thereby reduces the rate of dechlorination reactions. In this context, Mg^0 has a distinct advantage over Fe^0 in that the magnesium hydroxides produced are relatively more soluble (pKsp $Mg(OH)_2$ = 11.5 *vs* pKsp $Fe(OH)_2$ = 15.1) thereby decreasing the passivation of the corroding metal [19].
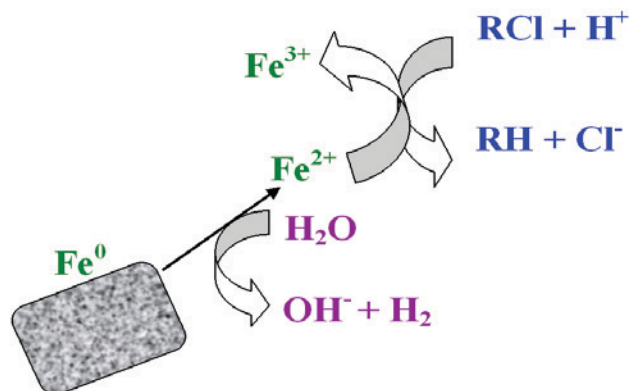

Fig. (2). Reductive dechlorination using Fe^0 – H_2O system in which Fe^{2+} acts as the dehalogenating agent (adapted from [1]).

Use of Nanoscale Zero-Valent Iron Particles (NZVI)

Nanoparticles (1-100 nm) which provide higher surface-area-to-volume ratio can lead to enhanced reactivity with environmental contaminants that degrade through adsorption mechanism. Zero-valent iron nanoparticles have been reported to be very effective for the transformation and detoxification of a wide variety of contaminants, such as arsenic [20], hexavalent chromium [21], chlorinated organic solvents and nitroaromatic compounds [22]. Shu *et al.* demonstrated reduction of azo dye, Acid Red Black 24 using chemically synthesized nanoscale zero-valent iron (NZSVI) particles [23].

Field-Scale Application of Zero-Valent Iron

Zero-valent iron has been applied to field-scale remediation of contaminated waters. Permeable reactive barriers (PRB) packed with iron particles have been positioned in the subsurface across the flow path of groundwater for facilitating reductive dehalogenation of halogenated contaminants. PRB technology represents an attractive alternative technology to traditional pump-and-treat systems and offers advantages such as low energy consumption and minimal operation and maintenance costs. Iron PRBs were first developed in USA and Canada [24]. Presently, several PRB configurations are commercially available around the world.

Disadvantages of Zero-Valent Systems in Effecting Dechlorination

Zero-valent metals such as iron, zinc or magnesium often result in the production of partially dechlorinated products which are sometimes more toxic than the parent compounds [25]. Also the rate of reactions slow down due to passivation of metals and remediation process may take several days [26]. In this context bimetallic systems provide distinct advantages.

3. BIMETALLIC SYSTEMS FOR REDUCTIVE REACTIONS

Rapid dehalogenation can occur if an effective hydrogenating catalyst (such as Pd) is combined with zero-valent metals as shown in Fig. (**3**) [25, 27-30]. Such systems combine the thermodynamic driving force associated with the corrosion of the reactive metals (like Mg^0 and Fe^0) with the catalytic hydrogenation characteristics of the second metal such as zero-valent palladium or silver [31]. The second metal primarily has the following functions: i) acts as a hydrogenating catalyst ii) prevents the formation of the oxide film on the surface of the metal [32] and iii) induces zero-valent metal to release electrons due to the difference in reduction potentials. The corrosion rate of the base metal is also expected to increase by the coated catalytic metal (such as palladium) as a result of galvanic reaction [33]. Table **2** shows

Table 2.   Application of Bimetallic Systems in the Degradation of Various Types of Pollutants

Category of Pollutant	Author(s) (Year)	Compound(s) Removed	Reaction System Used	Reaction Mechanism	Remarks
Chlorinated aromatic	Gautam and Suresh 2007 [35]	DDT	Mg^0/Pd system, acetone, 0.05% biosurfactant, acid	Reductive (complete) dechlorination to diphenyl ethane	Biosurfactant used for the solubilization of DDT
	Gautam and Suresh 2006 [28]	DDT, DDD and DDE in soil slurry	Mg^0/Pd (water-acetone / 0.05% biosurfactant- water with acid)	Reductive (complete) dechlorination of all three compounds to diphenyl ethane	Acetone & biosurfactant used for the solubilization of DDT, DDD and DDE
	Engelmann *et al.* 2001 [19]	DDT	Mg/Pd, acetone-water, acid	Reductive dechlorination to diphenyl ethane, diphenyl methane and tetraphenyl butane.	No toxic intermediates like DDD and DDE were produced
	Engelmann *et al.* 2003 [31]	PCB and DDT	Fe/Pd ; Mg/Pd	Reductive dechlorination to biphenyl and diphenylethane	Initially Fe/Pd produced mono- and di-chloro congeners followed by production of biphenyl byMg/Pd
	Grittini *et al.* 1995 [25]	PCB	Pd/Fe system, methanol/water/acetone phase	Reductive dechlorination of adsorbed PCB to Biphenyl	Reaction rate influenced by % Pd deposited on Fe, amount of Pd/Fe used and % of water in the system
	Patel and Suresh 2006b [29]	Pentachlorophenol (PCP)	Mg^0/Ag^0, acid	Sequential (complete) dechlorination to phenol	Efficiency of PCP (10 mg L^{-1}) removal was 35% in the absence of acid
	Patel and Suresh 2007 [30]	Chlorinated phenols	Mg^0 / Pd^0	Reductive dechlorination to phenol	Dechlorination rates increased with decrease in Cl atoms
	Kim and Carraway 2000 [36]	Pentachlorophenol	Pd/Fe, Pt/Fe, Ni/Fe and Cu/Fe	Removal by sorption and dechlorination to tetrachlorophenol	Rates of dechlorination by bimetals lower than untreated Fe
	Morales *et al.* 2002 [37]	Phenol	Pd/Mg and Pd/Fe	Hydrogenation	Cyclohexanone and cyclohexanol were the end products
	Zinovyev 2004 [38]	Lindane	Isooctane-base, a phase-transfer agent (Aliquat 336) and a metal catalyst (Pd/C, Pt/C and Raney-Ni)	Base-assisted dehydrochlorination followed by hydrodechlorination	Aliquat 336 produced a 10-fold rate increase, alkaline water avoids catalyst poisoning by neutralizing the hydrochloric acid formed.
Chlorinated aliphatic	Muftikan *et al.* 1995 [39]	CCl_4, $CHCl_3$ and CH_2Cl_2 di-,tri- and tetrachloro ethylenes	Pd/Fe	Reductive hydrodechlorination to ethane and methane	Dechlorination rates decreased with decrease in Cl atoms
	Feng and Lim 2005 [40]	CCl_4 and $CHCl_3$	Nanosized Pd/Fe and Fe	Reductive dechlorination	Reaction rates 2-8 times higher than that of commercial microscale Zn & Fe
	Wang and Zhang 1997 [32]	TCE and PCBs	Nanoscale Pd/Fe	Dechlorination to hydrocarbons and biphenyl	Surface-area-normalized rate constants were 10-100 times higher than those of commercially available iron particles
	Korte *et al.* 2000 [41]	Trichloroethane	Pd/Fe	Complete dechlorination	Formation of sulfide poisoned Pd
	Cheng and Wu 2000 [27]	Trichloroethylene	Zn/Pd and Zn/Ni	Reductive dechlorination	Degradation of TCE by Zn^0 was 10 times higher than that by Fe^0
	Fennelly *et al.* 1998 [11]	Trichloroethylene	Cu/Fe^0	Reductive elimination and radical/carbenoid coupling to 1,1-DCA, ethylene, cis 2-butene, 2-butyne	
	Fennelly *et al.* 1998 [11]	Trichloroethylene	Ni/Fe^0	Reductive elimination and radical/carbenoid coupling to cis 2-butene, ethylene, 1,1-DCA, trace of 2-butyne formed	
Textile dye	Patel and Suresh 2006a [42]	Reactive black 5, Sunset yellow FCF and Tartrazine dyes	Mg^0 / Pd^{+4}	Reductive cleavage of azo bonds to amines	Reaction followed first-order kinetics

the summary of literature available on the application of bimetallic systems for reductive remediation of various classes of pollutants. The hydrogenating catalyst may be spatially separated from the corroding zero-valent metal or doped on the latter (bimetallic system). Reductive hydrodechlorination follows the sequence: a) evolution of hydrogen gas by the reduction of protons which results through the corrosion of the base metal b) intercalation of hydrogen in the lattice of hydrogenating catalyst like palladium (Pd^0) to generate the powerful reducing species metal hydride (Pd-H) c) reductive dechlorination of the chlorinated compound by the metal hydride [34]. Dechlorination of pollutants by bimetallic systems is presumed to occur *via* nucleophilic substitution reactions and involves two steps. The overall rate of the reaction is strongly influenced by the type of substituent groups on the aromatic ring. The two general mechanisms for reductive dechlorination are considered in the following sub-sections.
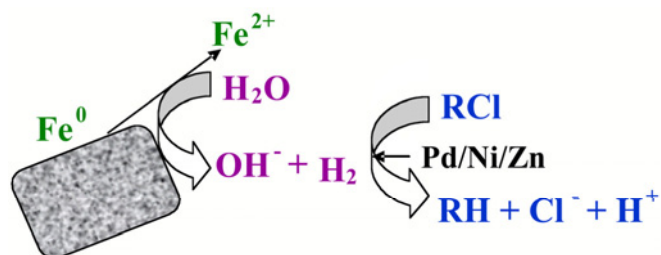

Fig. (3). Reductive dechlorination using Fe^0 – H_2O system and molecular hydrogen. (adapted from [1]).

Mechanism-1: The first step is the attack of nucleophilic species (such as silver hydride) on the aromatic ring to give the transient carbanion [29]. This is followed by the expulsion of halide ion from the carbanion, which is much faster as compared to the first step. The transient carbanion contains a tetrahedral carbon and the negative charge is distributed around the aromatic ring. Substituting groups (such as Cl atoms) that withdraw electrons will help to neutralize

(disperse) the negative charge on the ring and stabilize the carbanion. Thus, the greater the number of chlorine atoms on the ring (as in pentachlorophenol), the easier is the first nucleophilic substitution (and dechlorination) due to the enhanced stability of transition state.

Mechanism-2: The first step is possibly the slow and direct heterolytic cleavage of C-Cl bond accompanied by the formation of a transient carbocation on the aromatic ring [30]. In the second step the unstable carbocation combines rapidly with a nucleophile (such as palladium hydride) to complete the octet of the positively charged carbon. In the case of chlorophenols, the stability of transient carbocation and hence the overall rate of dechlorination is determined by the number of electron-withdrawing substituent groups such as chlorine atoms on the ring. More chlorine atoms on the ring (as in the case of pentachlorophenol) tend to intensify the positive charge on the aromatic ring, destabilizing the carbocation thereby reducing the overall rate of dechlorination reaction.

Examples of Reductive Degradation Reactions Mediated by Bimetallic Systems

Example-1: Reductive Dechlorination of DDT by Magnesium-Palladium Bimetallic System

Gautam and Suresh proposed the sequence of events leading to the reductive dechlorination of DDT to diphenylethane (DPE) by the bimetallic system, Mg/Pd system as shown in Fig. (**4**) [28]. First, zero-valent magnesium undergoes corrosion in the presence of water resulting in Mg^{2+} and electrons. These electrons are accepted by protons to produce molecular hydrogen which is absorbed by palladium to generate reactive species of hydrogen. The latter reacts with DDT molecules adsorbed on the surface of the bimetal resulting in the sequential removal of aromatic followed by aliphatic chlorine atoms to generate the hydrocarbon end product, diphenylethane (DPE).
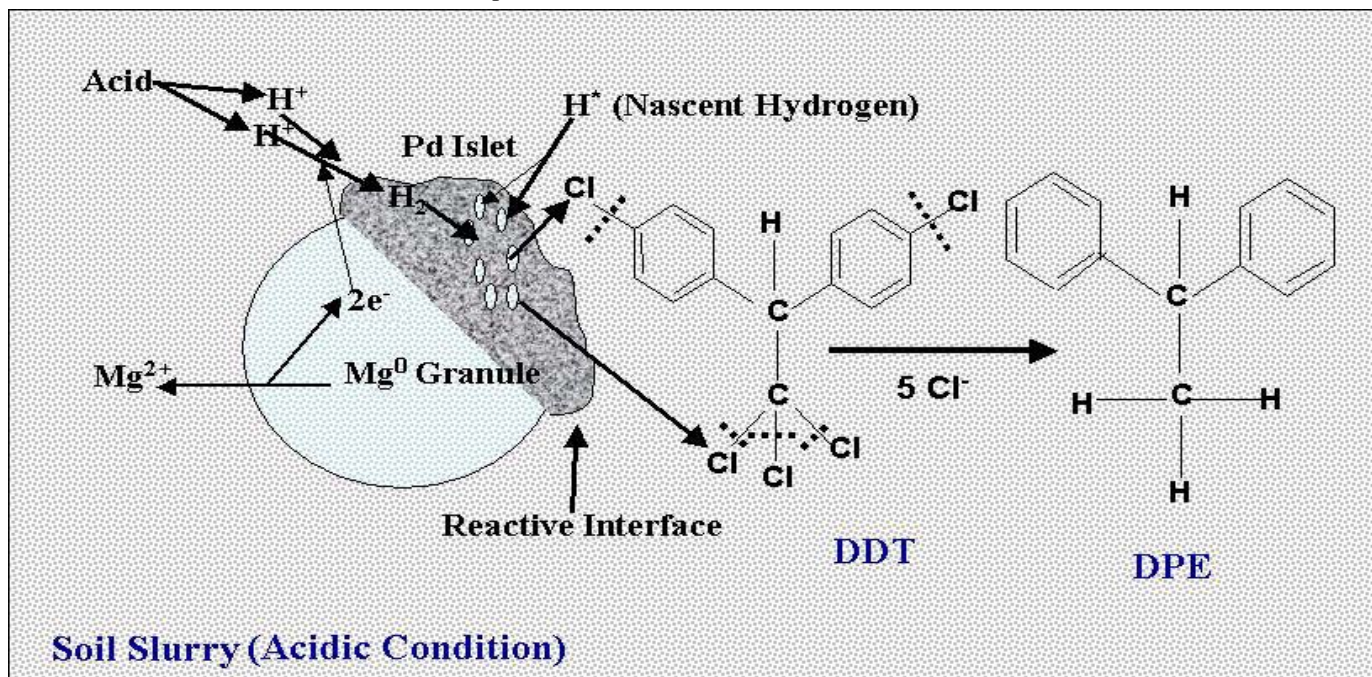

Fig. (4). Reductive dechlorination of DDT to diphenylethane (DPE) by magnesium–palladium system [28].

Example-2: Dechlorination of PCP by Magnesium-Silver Bimetallic System

Patel and Suresh reported more than 85% removal of 10 mg L^{-1} of pentachlorophenol (PCP) by magnesium/silver (206 mM/1.47 mM) bimetal system in the presence of acetic acid [29]. Dechlorination was found to be sequential and phenol was identified as ultimate hydrocarbon skeleton along with some accumulation of tetra, tri and dichlorophenols. Dechlorination reaction was found to follow second order kinetics. A diagrammatic sequence of events during the course of dechlorination of PCP by magnesium-silver bimetallic system is represented in Fig. (**5**).

Example-3: Reductive Decolourization of Reactive Black Dye

Patel and Suresh reported Mg/Pd (palladium in the form of K$_2$PdCl$_6$ or Pd^o-alumina pellets) mediated reductive reactions for decolourization of reactive black 5, sunset yellow FCF and tartrazine dyes [42]. The authors reported permanent and complete loss of visible range absorption peaks. The extent of colour removal exceeded 95 % within 24 h of reaction. The authors hypothesized that this heterogeneous phase catalytic process occurred at the interface between Mg^o/Pd^o or on Pd^o particles. LC-MS data suggested that the loss of colour was due to the reductive cleavage of –N=N– (azo) in the dye molecules (Fig. **6**).

Factors to be Considered for the Application of Bimetallic Systems

Some of the key factors that need to be considered for the field scale application of bimetallic systems are: a) effect of environmental parameters that affect the long term stability and performance of bimetallic systems b) concentration and cost of metals involved c) types of reaction products accumulated and d) toxicity of dissolved metal ions in the treated water, soil or slurry.

4. IMMOBILIZED NOBLE METALS FOR THE DEGRADATION OF POLLUTANTS

Among the noble metals, palladium is the best choice hydrogenating catalyst (such as in bimetallic systems) for the reductive transformation and degradation of various classes of pollutants (as is evident from Table **2**). However its commercial application is limited due to the fact that it is an expensive catalyst and its recovery after the reduction reaction is very poor. Moreover the presence of trace concentrations of palladium in treated water may exert toxic effects on biological systems. The above stated problems can be overcome by immobilizing the catalyst onto suitable supports which would enhance its reuse and recovery. Various types of supports have been used for the immobilization of palladium which includes inorganic ones such as alumina, silica, zeolites; metal oxides such as TiO$_2$, MgO, ZrO$_2$; and organic ones such as cellulose, chitin, chitosan, and aminoacids [43, 44]. Table **3** presents the literature available for the use of immobilized palladium as a catalyst for the degradation of chlorinated pollutants. Cagnola *et al.* (2004) reiterated the advantages of supported catalyst complexes compared to homogenous systems because of easy separation from the treated solution [45]. Morales *et al.* also observed that Pd supported on alumina could be easily recovered compared to the unsupported bimetallic systems [37]. However commercially available immobilized palladium catalysts such as palladium supported on carbon or Pd-alumina are very costly. Moreover, the selectivity of the catalyst to the target compound, the catalyst activity and stability of the catalyst are strongly influenced by the type of support material [43, 59].
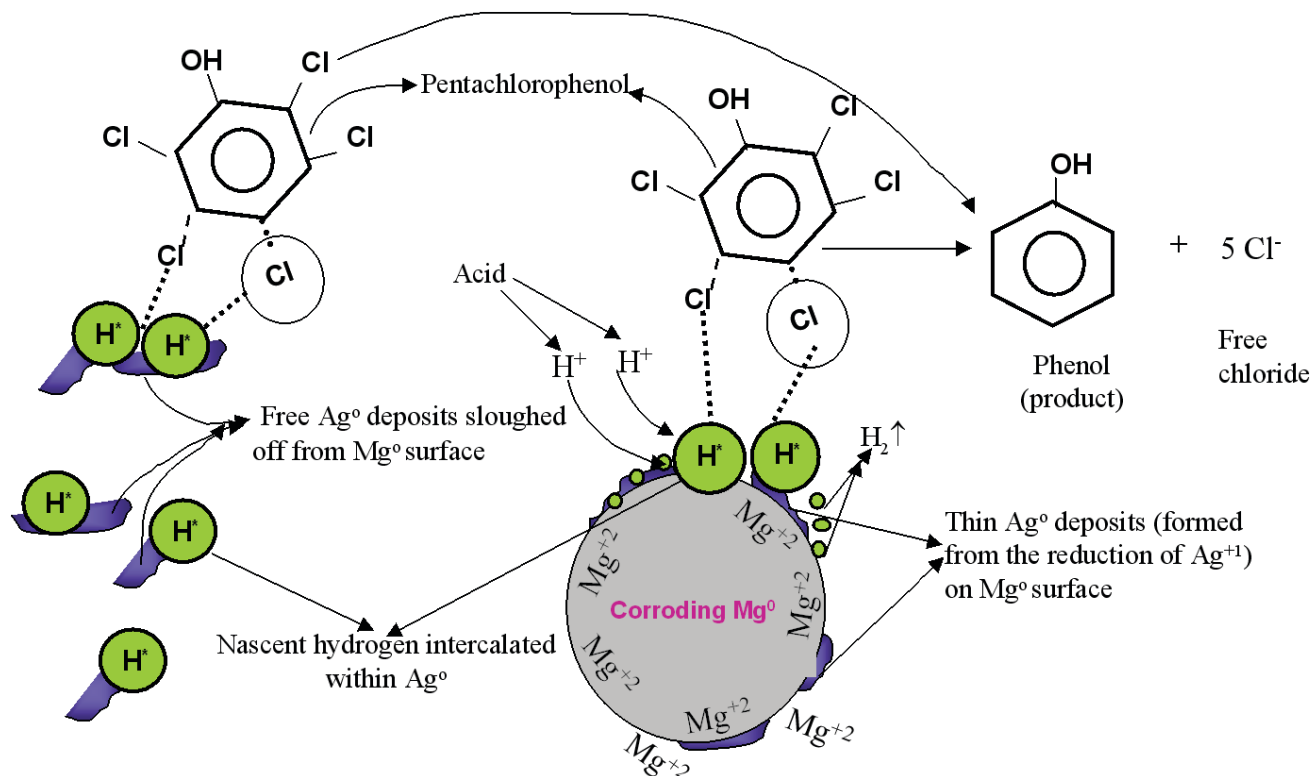

Fig. (5). Representation of events occuring during dechlorination of pentachlorophenol by Mg/Ag system [29].
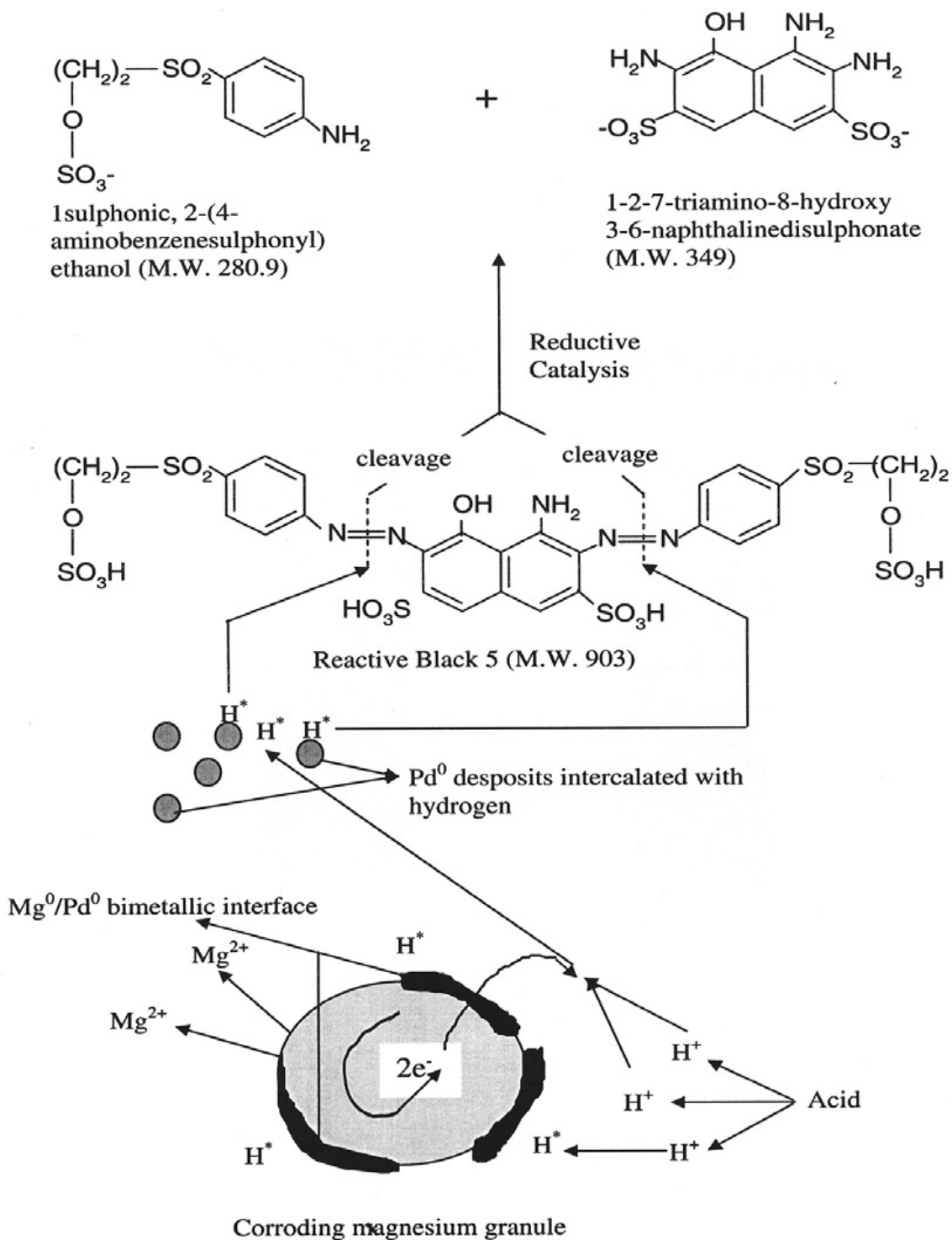
Fig. (6). Decolourization of reactive black 5 dye by magnesium-palladium system [42].

Most of the inorganic supports are also attacked and damaged by HCl released as a product of the dechlorination reaction. In addition inorganic supports also undergo unwanted reactions such as ion exchange, with HCl, leading to loss of selectivity and activity of the catalyst [43]. Reduction in the catalyst activity due to poisoning of support by chloride ions released from the catalyst precursor has also been reported [60]. Thus a catalyst support, which is resistant to corrosion by hydrogen halide, would ensure high activity and stability of palladium [43]. Apart from these, another important factor which should be taken into consideration while selecting a support is the ease and simplicity with which the catalyst can be immobilized on the support material.

Table 3. Dechlorination of Chlorinated Compounds by Palladium Immobilized on Various Support Materials

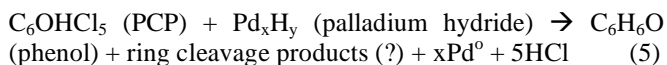| Author(s) and References	Compound(s) Degraded	Reaction System Used	Reaction Mechanism	Remarks
Schuth and Reinhard 1998 [5]	1,2 -dichlorobenzene, chlorobenzene, 4 -chlorobiphenyl, γ -hexachlorocyclohexane (Lindane), naphthalene and phenanthrene	Palladium on alumina in hydrogen-saturated water at room temperature and ambient pressure	Hydrodechlorination dehydrochlorination and (partial) hydrogenation to benzene	Dechlorination reactions faster than hydrogenation
Schreier and Reinhard 1995 [46]	Chlorinated ethylenes	Palladium on alumina and hydrogen	Hydrodehalogenation and hydrogenation to ethane	Presence of bisulfide poisoned the catalyst
Hoke *et al.* 1992 [47]	Chlorinated phenols	Palladium on carbon, ammonium hydroxide and hydrogen	Hydrodechlorination to phenol	Rate of dechlorination decreased with increase in chlorine substitution
Zhang *et al.* 2007a [48]	Octachlorodibenzo-p-dioxin (OCDD)	Palladium on carbon, H_2, ethanol–water solution of NaOH, 50°C, 3 h of reaction	Hydrodechlorination under mild conditions	96% of OCDD was degraded to low dechlorinated congeners. The yield of dibenzo-p-dioxin was 77%
Zhang *et al.* 2007b [49]	Polychlorinated dibenzo-*p*-dioxins (PCDDs)	Palladium on carbon, H_2, ethanol–water solution of NaOH, 50°C, 6 h of reaction	Hydrodechlorination under mild conditions	Chlorine-free products obtained
Ukizu *et al.* 2000 [50]	Chlorobenzene, *p* –chloro toluene, and 4-chlorobiphenyl	Rh - Platinum on carbon, NaOH solution in 2-propanol, anaerobic condition, 35° C	Dechlorination to benzene, toluene and biphenyl	Deactivation of catalyst due to accumulation of NaCl; reactivation of catalyst by washing with water
Author(s)	Compound(s) degraded	Reaction system used	Reaction mechanism	Remarks
Yuan and Keane 2004 [51]	Chlorophenols	Palladium on carbon and Palladium on aluminate	Hydrodechlorination to phenol	Reuse of Pd/C limited due to deactivation by HCl; limited loss of activity in case of Pd/Al_2O_3
Ukizu and Miyadera 1997 [52]	1,2,4-trichlorobenzene	Palladium on carbon, 2-propanol solution of NaOH, anaerobic condition	Hydrodechlorination to benzene	NaOH prevents catalyst deactivation and promotes 2-propanol dehydrogenation
Ukizu and Miyadera 2003 [53]	Polychlorinated dibenzo-*p*-dioxins and dibenzo furans	Palladium on carbon, 2-propanol solution of NaOH, anaerobic condition	Hydrodechlorination to chlorine-free products	NaOH promoted dechlorination reaction
Aramendia *et al.* 2001 [54]	Chlorobenzene	Palladium on PM2 (aluminium ortho phosphate and silica)	Hydrodechlorination to benzene	Addition of NaOH ineffective in neutralizing the HCl formed; NaOH damages the porous support and dissolves palladium metal
Patel and Suresh 2008 [55]	Pentachlorophenol (PCP)	Palladium immobilized on bacterial cellulose	Pentechlorophenol dechlorinated all the way to phenol	Approximately 12 L and 11 L of 40 mg L^{-1} PCP (pH 6.5) could be treated in RCCR with 99% and 80 % efficiencies in batch and continuous flow modes, respectively without any appreciable loss of the catalytic activity.
Hoke *et al.* 1992 [47]	PCP	Pd/C and hydrogen	Hydrodechlorination to phenol with an yield of 98%	Completely anaerobic conditions required. Reaction conducted in water + ethanol (1:1)
Roy *et al.* 2004 [56]	PCP	Pd-alumina and hydrogen	Hydrodechlorination and dearomatization of ring. Only product detected was cyclohexanone	Reaction conducted at room temperature and pressure in methanol + water (1: 99)
Monguchi *et al.* 2006 [57]	4-chlorophenol	Pd/C and hydrogen with triethylamine as an additive	Dechlorination to phenol with an yield of 92%	Reaction was incomplete in the absence of triethylamine
Mertens *et al.* 2007 [58]	Lindane	Pd^0 supported on the cells of *Shewanella oneidensis* with sodium formate as the electron donor	Partial and complete dechlorination. Dichlorobenzene and benzene were detected as end products. Complete removal of 50 mg L^{-1} of Lindane after 24 h of reaction	Reaction at atmospheric pressure and 28^0C
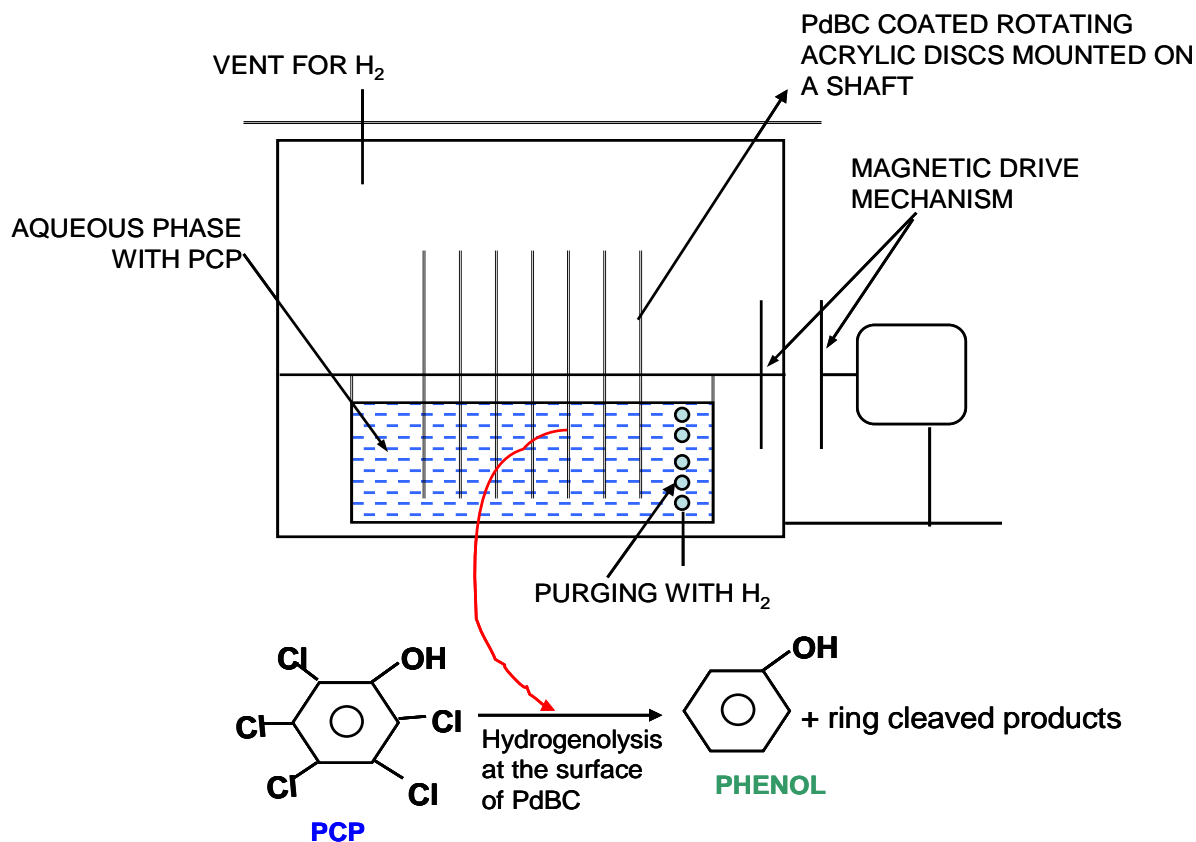
Fig. (7). Schematic diagram of rotating catalyst contact reactor (RCCR) used for treating water containing pentachlorophenol (PCP) [55]. PdBC = palladized bacterial cellulose.

Patel and Suresh developed a versatile reactor which employed a bio-inorganic composite catalyst [55]. A rotating catalyst contact reactor (RCCR) as shown in Fig. (**7**) was designed which consisted of palladized bacterial cellulose (PdBC) immobilized on circular acrylic discs for hydrodechlorination of pentachlorophenol (PCP). More than 99% of 40 mg L^{-1} PCP was dechlorinated to phenol in the presence of hydrogen in batch mode within 2 h of reaction (shown below) with stoichiometric release of free chloride as shown in equation 5.

C_6OHCl_5 (PCP) + Pd_xH_y (palladium hydride) $\rightarrow$ C_6H_6O (phenol) + ring cleavage products (?) + xPd^o + 5HCl   (5)

Approximately 12 L and 11 L of 40 mg L^{-1} PCP (pH 6.5) could be treated in RCCR with 99% and 80 % efficiencies in batch and continuous flow modes, respectively without any appreciable loss of the catalytic activity. These results suggested reusability of palladized bacterial cellulose which in turn is expected to substantially reduce the cost of treatment process. Thus RCCR seems to have high potential for treatment of ground water contaminated with chlorinated organic compounds. RCCR is simple and flexible with respect to: a) immobilization of bacterial cellulose onto rotating discs and b) *in-situ* reduction and immobilization of palladium onto bacterial cellulose and c) operation in batch or continuous flow mode. Scanning electron microscopy, energy dispersive x-ray spectroscopy and x-ray diffraction analyses suggested the irreversible deposition of nano-sized (average diameter of in the range of 100 to 150 nm) palladium (Pd^o) particles on the bacterial cellulose fibrils [55]. Quantitative energy dispersive spectroscopic (EDS) analyses further indicated that the element, palladium constituted ~ 23% of the total dry weight of PdBC. Dried palladized bacterial cellulose has been used as a material for electrodes in a fuel cell [61]. However, its application as a hydrodechlorination catalyst in a reactor operating under room temperature and atmospheric pressure has not been reported until recently.

5. CONCLUDING REMARKS

Zero-valent metals such as iron, zinc and magnesium have been extensively used for dechlorination reactions. The most important factors that govern the rate of reaction are pH of the reaction phase, precipitation of metal hydroxides and passivation of metal, surface area of the metal and hydrophobicity which encourages sorption of organics to the metal surfaces. Retrospection of the literature on the catalytic reductive degradation of various types of pollutants by bimetallic systems and immobilized catalysts illustrates that immobilization of the catalysts such as palladium onto suitable supports would prove to be a very cost-effective and efficient treatment method due to enhancement in their reusability. The support used for the immobilization of palladium should be chosen with care. The important factors to be taken into consideration are the simplicity of the immobilization process, the stability and reusability of the catalyst, prevention of damage to the support during the remediation process and application for reactor design to treat large volumes of contaminated water.

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