Catalytic Degradation of Substituted Phenols in Water by Chemically Synthesized Bimetallic Nanoalloys

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ABSTRACT

Stable oxide free nanoalloys of Fe-Pd, Fe-Mg_2 and Fe-Mo, synthesized by simple chemical approach, were found to have good catalytic activity towards degradation of three substituted phenols i.e. 2-chlorophenol (2-CP), 4-chlorophenol (4-CP) and 4-nitrophenol (4-NP). The room temperature studies carried out in the absence of sunlight had shown 100% degradation of 4-CP and 4-NP to environmental friendly degradation products by all the three nanoalloys as affirmed by GC-MS, while in case of 2-CP exceptions were found for Fe-Pd and Fe-Mo. Among the three nanoalloys, Fe-Mg_2 is the most effective and economic alternative to the existing catalysts as it results in 100% degradation of all the substituted phenols at ambient conditions of temperature and pressure and without the use of any other external source.

Keywords: Fe-Pd, Fe-Mg_2, Fe-Mo, substituted phenols, degradation

1 INTRODUCTION

Water contamination from various organic pollutants like substituted phenols is the burning issue of today that is posing concern owing to its environmental toxicity and non-biodegradable nature. These persistent pollutants are causing long term health hazard [1-4] and therefore, it is necessary to eliminate them from ecosystem. Potential amount of work has been done to degrade these pollutants into less toxic byproducts and nanoparticles owing to their high reactivity are known to have better catalytic activity compared to bulk materials [5,6]. Iron being very strong reductant [7] is predominantly used for this purpose [2] but several studies in cleanup of environmental pollutants have proved that bimetallic nanoparticles are effective than zero-valent metals [5,8] due to their easy diffusibility and high activity [9]. When Pd is used in conjunction with Fe [10,11] good dechlorinating activity is observed [12] and with substantial reduction in reaction time when nano Pd/Fe is employed [7]. In addition to Fe/Pd other bimetallic systems were also tested in search of cost effectiveness but no appreciable activity was found in case of Fe-Pt, Fe-Au and Fe-Cu [13,14]. Slightly improved results were achieved by optimizing the Ru/Fe wt.% to 1.5 [14] and using Ca-Fe composite at 300°C [15]. Significant enhancement in dechlorination activity was observed by introducing Ni-Fe bimetallic system [8,16]. All these procedures end up with dechlorination of the desired reactant in case of chlorinated pollutants, while for nitro compounds such oxidation/ reduction procedures are not well-known because of their non-effectiveness in properly degrading the reactant [17]. In order to enhance the degradation activity of chlorinated compounds and especially nitro compounds various other treatments were executed. Most of which require some necessary requirements to be fulfilled like presence of some specific solvent [18], additives [19] or external source like UV [20,21], ultrasound [19], day light [22], microwave [4] etc. or combination of these [1,23,24] in addition to being lengthy, tedious and costly [20,25]. Considering these aspects the present research was designed to synthesize nanoalloys that can cost effectively degrade these contaminants into environmental friendly products without employing tiresome procedures. Hence, offering an easy approach for treatment of these carcinogenic pollutants.

2 EXPERIMENTAL

2.1 Materials and Methods

All the reagents used in this study were of analytical grade and purchased from Fluka and Panreac. Phenols were supplied by Sigma-Aldrich while Anhydrous Sodium sulphate was purchased from Fluka.

2.2 Synthesis of Bimetallic Nanocatalysts

Stable bimetallic nanoalloys Fe-Pd [26], Fe-Mg_2 [27] and Fe-Mo were prepared as mentioned in previous studies by thermal decomposition of the homogeneous mixture of the bipyridine complexes of the component metals under inert atmosphere at 500°C. The resulting materials were

characterized using EDXRF, powder XRD, AFM and TEM. EDXRF confirms the Fe:Pd and Fe:Mo metal ratio to be 1:1 except in case of Fe-Mg in which it is 1:2. The particle size as affirmed by AFM and TEM was in range of 15-30nm for Fe-Pd, 30nm for Fe-Mg_2 and 48-66nm for Fe-Mo. XRPD confirms the *fcc* structure of Fe-Pd while Fe-Mg_2 and Fe-Mo nanoalloys are amorphous in nature.

2.3 Experimental Procedure

Stock solutions (1000ppm) of the phenols were prepared using acetone as solvent. From this 20ppm standard solution of all the phenols were prepared in distilled water. Batch experiments were conducted by taking 0.1g of nanoalloy in a Schlenk tube connected with inert vacuum line and covered with a black paper to avoid sunlight interference in the reaction. To this 5.0ml of distilled water was added and stirred for 10min in order to well disperse the particles in water. After that 5.0ml of standard solution (20ppm) of the phenol was added and contents were stirred for 48hrs at room temperature and then cannula filtered. The filtrate was taken in separating funnel and 0.1ml of 3M H_2SO_4 was added. After that the contents were chloroform extracted with vigorous shaking for 5min. The chloroform extract was then treated with 1.0g anhydrous sodium sulphate, filtered and volume was leveled up to 10ml with chloroform prior to GC-MS analysis [12].

For blank experiment same procedure was adopted, except that in place of phenols distilled water was used. Standards of phenols for GC-MS analysis were made by taking 5.0ml of standard solution (20mg/l) of the phenol with 5.0ml of distilled water and 0.1ml of 3M H_2SO_4 and extracted with (5ml×2) chloroform. After treating the extract with 1.0g anhydrous sodium sulphate volume was leveled up to 10ml and this was analyzed using GC-MS.

2.4 Analysis

The catalytic activity of the as—prepared samples was checked by analyzing the chloroform extracts with help of Agilent GC-MS model 6890N. The temperature program was as follows: Initial value 60°C, ramp at 40°C/min-100°C, then 2°C/min−150°C and finally 30°C/min-250°C. Highly pure grade (99.999%) helium gas was used as carrier gas with the constant flow rate of 1.2ml/min. Temperature of inlet and detector were 220°C and 280°C, respectively. Column used was DB-5. For measurements samples were withdrawn from syringe and a volume of 1.0µL solution was injected.

3 RESULTS AND DISCUSSION

The three nanoalloys Fe-Pd, Fe-Mg_2 and Fe-Mo were used as catalyst for studying the degradation of three phenols (2-CP, 4-CP and 4-NP), taken as representative from the huge number of organic pollutants, in aqueous system in absence of sunlight. The results obtained for each of the sample were tabulated (Table 1) along with peak retention time (R_t) and corresponding m/z values. The results obtained have indicated that all the alloys show good catalytic activity towards *degradation* of chloro- and nitro-phenols (Figure 1).

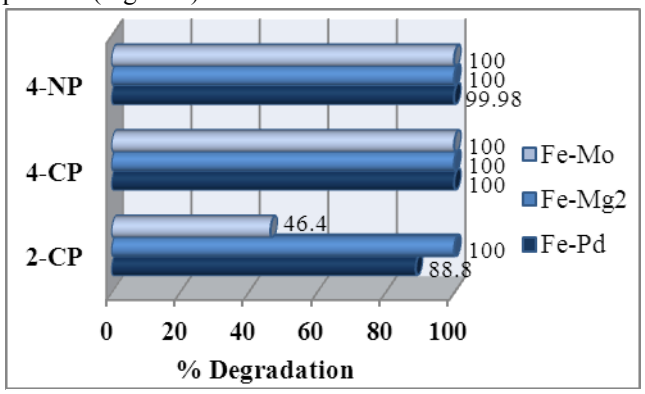


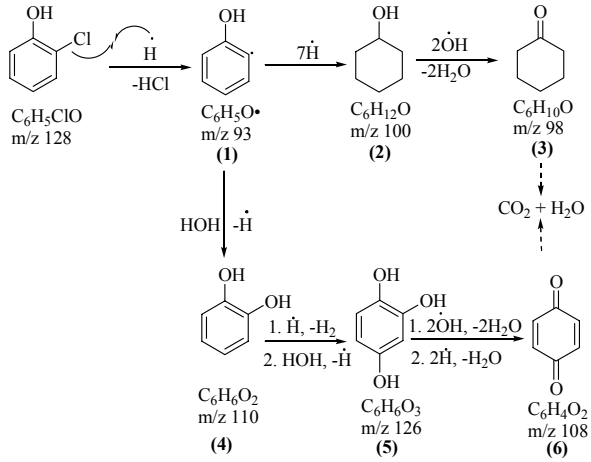
Figure 1: %age degradation of 2-CP, 4-CP and 4-NP

Based on GC-MS results and previous researches the following mechanism was proposed. In case of alloys, Fe is known to play primary role by producing hydrogen by water reduction (equation 1). Other metals (M = Pd, Mg or Mo) involved in the degradation along with Fe act as hydrogen collector [28], thus enhancing the reaction rate by providing catalytic sites to break H—H bond [9] resulting in formation of H˙ as depicted in equation 2. The hydrogen produced as a result plays an active part in degradation of CPs and NPs as presented in Scheme 1-3.

$$Fe + 2\,HOH \longrightarrow Fe^{+2} + H_2 + 2\,OH^- \quad (1)$$

$$M + H_2 \longrightarrow H^{\bullet} + H^{\bullet} \quad (2)$$

Schematic representation of degradation mechanism of 2-CP is presented in Scheme 1. It is obvious from the mechanism layout that 2-CP first degrades to phenol **(1)** by chloride abstraction with help of H˙ resulting in cleavage of C–Cl bond and elimination of HCl. **(1)** is degraded further following two paths.

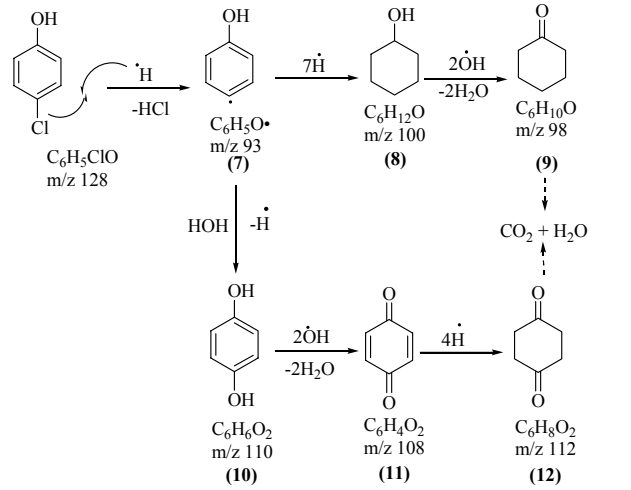


(1) Phenol (3) Cyclohexanone (5) Benzene-1,2,4-triol
(2) Cyclohexanol (4) Pyrocatechol (6) Cyclohexa-2,5-diene-1,4-dione

Scheme 1: Proposed mechanism of degradation of 2-CP

In first route reduction of **(1)** by H˙ results in **(2)**, oxidation of which by ˙OH gives **(3)** that undergoes ring opening leading to formation of aliphatic intermediates that ultimately degrades to CO_2 and H_2O. In second path, **(1)** attacks water molecule and forms **(4)** along with H˙. This radicle attacks para position of **(4)** followed by attack on water molecule to give **(5)** which on oxidation assisted by ˙OH and reduction by H˙ results in **(6)** that further degrade to CO_2 and H_2O by series of ring opening intermediates.

The degradation path followed by 4-CP (Scheme 2) is not much different from the 2-CP and starts with formation of **(7)** that degrades to environmentally friendly products by two possible path ways. First path is identical to that of 2-CP while the second path proceeds with attack of **(7)** on water resulting in **(10)**. This then oxidizes to **(11)** by ˙OH and reduced to **(12)** H˙. After that ring opening takes place and through various intermediate stages the final degradation to CO_2 and H_2O takes place.

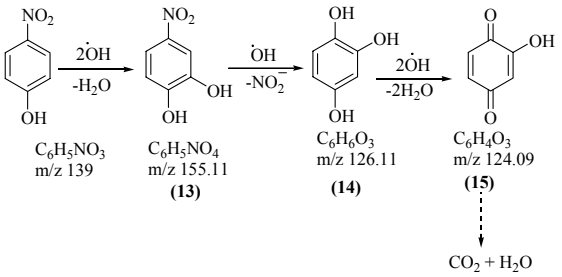


(7) Phenol (9) Cyclohexanone (11) Cyclohexa-2,5-diene-1,4-dione

(8) Cyclohexanol (10) Hydroquinone (12) Cyclohexane-1,4-dione

Scheme 2: Proposed mechanism of degradation of 4-CP

Degradation of 4-NP follows the path as given in Scheme 3. In this case OH˙ plays important role in degradation as against H˙ which is the main specie that has active role in degradation of chlorophenols'.



(13) 4-nitrobenzene-1,2-diol (14) Benzene-1,2,4-triol

(15) 2-hydroxycyclohexa-2,5-diene-1,4-dione

Scheme 3: Proposed mechanism of degradation of 4-NP

The ˙OH may be generated by following route [29]

$$Fe^0 \longrightarrow Fe^{2+} + 2e^-$$

$$Fe + 2\,HOH \longrightarrow Fe^{+2} + H_2 + 2\,OH^-$$

$$H^{\bullet} + O_2 \longrightarrow HOO^{\bullet}$$

$$2\,HOO^{\bullet} \longrightarrow H_2O_2 + O_2$$

$$H_2O_2 + e^- \longrightarrow {}^{-}OH + {}^{\bullet}OH$$

˙OH, hence produced, attacks the H on ortho position of 4-NP to produce water and 4-NP radical, that combines with another ˙OH to give **(13)**. Further attack of ˙OH on para position of **(13)** results in elimination of nitro group and formation of **(14)** which then degrades to **(15)** and finally to CO_2 and H_2O through series of ring opening reactions.

Hence, the degradation studies carried out in absence of sunlight have shown that all the alloys show good catalytic activity towards *degradation* of chloro- and nitro-phenols (Fig. 1) to environmentally friendly products. Of the three nanoalloys used in this study, remarkable activity is observed in case of Fe-Mg_2 towards 2-CP while in case of Fe-Pd and Fe-Mo %age degradation is 88.8% and 46.4%, respectively. 100% degradation of 4-CP is observed for all the nanoalloys. Considering this, it can be safely concluded that alloys having cheap and widely abundant metal like Mg can efficiently replace alloys having expensive metals like Pd which is known for its dechlorinating activity [7,10-12]. Similarly, in the case of 2-CP, Fe-Pd shows less catalytic activity as compared to the Fe-Mg_2 which has 100% degradation activity towards 2-CP. The complete degradation of CPs to CO_2 and H_2O even in absence of sunlight and without utilizing expensive techniques is an important aspect of this study. This is in contrast to earlier studies that *only* resulted in dechlorination of the harmful contaminants [12,15] and in some cases even lead to the formation of more harmful products [7,30]. This high catalytic activity of Fe-Mg_2 alloy can be attributed to higher redox potential of Mg in comparison to other metals that are alloyed with Fe. The same trend is also shown in degradation of 4-NP that is almost 100% for all the alloys. Thus, Fe-Mg_2 is better *economical alternative* to Fe-Pd for the complete and safe degradation of substituted phenols because of abundant nature of its' constitutes (Fe and Mg most abundant metals of earth crust) and hence easily available and inexpensive in addition to being environmental friendly.

4 CONCLUSION

Three nanoalloys Fe-Pd, Fe-Mg_2, Fe-Mo prepared by simple chemical approach are found to be highly active towards degradation of carcinogenic water pollutants i.e. 2-chlorophenol, 4-chlorophenol and 4-nitrophenol into environment friendly products like water and carbon dioxide at room temperature and even in absence of sunlight or any other aid. These nanoalloys show maximum activity for 4-CP, while Mg containing alloy show good catalytic activity towards degradation of 2-CP, 4-CP and 4-NP. Fe-Mg_2 due to its remarkable catalytic activity towards

all the substituted phenols is better economical and efficient alternative to already existing catalysts.

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Table 1: GC-MS results for phenols showing representative m/z values for the corresponding peak retention time, R_t

Nanoalloy	**2-Chlorophenol**			**4-Chlorophenol**			**4-Nitrophenol**		
	R_t	m/z	Species	R_t	m/z	Species	R_t	m/z	Species
Fe-Pd	3.375	93	**(1)**	2.911	98	**(9)**	5.273	155	**(13)**
	3.541	98	**(3)**	3.305	100	**(8)**	11.773	139	4-NP
	3.909	100	**(2)**	4.699	108	**(11)**	25.053	124	**(15)**
				10.446	110		26.550	126	**(14)**
$Fe\text{-}Mg_2$	3.357	93	**(1)**	2.727	93	**(7)**	5.268	155	**(13)**
	3.541	98	**(3)**	2.911	98	**(9)**	25.043	124	**(15)**
	3.901	100	**(2)**	3.305	100	**(8)**	26.557	126	**(14)**
				4.699	108				
				10.446	110				
Fe-Mo	3.533	98	**(3)**	2.911	98	**(9)**	5.270	155	**(13)**
	3.901	100	**(2)**	3.305	100	**(8)**	25.130	124	**(15)**
	5.980	128	2-CP	4.804	108	**(11)**	26.461	126	**(14)**
	10.954	110	**(4)**						
	26.550	126	**(5)**						