*Int. J. Environ. Res., 9(1):85-92,Winter 2015*
*ISSN: 1735-6865*

# Potential use of Foundry Sand as Heterogeneous Catalyst in Solar Photo-Fenton Degradation of Herbicide Isoproturon

**Kaur, M., Verma, A.* and Rajput, H.**

School of Energy and Environment, Thapar University, Patiala, India

Received 21 May. 2014; Revised 5 Sep. 2014; Accepted 31 Oct. 2014

**ABSTRACT:** This study deals with employing foundry sand (FS) as new low cost iron source in heterogeneous photo-Fenton process for the degradation of herbicide isoproturon (IPU) in aqueous solution. The characterization of the FS by EDS confirmed presence of iron (23%) required for photo-Fenton and simultaneously confirmed absence of any heavy metals which may be susceptible to leaching. The photo-Fenton effects of different reaction parameters like $H_2O_2$ concentration $[H_2O_2]_0$, operating pH, initial concentration of IPU $[C_0]$, FS dose, recycling of FS, effect of area/volume ratio were investigated. Results showed that the maximal removal efficiency were achieved when reaction parameters were $[H_2O_2]_0$= 2.2 mM, pH 3, FS dose=0.5 g/L, $[C_0]$ =25 mg/L. Under optimum condition, 97% degradation efficiency of IPU was achieved within 150 min of reaction. The catalyst recycling test was performed and FS was effectively recycled for 4 times with 20% reduction in degradation efficiency. SEM-EDS analysis of recycled FS confirmed morphology of FS unchanged. Solar baffled batch reactor (SBBR) with recirculation confirmed 70% degradation of IPU after 6 h. IPU mineralization was confirmed with TOC reduction, $NH_4^+$ generation along with formation of intermediates as confirmed through LC-MS.

**Key words:** Foundry sand, Herbicide isoproturon, Photo-Fenton, Degradation, Mineralization

## INTRODUCTION

Exposure to pesticides both occupationally and environmentally causes a range of human health problems increasingly linked to immune suppression, hormone disruption, diminished intelligence, reproductive abnormalities and cancer (Abhilash and Singh, 2009). Actually, less than 1% of the applied dose reaches the target crops, while the remainder ends up contaminating land, air, and, especially water (Malato *et al.,* 2001), thus posing a great threat for the quality of water resources (Guimarães *et al.*, 2014). Isoproturon is a phenylurea herbicide was considered as priority pollutant by the European Union (EU) (Directive 2008/ 32/EC) due to its high toxicity and also because of its low tendency to sorb to soil, leads to extremely easy transport in environment and can therefore easily cause contamination to both surface and ground water. Its half life in water is 30 days (DE, 1989), thus have high tendency toward bioaccumulation. Conventional treatments (Guimarães *et al.*, 2014) are either incapable, inefficient for pesticide treatment or merely transferring the pollutants from one phase to another. This has motivated many researches to find alternate environment friendly solution for the treatment. The success of advanced oxidation process (AOP) heterogeneous as well as homogenous photo catalysis for the degradation of pesticide has been widely accepted in literature (Malato *et al.* 1999; Pichat *et al.,* 2004; Farre *et al.,* 2005; Hincapie *et al.,* 2005; Tamimi *et al.,* 2008). Among these, solar photo-Fenton was particularly very efficient for degradation of pesticide as time required for degradation is less. The mechanism of homogenous photo catalysis is now well established and widely discussed in literature (Kwon *et al.,* 1999; Truong *et al.,* 2004) but they simultaneously add other pollutants to the water (iron sludge). With these concerns, efforts are shifted towards heterogeneous photo-Fenton reaction for degradation of bio-recalcitrant compounds so as to get rid of above discussed problems. Different types of waste materials have been tested as iron source in heterogeneous photo-Fenton degradation of different kind of pollutants (Lucking *et al.,* 1998; Chaudhuri and Sur, 2000; Mecozzi *et al.,* 2006; Djeffal *et al.,* 2013). The slow release of iron ions in case of heterogeneous photo-Fenton reactions limits undesired reaction in comparison with the conventional homogenous catalysis.

*Corresponding author E-mail: anoop.kumar@thapar.edu

Worldwide, Foundry sand is generated in large amounts (9-13 million tons annually) as an industrial by-product and its effective disposal is always a challenging job for the foundry industry (USEPA, 2002; Foundry Industry Recycling Starts Today (FIRST), 2006). A few studies have been reported in literature regarding its reuse potential such as in environmental remediation as adsorbent for different pollutants (Lee *et al.*, 2004; Lee *et al.*, 2004), in agriculture (Dungan and Dees, 2007) and use it in construction material (Bakis *et al.*, 2006; Siddique and Noumowe, 2008). The sand which is used to mold the molten metal after casting process becomes waste, i.e. waste foundry sand, consists primarily of silica sand, coated with a thin film of burnt carbon, residual binder (bentonite, sea coal, resins) residual iron particles and dust.

The objective of this study is to investigate the degradation of isoproturon using foundry sand (FS) as a new low-cost iron source for the heterogeneous photo-Fenton process. To the best our knowledge, this is the first reported study towards the use of foundry sand as heterogeneous catalyst in photo-Fenton degradation of pesticide. This would be of economic interest keeping in mind the high costs required for disposal of foundry sand which we are using as a catalyst that is commonly considered as a waste.

## MATERIALS & METHODS

Isoproturon (IPU), N,N-dimethyl-N'-[4-(1-methylethyl)phenyl] urea, Technical grade (95%), was obtained from Pioneer Pesticides Pvt. Ltd, Chandigarh (India) and used as such without any further purification. Waste Foundry sand was received as a gift sample from local industry and used as such as received without any further modifications. $H_2O_2$ (30% w/v) was purchased from SD Fine Chemicals Limited, India. 0.1 N $H_2SO_4$ was used for adjusting the pH of IPU solution. All the chemicals were of analytical grade and used as such without any further purification throughout the study. For the experimental study 25 mg/L IPU solution was used. For the preparation of all the solutions double distilled water was used.

The degradation studies were performed with UV-visible Spectrophotometer (Hitachi V- 500 UV/VIS (Japan)) double- beam spectrophotometer with isoproturon (IPU) having $\lambda_{max}$ at 239 nm. Degradation of IPU was also confirmed using HPLC [Shimazdu, SED-20A]. HPLC was performed on isocratic HPLC system using water:acetonitirile (60:40) as mobile system (flow rate 0.5 mL/min) with UV detector at 239 nm for isoproturon. The intermediate products were analyzed by Agilent series LC-MS equipped with an ESI source. The column used was Exclipse XDB C-18 and the mass spectrum was operated in positive ion mode. For characterization of foundry sand (FS), scanning electron microscope (SEM) was used as shown in Fig. 1(a).Energy-dispersive X-ray spectroscopy (EDS) was performed for foundry sand to determine its chemical composition using same instrument Fig. 1(b) which is reported in Table 1. The analysis showed absence of any heavy metals which is susceptible to leaching simultaneously showed good percentage of iron (23%) required for photo-Fenton studies.

In this study, work has been done on two type batch reactors, one was shallow pond batch slurry reactor and other was solar baffled batch reactor (SBBR) with recirculation. The shallow pond batch slurry reactor as shown in Fig. 2(a) was made up of borosil glass, 16 cm in diameter and 5.2 cm in height

**Table 1. Mean composition of foundry sand**

| Element | Na K | Mg K | Al K | Si K | K K | Ca K | Ti K | Fe K | Cu K | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| **Weight%** | 1.93 | 1.21 | 7.85 | 58.10 | 1.77 | 1.49 | 1.36 | 23.16 | 3.13 | 100 |

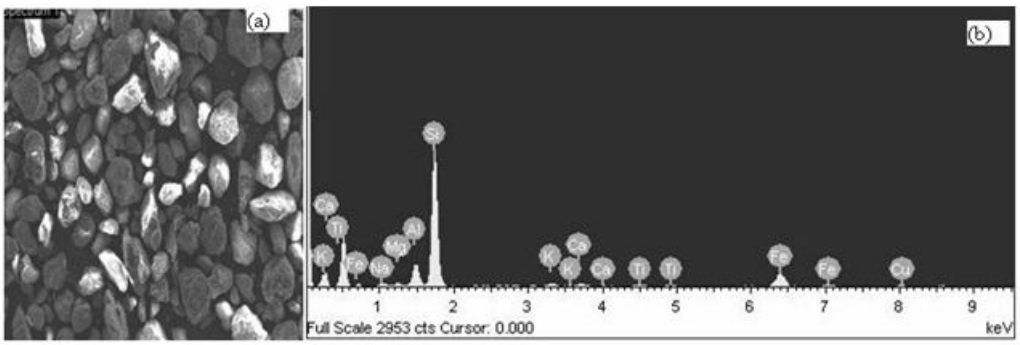


**Fig. 1. SEM Analysis**

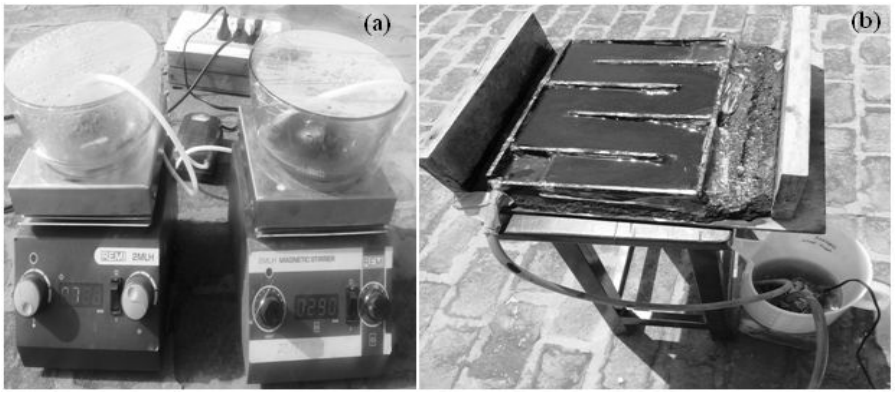


**Fig. 2. Batch Reactors**

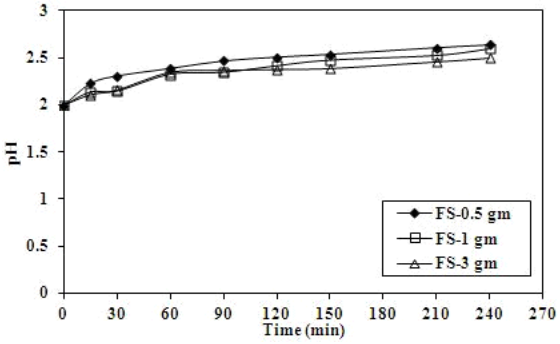


**Fig. 3. PH over time**

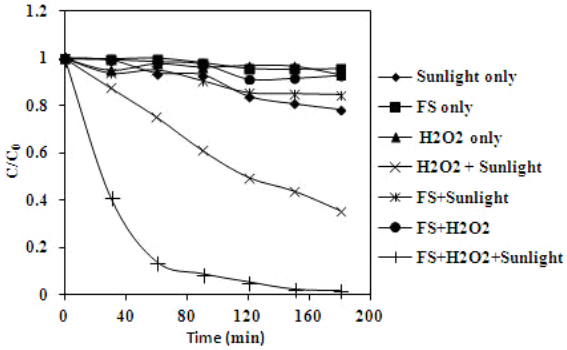


**Fig. 4. Herbicide oxidation**

with a capacity of 1200 mL. For heterogeneous solar photo-Fenton studies, 200 ml of IPU solution (25 mg/L) was taken in this reactor at pH 3 and known amount of Fenton reagent (FS+$H_2O_2$) was added. Samples were taken after regular intervals and analyzed for degradation studies. The experiments were also performed using baffled batch reactor with recirculation as shown in Fig. 2(b), was made up of concrete (20 x 30cm) with four equally spaced baffles. The baffles were made up of cast iron fitted in batch reactor to increase the retention time of the solution to be treated. The base of the reactor was covered with plastic sheet as concrete will increase the pH of solution which ultimately stops Fenton reaction. All the solar experiments were carried during timings 10.00 A.M. to 3.30 P.M. in months of March to May, 2014 at Patiala, Punjab [India]. Experiments were repeated thrice to check the reproducibility of results and average values are reported.

## RESULTS & DISCUSSION

One of the major limitations of using different heterogeneous catalyst in photo-Fenton studies is variation in pH during the reaction. Normally the pH of the solution increases with time after addition of heterogeneous catalyst, which ultimately stops Fenton reaction (Mecozzi *et al.*, 2006). In this context, the change in pH studies with time has been performed using different amount of foundry sand. The initial pH was adjusted at pH 2 and was continuously monitored for 180 min after addition of different foundry sand concentration. There was no significant change in the pH even after 180 min (Fig. 3). This eliminates the necessity of continuous pH adjustment i.e. in the range of 2-3 pH for photo-Fenton studies.

Before the detailed investigation regarding the heterogeneous Fenton catalytic activity of foundry sand on the herbicide degradation, different preliminary experiments were performed to evaluate the benefit and efficiency of each condition. Preliminary experiments were carried out as follows:

(1) Sunlight only (2) FS only (3) $H_2O_2$ only (4) $H_2O_2$ +sunlight (5) FS + sunlight (6) FS+ $H_2O_2$ (7) FS + $H_2O_2$ +sunlight

Sunlight alone was not efficient process since less than 25 % degradation of isoproturon within 180 min was observed. Negligible degradation (4.16%) was achieved with foundry sand only in 180 min thus confirming negligible adsorption. From the results it

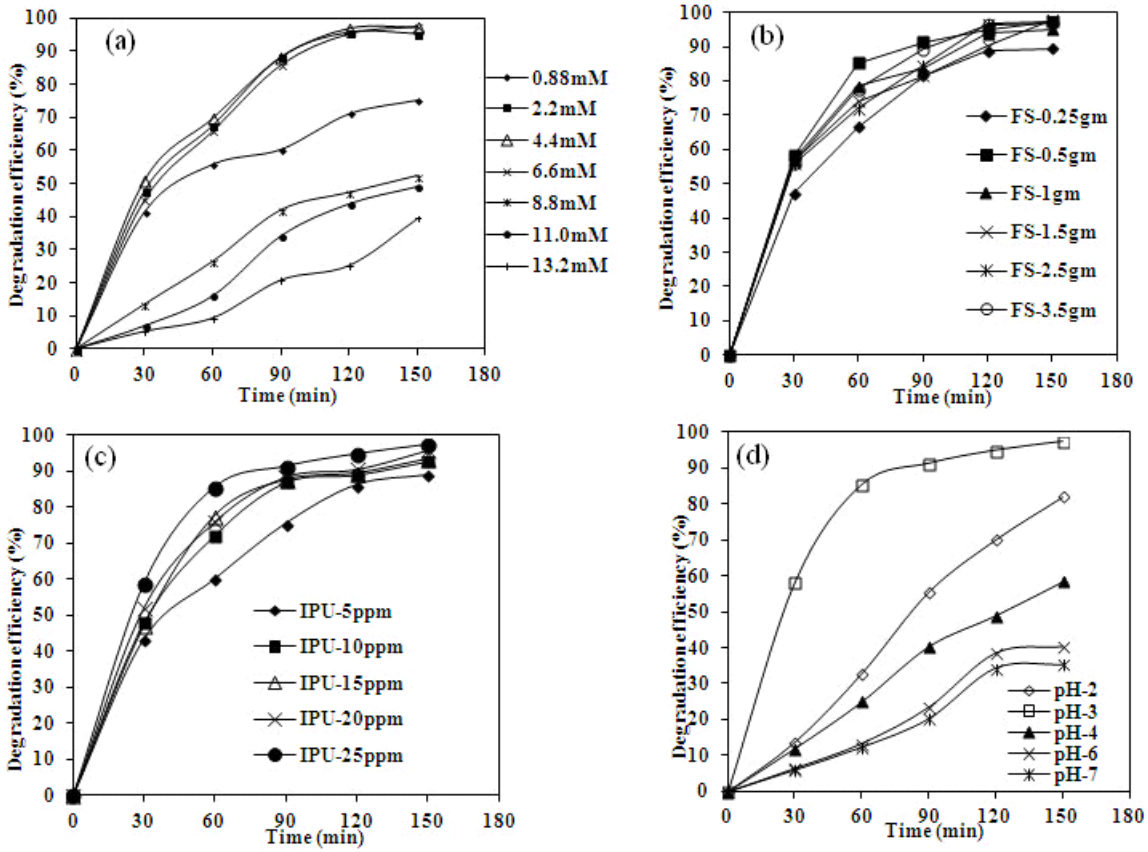


**Fig. 5. Degradation over time**

was observed that herbicide was resistant to the oxidation from $H_2O_2$ alone (Fig. 4). The combined action of $H_2O_2$ and sunlight lead to 64.4% degradation in 180 min. Less than 20 % degradation in 180 min was achieved with combination of foundry sand and sunlight. In Fenton process (FS+ $H_2O_2$), around 8% degradation was achieved in 180 min. Maximum degradation efficiency 97 % was observed in solar photo-Fenton process (FS+ $H_2O_2$ + sunlight).

The relative efficiencies of the above combinations are in following order:

FS + $H_2O_2$ +sunlight> $H_2O_2$ +sunlight> sunlight only > FS + sunlight> FS + $H_2O_2$ > $H_2O_2$ only> FS only.

Thus from the studies, it was confirmed for getting higher degradation efficiency solar photo-Fenton came out to be best treatment for isoproturon.

For completing any Fenton reaction stoichiometry amount of $H_2O_2$ is very important. Amount less or more than stoichiometry amount of $H_2O_2$ generally leads to lesser degradation rates. With excessive $H_2O_2$, it can react with OH radicals and inhibit Fenton reaction (1).

$$H_2O_2 + OH^{\cdot} \longrightarrow H_2O + HO_2^{\cdot} \qquad (1)$$

The excess amount also reacts with ferric ions yielding Fe (III) - hydroperoxy (Guimarães *et al.*, 2014), thus reducing the number of ferrous ions required for Fenton reaction. Ferric ions reduced to ferrous ions in the presence of iron i.e. Fenton reaction. In this view, $H_2O_2$ was varied from 0.0 mM to 13.2 mM for degradation of isoproturon by keeping the other operating condition fixed (pH 3, $C_0$ = 25 mg/L, and FS = 2 gm). The initial increase of $H_2O_2$ concentration up to 2.2 mM lead to increase in degradation rate to 90% after 90 min as expected because more OH radicals will be formed. The removal efficiency was almost constant till 6.6 mM, decreased thereafter as $H_2O_2$ concentration was increased from 6.6 mM to 13.2 mM as shown in fig. 5(a). Thus, the $H_2O_2$ concentration 2.2 mM was used for further experiments (Verma *et al.*, 2013).

The effect of foundry sand concentration on degradation of isoproturon is shown in fig. 5(b). Amount of foundry sand was varied in the range of 0.25-3.5 gm while keeping other operating condition unchanged i.e. pH 3, $H_2O_2$=2.2 mM, $C_0$ = 25 mg/L and volume of solution 200 mL. The herbicide degradation increased with increasing foundry sand concentration. The 86% degradation of herbicide was achieved with

foundry sand concentration of 0.5 gm after 60 min. On the other hand, increasing foundry sand above 0.5 gm may inhibit the process efficiency due to the scavenging of hydroxyl radical (2) (Yang *et al*., 2013).

$$\cdot OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad (2)$$

The effect of initial IPU concentration on the photo-Fenton process was observed, since pollutant concentration is an important parameter in wastewater treatment. As shown in Fig. 5(c), the efficiency of degradation increased with the increase in the pesticide concentration. The increase of pesticide concentration from 5 to 25 mg/L increased the degradation efficiency from 88% to 97% after 150 min. A higher concentration increases the number of IPU molecules per volume unit, increases the probability of collision between isoproturon molecule and oxidizing species, which lead to enhancement in the degradation efficiency (Daud and Hameed, 2010).

Fig. 5(d) illustrates the effect of pH on the IPU degradation using FS as heterogeneous catalyst. The experiments were carried out at pH range of 2-7 keeping other operating conditions fixed at FS= 0.5 gm and $H_2O_2$ = 2.2 mM. It was observed that maximum degradation efficiency (97.32%) was found at pH-3. However, further increasing pH from 3 to 7 resulted in decreased degradation efficiency (35.21%). The reduction in efficiency at high pH value might be due to the precipitation of iron as $Fe(OH)_3$ thereby lowering its ability to catalyze $H_2O_2$ (Saritha *et al.,* 2007) and lower the transmission of the radiation (Saritha *et al.,* 2007). Secondly, the decrease in degradation efficiency might be due to the dissociation and auto-decomposition of $H_2O_2$ (Tamimi *et al.,* 2008). It was also known that there was decrease in the oxidation potential of OH radical with increasing pH (Tamimi *et al.,* 2008). The slight reduction in degradation efficiency at pH lower than 3 was due to OH radical scavenging of $H^+$ ions (3).

$$OH^{\cdot} + H^+ + e^- \rightarrow H_2O \quad (3)$$

For the field applications of heterogeneous solar photo-Fenton, the stability of the catalyst is very important. In this regard, the catalytic activity of the foundry sand for subsequent cycles for degradation of isoproturon i.e. Recycling studies were conducted. After completion of each run, foundry sand was separated from solution by filtration and then washed with distilled water, dried at $80^0$C for 1h and was reused for next run with fresh isoproturon solution. The foundry sand was effectively recycled for four times with 20% reduction in degradation efficiency. The morphology of recycled FS was unchanged as clear from SEM-EDS (fig. 6 (a) and (b)). The reduction in efficiency of catalyst might be due to accumulation of intermediates formed during oxidation, surface deposition and loss of active phase leaching (Daud & Hameed, 2010). This reduction in degradation

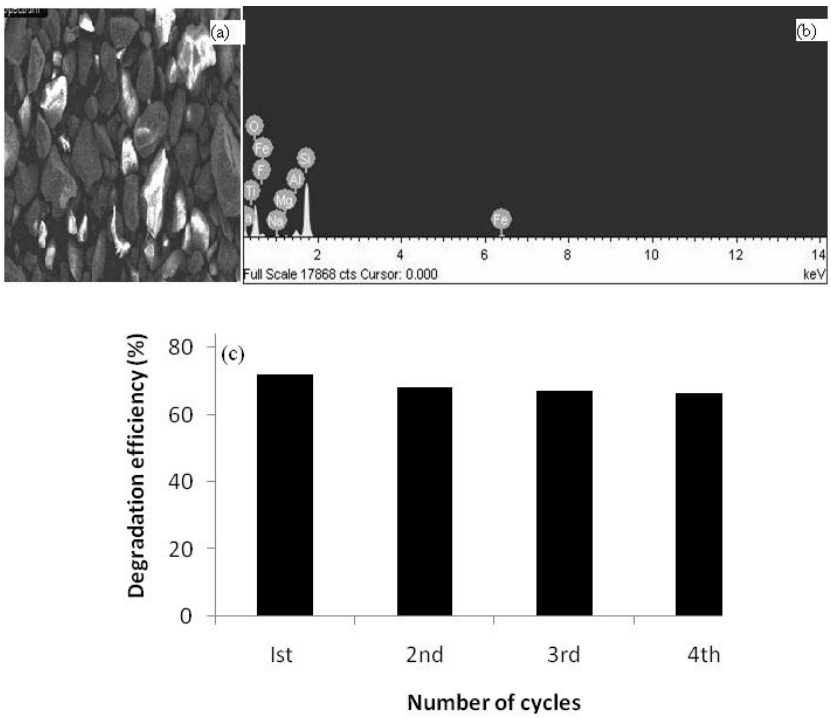


**Fig. 6. SEM -EDS Analysis**

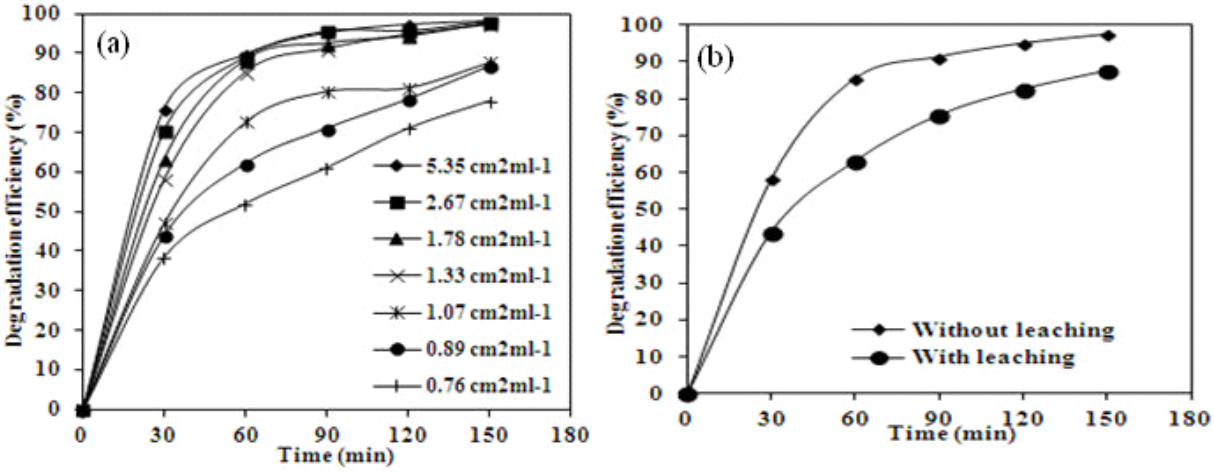


**Fig. 7. Degradation over time**

efficiency might also be due to some loss in weight of FS during filtration (nearly 5%) as clear from fig. 6(c). Leachate after every cycle was tested for the total dissolved iron concentration and in every case it was found less than 3 mg/L i.e. the discharge limit (EPA, 1986).

For field scale applications of solar photo-Fenton process using foundry sand as catalyst, the depth of reactor is very important. Generally for more solar light penetration, less depth and more area is recommended. This can be achieved by both keeping the volume constant and area varied or by keeping area constant and volume varied. In our studies, we varied the volume by keeping the aperture constant. In this view, A/V variations of slurry pond reactor were varied from 0.76 to 5.35 $cm^2$/mL. The degradation efficiency increased with the reduction in the volume of the sample to be treated i.e. less depth (fig. 7(a)). Actually, reducing the volume increases A/V ratio thus enhancing surface area of solution leading to increase in path length of photons resulting in more OH radicals (Verma *et al.*, 2013). Generally, in photo-Fenton studies, handling of iron sludge adds other pollutants to the water which can pose threat to environment. In this view, efforts have been done to leach out iron from foundry sand in dissolved iron form to catalyze the photo-Fenton studies. In our studies, leaching experiment was carried out by adding 0.5gm of foundry sand into 200ml of isoproturon solution using stirring overnight. After filtration through blotting sheet, the reaction was started by adding 2.2 mM $H_2O_2$ at pH-3. The degradation achieved was 85% after 150 min of solar photo-Fenton treatment with iron concentration 2.5 mg/L as shown in fig. 7(b).

Experiment was carried out in a SBBR designed for the degradation of IPU, as shown in Fig. 2b. The optimized parameters under which the reaction was carried out were $[C]_0$ = 25 mg/L ; $[H_2O_2]_0$ = 2.2 mM; FS dose = 0.5 gm; pH 3. To limit the variation in pH during the photo-Fenton process, the bottom surface of reactor was covered with plastic and 70% degradation efficiency was achieved using this designed system after 6 h. Baffles were introduced into the reactor in order to increase the contact time between IPU, FS and sunlight for achieving higher degradation rates. Reactors with inner layer of plastic can be a feasible alternative for the construction of reactor to limit pH variations during the reaction (Verma *et al.*, 2014).

For complete mineralization, generally formation of $CO_2$ along with generation of anions and cations are preferable indicators [28].

In present study, we have measured the TOC reduction along with $NH_4^+$ generation. TOC reduction was 85% after 3 h of solar-photo-Fenton treatment of IPU. The release of $NH_4^+$ was 69% during first hour of treatment and after that it achieved a constant value of 82% after 3 h of treatment. For the confirmation of intermediates, the LC-MS analysis of the treated sample was performed. Analysis confirmed the formation of various intermediates (i) monodemethylisoproturon (ii) didemethylisoproturon (iii) 3-hydroxy isoproturon during solar-photo-Fenton treatment of IPU; same have been reported in our previous studies (Verma *et al.*, 2014, Verma *et al.*, 2014).

## CONCLUSIONS

In this study, attempt has been made for using FS as heterogeneous catalyst in photo-Fenton process for degradation of IPU.

- The results confirmed effective use of FS as iron source in photo-Fenton degradation studies of herbicide IPU.

- The best degradation efficiency of 97% was achieved at $[H_2O_2]_0$= 2.2 mM, pH 3, FS dose=0.5 g/L, $[IPU]_0$= 25 mg/L.
- 70 % degradation efficiency was achieved in SBBR with recirculation using optimized parameters. The pH of reaction remains unaltered with reactor having inner plastic lining.
- The advantages of this system are high degradation efficiency, simple handling, environmental friendly, and low cost waste as iron source.

**ACKNOWLEDGEMENTS**

The study was supported by grant from Defence Research and Development Organization (ERIP/ER/ 1003860/M 101/1281), New Delhi and The Institution of Engineers (India) [Project I.D PG2013009].

**REFERENCES**

Abhilash, P. C. and Singh, N. (2009). Pesticide use and application: an Indian scenario. Journal of Hazardous Materials, **165**,1-12.

Bakis, R., Koyuncu, H. and Demirbas, A. (2006). An investigation of waste foundry sand in asphalt concrete mixtures. Waste Management & Research, **24**, 269–274.

Chaudhuri, S. K. and Sur, B. (2000). Oxidative Decolorization of Reactive Dye Solution Using Fly Ash as Catalyst. Journal of Environmental Engineering, **126 (7)**, 583–594.

Daud, N. K. and Hameed, B. H. (2010). Decolorization of Acid Red 1 by Fenton-like process using rice husk ash-based catalyst. Journal of Hazardous Materials, **176**, 938-944.

DE, (1989). Department of the Environment, London, Pesticides in water supplies. (DoEReference: WS/45/1/1).

Djeffal, L., Abderrahmane, S., Benzina, M., Siffert, S. and Fourmentin, S. (2013). Efficiency of natural clay as heterogeneous Fenton and photo-Fenton catalyst for phenol and tyrosol degradation. Desalination and Water Treatment, **52**, 2225-2230.

Dungan, R. and Dees, N. (2007). Use of Spinach, Radish, and Perennial Ryegrass to assess the availability of metals in waste foundry sands. Water, Air, & Soil Pollution, **183**, 213–223.

European commission, Decision no. 2455/2001/EC, Directive 2008/32/EC, in press.

Farre, M. J., Franch, M. I., Malato, S., Ayllon, J. A., Peral, J. and Domenech, X. (2005). Degradation of some biorecalcitrant pesticides by homogeneous and heterogeneous photocatalytic ozonation. Chemosphere, **58**, 1127–1133.

FIRST, (2006). Foundry Industry Recycling Starts Today, On-line information accessed October 2, 2006 at http:// www.foundryrecycling.org/org/whatis.html.

Guimarães, B.S., Kleemann, N., Caldas, S.S., Costa, F.P., Silveira, M.A.K.., Duarte, F.A. and Primel, E.G. (2014). Environmentally friendly system for the degradation of multipesticide residues in aqueous media by the Fenton's reaction. Environmental Science and Pollution Research, **21**, 584-592.

Hincapie, M., Maldonado, M.I., Oller, I., Gernjak, W., Sanchez-Perez, J.A., Ballesteros, M.M. and Malato, S. (2005). Solar photocatalytic degradation and detoxification of EU priority substances. Catalysis Today, **101**, 203–210.

Kwon, B.G., Lee, D.S., Kang, N. and Yoon, J. (1999). Characteristics of p-chlorophenol oxidation by Fenton's reagent. Water Research, **33**, 2110–2118.

Lee, T., Benson, C. and Eykholt, G. (2004). Waste green sands as reactive media for groundwater contaminated with trichloroethylene (TCE). Journal of Hazardous Materials; B, **109**, 25–36.

Lee, T., Park, J. and Lee, J. (2004). Waste green sands as reactive media for the removal of zinc from water. Chemosphere, **56**, 571–581.

Lucking, F., Koser, H., Jank, M. and Ritter, A. (1998). Iron powder, graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxide. Water Research, **32**, 2607–2614.

Malato, S., Blanco, J., Richter, C., Milow, B. and Maldonado, M. I. (1999). Pre-industrial experience in solar photocatalytic mineralization of real wastewater. Application to pesticide containers recycling. Water Science and Technology, **40**, 123–130.

Malato, S., Caceres, J., Agüera, A., Mezcua, M., Hernando, D., Vial, J. and Fernández-Alba, A. R. (2001). Degradation of imidacloprid in water by photo-Fenton and $TiO_2$ photocatalysis at a solar pilot plant: a comparative study. Environmental Science & Technology, **35**, 4359-66.

Mecozzi, R., Palma, L. D., Pilone, D. and Cerboni, L. (2006). Use of EAF dust as heterogeneous catalyst in Fenton oxidation of PCP contaminated wastewaters. Journal of Hazardous Materials; B, **137**, 886–892.

Pichat, P., Vannier, S., Dussaud, J. and Rubis, J. P. (2004). Field solar photocatalytic purification of pesticides-containing rinse waters from tractor cisterns used for grapevine treatment. Solar Energy, **77**, 533–542.

Saritha, P., Aparna, C., Himabindu, V. and Anjaneyulu, Y. (2007). Comparison of various advanced oxidation processes for the degradation of 4-chloro-2 nitrophenol. Journal of Hazardous Materials, **149**, 609-614.

Siddique, R. and Noumowe, A. (2008). Utilization of spent foundry sand in controlled low strength materials and concrete. Resources, Conservation and Recycling, **53**, 27–35.

Tamimi, V. M., Qourzal, S., Barka, N., Assabbane, A. and Ait-Ichou, Y. (2008). Methomyl degradation in aqueous solutions by Fenton's reagent and the photo-Fenton system. Separation and Purification Technology, **61**, 103-108.

Truong, G.L., Laat, J. D. and Legube, B. (2004). Effects of chloride and sulfate on the rate of oxidation of ferrous ion by $H_2O_2$. Water Research, **38**, 2383–2393.

USEPA, (2002). U.S. Environmental Protection Agency, Beneficial Reuse of Foundry Sand: A Review of State Practices and Regulations.

Verma, A., Prakash, N. T. and Toor, A. P. (2014). Photocatalytic Degradation of Herbicide Isoproturon in $TiO_2$ Aqueous Suspensions: Study of Reaction Intermediates and Degradation Pathways. Environmental Progress & Sustainable Energy, **33 (2)**, 402-409.

Verma, A., Sheorn, M. and Toor, A. P. (2013). Titanium dioxide mediated photocatalytic degradation of malathion in aqueous phase. Indian Journal of Chemical Technology, **20**, 46-51.

Yang, S., Yu, H., Chen, Y., He, F., Li, X. and Lu, K. (2013). The degradation pathway of aminosilicone polymer in aqueous microemulsion by Fenton process. Polymer Degradation and Stability, **98**, 464-470.

Verma, A., Prakash, N. T. and Toor, A. P. (2014). An efficient $TiO_2$ coated immobilized system for the degradation studies of herbicide isoproturon: Durability studies. Chemosphere, **109**, 7-13.