1   **Comment on "Reductive dechlorination of γ-hexachloro-cyclohexane using Fe–Pd**

2   **bimetallic nanoparticles" by Nagpal et al. [J. Hazard. Mater. 175 (2010) 680–687]**

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7   **Abstract**

8   The author used a recent article on lindane (γ-hexachloro-cyclohexane) reductive

9   dechlorination by Fe/Pd bimetallics to point out that many other of published works in several

10   journals do not conform to the state-of-the-art knowledge on the mechanism of aqueous

11   contaminant removal by metallic iron (e.g. in Fe^0/H_2O systems). It is the author's view that

12   the contribution of adsorbed Fe^{II} to the process of contaminant reduction has been neglected

13   while discussing the entire process of contaminant reduction in the presence of bimetallics.

14   **Keywords:** Adsorption; Bimetallic Co-precipitation; Iron corrosion; Zerovalent iron.

15   **1   Introduction**

16   Nagpal and his colleagues recently presented a very informative article on the chemical

17   reduction (reductive dechlorination) of lindane (γ-hexachloro-cyclohexane) in aqueous

18   solution using Fe/Pd bimetallic nanoparticles [1]. It is argued in the present work that this

19   study (i) used an inappropriate experimental design/procedure and (ii) failed to recognise the

20   results of several recent publications on contaminant removal using Fe^0-based materials as

21   will be shown below.

22   **2   Reactive species present in a Fe^0/H_2O system**

23   The diversity of reactive species in a conventional Fe^0/H_2O system (micro-sized Fe^0) has been

24   extensively discussed during the past 20 years [2-5]. In typical conditions, the Fe^0/H_2O

25   system is comprised of metallic iron and its associated corrosion products. Iron corrosion

26   products, in dissolved or adsorbed forms, include: (i) primary species, such as Fe^{II}, H or H_2,

27   which are also reducing agents (co-reductants), (ii) secondary species, such as Fe^{III} or

28   Fe^{II}/Fe^{III} oxide/hydroxides, which may be reducing agents (e.g. green rust) or adsorbents

29   (green rust, Fe^{III}-hydroxides), and (iii) other corrosion products which result from

30   transformations or combinations of primary and secondary corrosion products (FeOOH,

31   Fe_3O_4, Fe_2O_3). Other corrosion products include $HO^{\bullet}$ radicals which are known for their

32   oxidative capacity for organic chemicals [4-9].

33   It can therefore be implied that depending on solution conditions contaminants in the Fe^0/H_2O

34   system can be either adsorbed, oxidized or reduced [9]. As the Fe^0/H_2O system can be

35   regarded a dynamically evolving system and it remains highly difficult to separate the relative

36   contributions of each individual reaction [4]. For example: (i) during precipitation, iron

37   hydroxides and oxides will enmesh available (organic and inorganic) contaminants and/or

38   their reaction products (co-precipitation) [10,11], and (ii) iron oxides will serve as adsorption

39   sites for self-catalytic reactions using H_2/H and/or Fe^{II} [12,13]. Reducible contaminants, such

40   as lindane, could therefore be adsorbed and/or co-precipitated before or after reduction. As a

41   result, it can be stated that the relative contributions of co-reductants, such as adsorbed Fe^{II}

42   and H_2/H, could be much greater then Fe^0 due to their increased accessibility to the aqueous

43   contaminant [5-7,13]. It is argued in the present work that this was not appropriately

44   presented/discussed by Nagpal et al. [1].

45   The conventional Fe^0/H_2O system is modified by Nagpal et al. [1] in two ways: (i) by the use

46   of nano-sized particles and (ii) by the use of plating Pd^0 (Pd/Fe bimetallic system). While a

47   smaller particle size unequivocally enhances reaction kinetics, the prevailing effects of the

48   presence of Pd^0 on Fe^0 surface has been challenged [8] but not considered in their

49   presentation by Nagpal et al. [1].

50   **3   Effects of Pd^0 on the performance of Fe^0/H_2O systems**

51   Nagpal et al. [1] attributed enhanced lindane degradation efficiency to "increased catalytic

52   reactivity due to the presence of Pd^0 on the surface". This statement is intrinsically valid but

53   the prevailing mechanism (lindane hydrodechlorination on Pd^0 surface) has been challenged

54   [8]. Results from [8] suggest that (i) dissolved Pd^{II} species will be enmeshed in the mass of

55   precipitating iron hydroxides/oxides, and (ii) Pd^0 will be covered by surface oxide phases that

56   will retard any potential catalytic activities. In both cases the net result is a decrease in the

57   contaminant degradation efficiency as a function of time. This argument provides strong

58   evidence to suggest that, unlike bimetallic composites, coated bimetallic materials are

59   fundamentally inappropriate for long-term reactivity applications. The fundamental suitability

60   of Fe^0 composites for water treatment and their superiority over conventional Fe^0 materials

61   has been demonstrated by Hussam et al. [14,15]. These authors replaced conventional iron

62   shavings by a composite iron material (CIM: 92 - 94 % Fe, 4 - 5 % C, 1 - 2 % SiO_2, 1 - 2 %

63   Mn, 1–2% S, P) and could transform a highly efficient but not sustainable system (3-Kolshi

64   filter) into a highly functional and sustainable system (SONO filter) [15]. Actually, SONO

65   filters initially designed for arsenic removal has been shown efficient in removing a large

66   spectrum of contaminants including bacteria, nitrates, pesticides and viruses [16,17].

67   Beside the reaction mechanism for the hydrodechlorination on Pd^0 surfaces reported by [1], it

68   can be argued that there is another possible explanation for the enhanced degradation

69   efficiency observed. In the initial stages of the reaction, highly reactive iron hydroxides are

70   produced and these can adsorb dissolved Fe^{II} to produce structural Fe^{II} (adsorbed Fe^{II} or

71    $Fe^{II}_{(s)}$). As the electrode potential for the redox couple $Fe^{III}_{(s)}/Fe^{II}_{(s)}$ varies from -0.65 to -0.36

72   V compared to $E^0 = -0.44$ V exhibited by Fe^0 ($Fe^{II}_{(aq)}/Fe^0_{(s)}$) it can therefore be stated that the

73   formation of structural Fe^{II} on the surface of the material during the initial stages of the

74   reaction could represent a further mechanism for the enhanced (catalytic) reduction of lindane

75   observed. Adsorbed Fe^{II} is always superior to molecular hydrogen ($E^0 = 0.00$ V) as a reducing

76   agent [7].

77   It can also be suggested that the experimental conditions employed by Nagpal et al. [1] were

78   not appropriate for the conclusions drawn.

79 **4   Suitability of the experimental design for Fe/H₂O reactions**

80   Due to the aforementioned complex mechanism of Fe^0 oxidative corrosion, research into the

81   Fe^0/H_2O system is typically characterised by a pragmatic approach, and often a high degree of

82   variation in solution conditions between experiments (Table 1). For example, (i) at present

83   there is no universal Fe^0 reference material available; (ii) nano-sized Fe^0 materials are used

84   for their increased reactivity, (iii) Fe^0 bimetallic systems are also used for their increased

85   reactivity. Accordingly, it can be stated that, when using nano-scale bimetallic Fe^0, two

86   variants exist that have strong bearings on nanoparticulate reactivity.

87   Batch experiments of Nagpal et al. [1] were performed with 15 mL solutions of 5 mg/L

88   lindane ($C_6H_6Cl_6$: 290,83 $g \cdot mol^{-1}$). The solutions contained 100 to 500 mg/L of Fe/Pd

89   nanoparticles (Fe: 56 $g.mol^{-1}$). With a Fe^0:lidane molar ratio therefore ≥7000 in all systems

90   studied, it can be suggested that this experiment may be inappropriate as a "real-world"

91   analogue, as it would be difficult to maintain such a large Fe^0:contaminant molar ratio in the

92   subsurface.

93   The authors also employed an agitator to maintain nanoparticle suspension during the

94   experiment. This poses an uncertainty with respect to ensuring consistent mixing throughout

95   the reaction. Table 1 clearly shows the diversity of used experimental designs on the basis of

96   selected works referenced by Nagpal et al. [1]. In general, the investigation of processes

97   yielding aqueous contaminant removal by Fe^0 has been biased by the use of irrelevant

98   experimental conditions [5,22]. In particular, the use of experimental designs disturbing the

99   formation of an oxide scale in the vicinity of Fe^0 has significantly disturbed mechanistic

100   investigation and contributed to general acceptance of the view that Fe^0 is a reducing agent

101   (direct reduction). However, even though Fe^0 could generate reducing species (Fe^0, H/H_2) that

102   may quantitatively reduce relevant contaminants, the primary objective of water treatment is

103   contaminant removal and not contaminant reduction. Accordingly, even reduced species must

104   be physically removed from the aqueous phase. The next section will give an overview on the

105   acceptance on the concept that contaminants are quantitatively removed by adsorption and co-

106   precipitation.

107   **5   Acceptance of the adsorption co-precipitation concept.**

108   Although the concept that in Fe^0/H_2O systems contaminants are quantitatively removed by

109   adsorption, co-precipitation and size-exclusion has been presented in several peer-reviewed

110   communications and has been independently confirmed as summarized in ref. [7], this

111   concept is not yet really accepted in the scientific community [23-25]. Although the concept

112   is based on thermodynamic considerations and has considered several aspects of aqueous iron

113   corrosion, some authors have criticized that mentioned communications are using self-citation

114   [24] or that the concept is lacking experimental support for organic contaminants [24,25].

115   The argument that organic compounds (known to adsorb very little onto iron oxides) are not

116   going to be sequestered and co-precipitated in the same fashion as metals, is not acceptable

117   for at least four reasons:

118   (i) Organic compounds are in trace in an "ocean" of iron oxides and hydroxides [4]. Despite

119   low affinity, organic compounds will be collected by in-situ generated iron corrosion products

120   and/or removed from the aqueous phase by size exclusion. A direct evidence is given by Lai

121   et al. [26] who reported on quantitative removal of 1,2-dichloroethane and dichloromethane in

122   Fe^0 reactive walls although both compounds were "proven to be not treatable by Fe^{0}". This

123   observation was attributed to enhanced adsorption or microbial degradation.

124   (ii) Organic compounds have been successfully removed by electrocoagulation (using Al or

125   Fe). The similitude between electrocoagulation and contaminant removal in Fe^0/H_2O system

126   is well-documented [27,28]. For example, Bojic et al. [27] reported that the mechanism of

127   action of alloyed metallic aluminium (Al^0) for contaminant removal is based on the "several

128   physico-chemical processes and the in situ formation of the coagulant". The major processes

129   being adsorption, reduction, hydrogenation, hydrolysis and coagulation, operating

130   synergistically to (degrade and) remove variety of aqueous contaminants. Noubactep [4-7] has

131   segregated between removal (adsorption, coagulation, size-exclusion) and transformation

132   (reduction, hydrogenation and hydrolysis) mechanisms and argued that even transformed

133   species are removed by adsorption, co-precipitation or size-exclusion.

134   (iii) The adsorption/co-precipitation concept has been validated by Noubactep using

135   methylene blue ($C_{16}H_{18}N_3SCl$) as model contaminant [29,30]. The model was further

136   independently confirmed using clofibric acid ($C_{10}H_{11}ClO_3$) and diclofenac ($C_{14}H_{11}Cl_2NO_2$)

137   [31,32].

138   (iv) The adsorption co-precipitation concept has been indirectly validated by giving a better

139   interpretation on data on thiobencarb ($C_{12}H_{16}ClNOS$) [33], triazoles ($C_2H_3N_3$) [34],

140   Ethylenediaminetetraacetic (EDTA, $C_{10}H_{16}N_2O_8$) [35], tartrate ($C_4H_4O_6^{2-}$) and glycine

141   ($C_2H_5NO_2$) [36].

142   In conclusion, it is over to the scientific community to disprove (or improve) the

143   adsorption/co-precipitation concept. A recent paper by Gillham et al. [37] has stated that

144   "there are ongoing discussions on the mechanism of contaminant removal processes by

145   metallic iron". The present work is part of these discussions.

146   **6   Concluding remarks**

147   While presenting scientific work, authors should always use objectivity and clarity in

148   formulating their conclusions. Despite supported by a peer review system, this however never

149   ensures 100% validity of published work [38].

150   The author's view is that the study by Nagpal et al. [1] has overlooked the role of structural

151   Fe^{II} in the chemical transformation and the removal of aqueous contaminants in bimetallic

152   systems [8]. The concept employed by Nagpal et al. [1] has already been proven to be

153   deficient [4-8]. The alternative concept, the adsorption/co-precipitation concept, is largely

154   presented in the Journal of Hazardous Materials and has been demonstrated by independent

155   researchers [13,31,32]. Considering this, the current author would like to appeal to subsequent

156   authors, peer-reviewers, and referees to consider the above arguments. The presented

157 comments with respect to the work of Nagpal et al. [1] can also be applied to several recent

158 publications using Fe^0 and Fe^0 bimetallic systems for water treatment in various journals.

159 To conclude the author supports the comments of Tien [39] who is paraphrased as "The

160 viability and the acceptability of Fe^0-based remediation technology depends largely on the

161 quality of its investigators and the work they produce. The fact that within the Fe^0 remediation

162 community, some authors have the choice to: (i) select references to "accurately" present their

163 results, and (ii) possibly select journals to the same purposes must be a concern to all

164 members of the community."

165 Considering the comments outlined in the current work, it is the author's view that critical

166 analysis of future and concurrent publications is required in order to ensure the effective

167 advance of research associated within the Fe^0/H_2O system [40].

171 **References**

172 [1] V. Nagpal, A.D. Bokare, R.C. Chikate, C.V. Rode, K.M. Paknikar, Reductive

173 dechlorination of γ-hexachlorocyclohexane using Fe–Pd bimetallic nanoparticles, J.

174 Hazard. Mater. 175 (2010), 680–687.

175 [2] L.J. Matheson, P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron

176 metal, Environ. Sci. Technol. 28 (1994), 2045–2053.

177 [3] A.D. Henderson, A.H. Demond, Long-term performance of zero-valent iron permeable

178 reactive barriers: a critical review, Environ. Eng. Sci. 24 (2007), 401–423.

179 [4] C. Noubactep, An analysis of the evolution of reactive species in Fe^0/H_2O systems, J.

180 Hazard. Mater. 168 (2009) 1626–1631.

181 [5] C. Noubactep, A critical review on the mechanism of contaminant removal in $Fe^0–H_2O$

182 systems, Environ. Technol. 29 (2008) 909–920.

183   [6] C. Noubactep, Elemental metals for environmental remediation: learning from
184   cementation process, J. Hazard. Mater. 181 (2010) 1170 –1174.

185   [7] C. Noubactep, The fundamental mechanism of aqueous contaminant removal by metallic
186   iron, Water SA 36 (2010) 663–670.

187   [8] C. Noubactep, On the operating mode of bimetallic systems for environmental
188   remediation, J. Hazard. Mater. 164 (2009), 394–395.

189   [9] D.F. Laine, I.F. Cheng, The destruction of organic pollutants under mild reaction
190   conditions: A review, Microchem. J. 85 (2007) 183–193.

191   [10] R.J. Crawford, I.H. Harding, D.E. Mainwaring, Adsorption and coprecipitation of
192   multiple heavy metal ions onto the hydrated oxides of iron and chromium, Langmuir 9
193   (1993) 3057–3062.

194   [11] K. Eusterhues , T. Rennert , H. Knicker, I. Kgel-Knabner, K.U. Totsche, U.
195   Schwertmann, Fractionation of organic matter due to reaction with ferrihydrite:
196   Coprecipitation versus adsorption, Environ. Sci. Technol. 45 (2011) 527–533.

197   [12] L. Charlet, D. Bosbach, T. Peretyashko, Natural attenuation of TCE, As, Hg linked to the
198   heterogeneous oxidation of Fe(II): an AFM study, Chem. Geol. 190 (2002) 303–319.

199   [13] Y. Jiao, C. Qiu, L. Huang, K. Wu, H. Ma, S. Chen, L. Ma, L. Wu, Reductive
200   dechlorination of carbon tetrachloride by zero-valent iron and related iron corrosion,
201   Appl. Catal. B: Environ. 91 (2009) 434–440.

202   [14] A. Hussam, A.K.M. Munir, A simple and effective arsenic filter based on composite iron
203   matrix: Development and deployment studies for groundwater of Bangladesh, J.
204   Environ. Sci. Health A 42 (2007) 1869–1878.

205   [15] A. Hussam, Contending with a development disaster: SONO filters remove arsenic from
206   well water in Bangladesh, Innovations 4 (2009) 89–102.

207   [16] S. Tuladhar, L.S. Smith, SONO filter: An excellent technology for save water in Nepal,
208   SOPHEN 7 (2009) 18–24.

209 [17] S. Tuladhar, Er.B. Man Shakya, A study on the performance of SONO filter in reducing

210 different drinking water quality parameters of ground water: A case study in Ramgram

211 municipality of Nawalparasi District, Nepal. Paper presented at the Regional

212 Conference on Appropriate Water Supply, Sanitation and Hygiene (WASH) Solution for

213 Informal Settlements and Marginalized Communities, Kathmandu, Nepal, May 19-21,

214 (2010) 297–310.

215 [18] Y. Kim, E.R. Carraway, Dechlorination of pentachlorophenol by zero valent iron and

216 modified zero valent irons, Environ. Sci. Technol. 34 (2000) 2014–2017.

217 [19] Y.-H. Tee, L. Bachas, D. Bhattacharya, Degradation of trichloroethylene and

218 dichlorobiphenyls by iron-based bimetallic nanoparticles, J. Phys. Chem. C 113

219 (2009) 9454–9464.

220 [20] Y. Liu, S.A. Majetich, R.D. Tilton, D.S. Sholl, G.V. Lowry, TCE dechlorination rates,

221 pathways, and efficiency of nanoscale iron particles with different properties, Environ.

222 Sci. Technol. 39 (2005) 1338–1345.

223 [21] Z. Wang, P. Peng, W. Huang, Dechlorination of _-hexachlorocyclohexane by zero-valent

224 metallic iron, J. Hazard. Mater. 166 (2009) 992–997.

225 [22] C. Noubactep, T. Licha, T.B. Scott, M. Fall, M. Sauter, Exploring the influence of

226 operational parameters on the reactivity of elemental iron materials, J. Hazard. Mater.

227 172 (2009) 943–951.

228 [23a] M. Ebert , V. Birke, H. Burmeier, A. Dahmke, P. Hein, R. Köber, H. Schad, D. Schäfer,

229 M. Steiof, Comments on the articles "the end of a myth" and "on the operating mode of

230 reactive walls" by Dr. Chicgoua Noubactep, (in German) Wasser, Luft und Boden

231 (Terratech) 7-8 (2007) 4–5.

232 [23b] M. Elsner, D.M. Cwiertny, A.L. Roberts, B.S. Lollar, Response to Comment on

233 "1,1,2,2-tetrachloroethane reactions with OH-, Cr(II), granular iron, and a copper-iron

234   bimetal: Insights from product formation and associated carbon isotope fractionation",

235   Environ. Sci. Technol. 41 (2007) 7949 –7950

236   [24] S.-H. Kang, W. Choi, Response to comment on "oxidative degradation of organic

237   compounds using zero-valent iron in the presence of natural organic matter serving as an

238   electron shuttle", Environ. Sci. Technol. 43 (2009) 3966–3967.

239   [25] P.G. Tratnyek, A.J. Salter, Response to comment on "Degradation of 1,2,3-

240   trichloropropane (TCP): Hydrolysis, elimination, and reduction by iron and zinc",

241   Environ. Sci. Technol. 44 (2010) 3198 –3199.

242   [26] K.C.K. Lai, I.M.C. Lo, V. Birkelund, P. Kjeldsen, Field monitoring of a permeable

243   reactive barrier for removal of chlorinated organics, J. Environ. Eng. 132 (2006) 199–

244   210.

245   [27] A.Lj. Bojic, D. Bojic, T. Andjelkovic, Removal of Cu^{2+} and Zn^{2+} from model

246   wastewaters by spontaneous reduction–coagulation process in flow conditions, J.

247   Hazard. Mater. 168 (2009) 813 –819.

248   [28] C. Noubactep, A. Schöner, Metallic iron for environmental remediation: Learning from

249   electrocoagulation, J. Hazard. Mater. 175 (2010) 1075–1080.

250   [29] C. Noubactep, Characterizing the discoloration of methylene blue in Fe^0/H_2O systems, J.

251   Hazard. Mater. 166 (2009) 79–87.

252   [30] C. Noubactep, A.-M.F. Kurth, M. Sauter, Evaluation of the effects of shaking intensity

253   on the process of methylene blue discoloration by metallic iron, J. Hazard. Mater. 169

254   (2009) 1005–1011.

255   [31] A. Ghauch, H.Abou Assi, A. Tuqan, Investigating the mechanism of clofibric acid

256   removal in Fe^0/H_2O systems, J. Hazard. Mater. 176 (2010), 48–55.

257   [32] A. Ghauch, H. Abou Assi, S. Bdeir, Aqueous removal of diclofenac by plated elemental

258   iron: Bimetallic systems, J. Hazard. Mater. 182 (2010) 64–74.

259   [33] C. Noubactep, Comments on "Removal of thiobencarb in aqueous solution by zero

260   valent iron" by Nurul Amin et al. [Chemosphere 70 (3) (2008) 511–515], Chemosphere

261   72 (2008) 325–327.

262   [34] C. Noubactep, Comments on "Sorption of triazoles to soil and iron minerals" by Y. Jia et

263   al. [Chemosphere 67 (2007) 250–258], Chemosphere 71 (2008) 802–806.

264   [35] C. Noubactep, Comments on "Decontamination of solutions containing EDTA using

265   metallic iron" by Gyliene O., et al. [J. Hazard. Mater. (2008)], J. Hazard. Mater. 165

266   (2009) 1261–1263.

267   [36] C. Noubactep, Comments on "Decontamination of solutions containing Cu(II) and

268   ligands tartrate, glycine and quardol using metallic iron" [J. Hazard. Mater. (175 (2010)

269   452–459)], J. Hazard. Mater. 177 (2010) 1165–1166.

270   [37] S.-W. Jeen, R.W. Gillham, A. Przepiora, Predictions of long-term performance of

271   granular iron permeable reactive barriers: Field-scale evaluation, J. Contam. Hydrol,

272   123 (2011) 50–64.

273   [38] J.R. Wilson, Responsible authorship and peer review, Sci. Eng. Ethics 8 (2002), 155–

274   174.

275   [39] C. Tien, Remarks on adsorption manuscripts revised and declined, Sep. Purif. Technol.

276   54 (2007), 277–278. or J. Hazard. Mater. 150 (2008), 2–3.

277   [40] A. Berthod, So What? or required content of a review article, Sep. Purif. Rev. 38 (2009)

278   203–206.

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280

280 **Table 1**: Selected experimental conditions of Nagpal et al. [1] and references therein [19-22].

281   The experimental designs further differ regarding the availability of oxygen

282   (anoxic/oxic), the mixing type and mixing intensity, and experimental duration. V

283   is the used volume of solution and $\rho_{Material}$ the material loading. The proportion of

284   plating metal in bimetallic systems has not been considered.

Contaminant (X)	M_X (g/mol)	Material	V (mL)	[X] (mM)	$\rho_{Material}$ (mM)	Material/X (-)	Ref.
Lindane	290.83	nano-Fe/Pd	15	0.017	119	6925	[1]
		nano-Fe/Pd	15	0.017	595	34623	
Pentachlorophenol	266.34	micro-Fe	10	0.038	1786	47619	[18]
		micro-Fe/Pd	10	0.038	1786	47619	
		micro-Fe/Pt	10	0.038	1786	47619	
		micro-Fe/Ni	10	0.038	1786	47619	
		micro-Fe/Cu	10	0.038	1786	47619	
Trichloroethylene	131.39	nano-Fe/Pd	40	0.076	45	587	[19]
		nano-Fe/Ni	40	3.805	45	12	
Trichloroethylene	131.39	micro-Fe	100	0.220	7	32	[20]
		micro-Fe	100	0.210	7	31	
Lindane	290.83	micro-Fe	5	0.024	89	3720	[21]
		micro-Fe	5	0.024	179	7440	
		micro-Fe	5	0.024	357	14881	

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