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In-situ dual effect of novel Fe-TiO_2 composite for the degradation of phenazone

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ABSTRACT

Study presents the applications of innovative, inexpensive composite made up of Fuller's Earth (FE) and Foundry Sand (FS) for incorporating in-situ dual effect (photocatalysis and photo-Fenton). FE and FE + FS beads have been contrived for the degradation of pharmaceutical drug Phenazone (PHZ) which persists even in drinking and groundwater. The composite material possesses the inherent property of presence of iron content which leaches in the acidic medium (leading to photo-Fenton) along with surface coated TiO_2 (leading to photocatalysis) thus exhibiting the dual effect. 60% of synergy was observed with dual effect over photocatalysis and photo-Fenton. Box Behnken Design (BBD) was used to optimize the parameters and % degradation, nitrate ions concentration and nitrite ions concentration were used as responses. Kinetics studies revealed the increase in the reaction rate to 5 folds, thus envisages degradation to be achieved at a faster pace. The beads were durable enough to be recycled up to 35 recycles while maintaining their catalytic activity. The retention of iron and TiO_2 in recycled beads was further confirmed through various characterizations of XRD, SEM-EDS, and UV-DRS. Further mineralization studies were conducted and reduction in COD and TOC was carried out. Various intermediates were analyzed through GC–MS and reaction mechanism was suggested for the mineralization of PHZ.

1. Introduction

Although numerous applications of advanced oxidation process AOP's have been cited in literature in context to degradation of the wide variety of pollutants [1–3], yet its commercial applications have been in limbo. Almost all the studied techniques have either individual drawbacks like cumbersome separation of TiO_2, larger quantity of catalyst being utilized, Iron sludge production, high dose of H_2O_2 or process drawbacks like electron hole recombination [4]. Moreover, these processes have the potential drawback of being scaled-up with major concerns like increase in the treatment time, compact design of the process, mass transfer limitations along with all other factors.

Over the past few years, work have been reported on the fixed-bed photocatalysis (heterogeneous and homogeneous), where the catalyst is being coated on some material and subsequently used for degradation [5]. Studies related to fixing of catalyst on supports and their subsequent use in the degrading pollutants have been extensively cited in the literature [6–9]. In all these cases, durability, recyclability, cost of the support material has not been studied effectively. Moreover, concerns regarding the increase in treatment time due to mass transfer limitations, slow reaction rates, along with durability, cost of support materials still to be answered in fixed bed photocatalysis.

Hence, most of the research is always being focused towards the reduction in the treatment time along with cost optimization of the process. In this context, the present study reports the innovative concept of the dual process of photocatalysis and photo-Fenton taking place at same place and same time for the degradation of recalcitrant pollutant. The dual process has excellent degradation efficiency but has not been explored well yet. The cost of the process and a high dose of chemicals can be substantially reduced if the two different processes (photo-Fenton and photocatalysis) are coupled together in one system which would consequently increase the degradation rate as well. The concept of dual effect has been recently suggested by few studies for enhancing the degradation efficiency [10,11]. The improved degradation efficiency by the introducing dual effect can be attributed to the production of sufficient amount of hydroxyl radicals generated simultaneously by both ongoing processes. The basic mechanism of dual process taking place might be explained as shown in Eqs. (1)–(8). The major problem of electron-hole recombination is solved in this novel effect as the electrons generated in the photocatalysis helps in the

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conversion of Fe^{3+} to Fe^{2+} as shown in Eqs. (7) and (8). Scavenging effect of the H_2O_2 is explained using Eq. (9).

$$Fe^{2+}_{aq} + H_2O_2 \rightarrow Fe^{3+}_{aq} + OH^- + \cdot OH \tag{1}$$

$$Fe^{3+}_{aq} + H_2O_2 + H_2O \rightarrow Fe^{2+}_{aq} + H_3O^+ + HO_2^- \tag{2}$$

$$Fe^{3+}_{aq} + H_2O \xrightarrow{h\nu} Fe^{2+}_{aq} + H^+ + \cdot OH \tag{3}$$

$$TiO_2 \xrightarrow{h\nu} e^- + h^+ \tag{4}$$

$$TiO_2 + H_2O \rightarrow TiOH^- + \cdot OH \tag{5}$$

$$TiOH^- + h^+ \rightarrow TiHO^{\cdot} \tag{6}$$

$$TiO_2 + O_2 + e^- \rightarrow TiO_2 + O_2^- \tag{7}$$

$$Fe^{3+}_{aq} + e^- + H_2O \rightarrow Fe^{2+}_{aq} + H^+ + \cdot OH \tag{8}$$

$$\cdot OH + H_2O_2 \rightarrow HO_2 + H_2O \tag{9}$$

In the present study the novel concept of the dual process for the degradation of pharmaceutical compound Phenazone (PHZ) has been introduced. Phenazone is non-steroidal antipyretic, anti-inflammatory drug (NSAIDS) [12] most commonly used for reduction in fever, ear infections, and skin infections and for relieve of pain. NSAIDS have been found in surface water [13], groundwater and even in drinking water [14]. Even at low concentration of drugs, they can pose threat to living beings due to resistance caused by these in the bacteria and are harmful to the aquatic species. Its presence in natural waters clearly indicates the inefficacy of conventional treatment methods [15].

In the present study, innovative noble inert composite material has been selected for TiO_2 immobilization i.e. Fuller's Earth (FE) (Fig. 1a), which is also a good source of natural iron oxides. Further to make the process more lucrative from the applications point of view, waste material of the industry i.e. Foundry Sand (FS) (Fig. 1b) has been used as an alternative additional iron source. In this way, a novel support material has been developed capable of incorporating in-situ dual effect (photocatalysis and photo-Fenton) at the same place. This is the first reported study incorporating both the processes for the degradation of the pharmaceutical compound PHZ. Moreover the study of durability of composite material has been given main attention in the reported study to boost its scale-up applications. Box Behnken Design (BBD) has been used to optimize and analyze the responses [16,17]. Various parameters like treatment time, H_2O_2 dose, the surface area covered have been used.

2. Material and methods

2.1. Materials

Phenazone (PHZ) > 98% purity, was obtained from TCI Chemicals, India. Degussa TiO_2-P25 (Rutile/Anatase 30:70) was obtained from Evonik (India) while Hydrogen Peroxide (H_2O_2) (30% w/v), an oxidant was bought from Ranbaxy (India). Waste foundry sand (FS) was collected as such from a local industry, Patiala (India). Fuller's earth was acquired from local vendor, Patiala (India). Sodium acetate, > 98.5% purity and acetic acid, > 99.5% purity, acquired from TCI Chemicals (India) was used for preparing acetate buffer. Sodium carbonate (anhydrous), > 98.5% purity was procured from Loba Chemie Pvt Ltd (India). For all lab-scale experiments, UV tubes (36 W × 7, UV-A, Philips) were used. All aqueous solutions were prepared with double distilled water.

2.1.1. Composite material for dual effect studies

Dual effect of photocatalysis and photo-Fenton was proposed using two types of composite beads which were made up of FE and FE + FS (actual photographs depicted in Fig. 2(i) and Fig. 2(ii) respectively). FE and FS are the natural source of iron oxides which was subsequently confirmed by their characterization. Fuller's Earth beads (spherical in shape) were made manually and subsequently baked at 800 °C for 2 h for gaining the strength. The bead size was measured by taking randomly 15–20 beads then the average diameter was quoted by measuring the diameter in multiple directions using a screw gauge. The average diameter came out to be 12.20 mm. Density of the FE + FS composite beads came out to be 1675 kg/m^3. Composite beads were prepared by coating TiO_2 on the surface of beads using dip coating method two times [8,18]. The weight % of TiO_2 to the beads came out to be 4%. XRD of the uncoated beads and TiO_2 coated beads confirmed the presence of iron oxides in both types of beads (Fig. 3). SEM-EDS images confirmed that the coating of TiO_2 was uniform and EDS confirmed the presence of iron with TiO_2 in freshly coated beads (Fig. 2(a)–(c)). Elemental mapping of the Ti, O and Fe catalyst used is depicted in Figs. S1–S3. The presence of Fe along with TiO_2 [19–22] confirmed the dual process.

For the comparison, the FE + FS composite beads were made by keeping the proportion of Fuller's earth and Foundry sand as (2:1). XRD of the uncoated beads of FE + FS confirmed the presence of iron even after heating. Similarly here the SEM images showed TiO_2 coating was appropriate and uniform. EDS also confirmed Ti and Fe in the coated beads (Fig. 2).

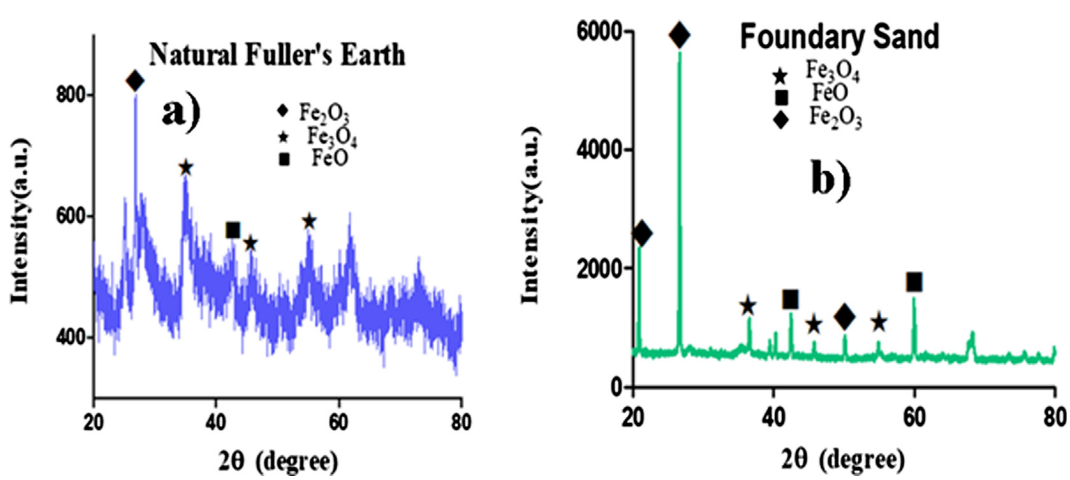

Fig. 1. XRD pattern of (a) Natural Fuller's Earth and (b) Foundry Sand.