# Photo-catalytic degradation of emerging pharmaceutical pollutants using bimetallic Pd-magnetite nanoparticles

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# Introduction

In recent years, concern has been growing on due to contamination of aquatic environment by pharmaceutical compounds. They are biologically active in trace quantities and retain their behavior when discharged into aquatic environment which may leads to increase in potential risk to environment and health hazards. Studies have shown that complete removal of pharmaceutical compounds is difficult to accomplish by conventional wastewater techniques (1, 2). Non-Steroidal Anti-Inflammatory Drug (NSAID) Ibuprofen (IBP) is one of the most consumed medicine and several reports have indicated its presence in effluents of wastewater treatment plant. In spite of its high biodegradation rate, risk remains still high due to generation of toxic by-products during its biological oxidation. Clofibric acid (CFA), a primary metabolite of lipid regulator drug clofibrate, occurs in surface and groundwater due to its polar character. Although its biological effects are not completely understood, it is associated with endocrine disruption through interference with cholesterol synthesis (3). Recent performed studies indicate that Advanced Oxidation Processes (AOPs) could be an interesting and effective technology for removal of recalcitrant contaminants.

Among the various AOPs, heterogenous Fenton like process in combination with UV light is highly efficient in waste water treatment. The present work investigates the efficiency of the combined approach, heterogeneous Fenton reaction with "in-situ" hydrogen peroxide generation from formic acid and oxygen using Pd-magnetite nanoparticles (NPs) in presence of UV/UV-vis light for oxidative degradation of ibuprofen. Photolysis and photo catalytic degradation of ibuprofen was also studied using UV/UV-vis light and simulated solar light.

## **Materials and Methods**

### **Catalyst preparation:**

Magnetite-Palladium Nanoparticles (NPs): Magnetite ( $Fe^{2+/}Fe^{3+}$ ) - Pd NPs were prepared using appropriate amounts of FeSO<sub>4</sub>.7H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, ammonium hydroxide, hydrazine hydrate as reducing agent and PVP as stabilizer (molar ratio  $Fe^{2+}/Fe^{3+}$ : PVP -1:3) in water at 80°C. NPs obtained were cooled and recovered by centrifugation after several washes with water, and kept in ethanol for overnight with continuous stirring. The required quantity of Pd(NO<sub>3</sub>)<sub>2</sub> was further added to obtain the Fe:Pd molar ratio of 50:1 and reduced with hydrazine hydrate. 30wt % NPs was supported on Y-Al<sub>2</sub>O<sub>3</sub>

#### Catalytic Tests:

The degradation reaction of IBP (5mg/L) or CFA (10 mg/L) was carried out with 500 ml of volume, 0.2g/l catalyst and 10mM formic acid. Oxygen was passed bubbling (20 ml/min). Reactions were performed at ambient conditions (25°C and atmospheric pressure) for 3h in presence and absence of a low pressure mercury lamp (254 nm,17W) or simulated Solar light (Xe lamp, 1500W). Samples were withdrawn at regular interval of time and analyzed by UPLC-Mass spectrometry equipped with auto-sampler and photo-diode array detector (Waters) interfaced to an API 5000 mass Spectrometer (AB Sciex) by means of an ESI interface.

# **Results and Discussion**

Table 1 shows mineralization degree of IBP obtained by photocatalysis with different concentration of magnetite-Pd/ Y-Al<sub>2</sub>O<sub>3</sub> catalyst in presence of UV light and simulated solar light. It has been observed that in presence of UV light with lower concentration of catalyst

(0.02 g/L), a high mineralization degree was obtained, with complete conversion of IBP in 30 min of reaction, as shown in Figure 1.Whereas, with increase in catalyst concentration degree of mineralization decreases. In case of photolysis of IBP by UV light and simulated solar light, 100 and 73% conversion of IBP was obtained in 15 min and 3h respectively

Table 1. % Mineralization of IBP	at 3h using different ca	atalyst amounts and light source
	0	

Catalyst concentration	% mineralization at 3h	
	UV light (254nm)	Simulated solar light
0.02g/L	80	62.2
0.05g/L	63	40
0.2g/L	7	34.5
0.02g/L (without light)	0	0
Photolysis	37	0

In Fig 1& 2, numbers (1) and (2) indicate stages of sampling done prior to start of reaction: (1) IBP solution and catalyst stirred for 30 min to check adsorption; (2) Introduction of light and consider initial time  $t_0$ .



of presence UV light -254nm.

**Figure 2**. Decomposition of IBP in presence of simulated solar light.

Photo catalytic degradation of ibuprofen was also carried in presence of UV light (254nm) and "in-situ" generated  $H_2O_2$  using formic acid and oxygen with different concentration of catalyst. With 0.2g/L of catalyst concentration 100% IBP removal was observed within 30 minute of reaction. However, high adsorption of IBP was observed over catalyst under acidic pH. Concerning results obtained with CFA, 100% removal in 90 min with light and 60% removal in 3h without light were observed. Further study will be focused on intermediates formed during photocatalysis of IBP and CFA degradation by photocatalysis.

#### Significance

Magnetite-Pd nanoparticles in presence of UV light are able to decompose and mineralize IBP. Catalyst concentration plays an important role in photo catalytic reaction. Sunlight showed to be a proper source of radiation for this process. It could be interesting to evaluate the mechanism and intermediate formed during photo catalytic reaction of IBP. Degradation of CFA by photocatalysis could be an efficient process to further focused on. **References** 

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