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Invited paper

Synergistic effect of dual process (photocatalysis and photo-Fenton) for the degradation of Cephalexin using TiO_2 immobilized novel clay beads with waste fly ash/foundry sand

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ABSTRACT

Novel composite clay beads mixed with foundry sand (FS)/fly-ash (FA) were used as support materials for fixing the catalyst TiO_2 and subsequently used as iron source. The in-situ iron generation in case of beads that contained either FS/FA or both induced dual effect (photo-Fenton and photocatalysis) in the same treatment unit thus leading to synergistic effect for the degradation of antibiotic Cephalexin. Composite beads (FS/FA/TiO_2) showed relatively best results (89% degradation) as compared to FS/TiO_2 (79%) or FA/TiO_2 (81%) at optimized conditions. From the kinetics data, there was 30–45% increase in first order rate constant in case of FS/FA/TiO_2 beads pertaining to dual effect. The stability of the catalyst even after 35 recycles, as confirmed through SEM/EDS and XRD analysis; justified its claim for field-scale applications. Further, mineralization of pollutant was validated by reduction in COD (82%) along with generation of various anions whereas intermediate products were identified through GC–MS analysis.

1. Introduction

There have been recent concerns related to the management and handling of industrial waste like foundry sand (FS) and fly-ash (FA) as they can pose serious threats to the society. With established environmental and health impacts of these kinds of waste, there is widespread demand of efficient handling of these waste. Worldwide generation of FA and FS is approximately 131 and 13 million tonnes per year, respectively [1,2]. Their effective management in terms of recycling/reuse is a need of the hour as large amounts of chemicals and manpower have been required to handle this kind of environmental concern. The studies pertaining to the utilization of such kind of waste as construction material [3] or as adsorbents for contaminants [4,5] have been reported. With known composition of iron, aluminium, FS/FA can be effectively used for wastewater treatment. Very few studies have demonstrated the efficacy of waste FA and FS to be recycled and used as low-cost alternative iron source in water treatment technologies [6,7]. However, the present study innovates the in-situ dual effect concept using FS and FA for treating the non-biodegradable waste with reduction in treatment time.

The increasing emphasis on the development of environment friendly and effectual treatment methods to completely eliminate recalcitrant organic pollutants from wastewater has prompted the scientists to investigate new innovative modifications that can be implanted in the present advanced wastewater treatment technologies. Among advanced oxidation processes, one of the economic alternative that has shown promising results in the field of wastewater treatment is the photo-Fenton process that produces hydroxyl radicals through the catalytic activity of Fe^{2+}/Fe^{3+} in the presence of hydrogen peroxide [8–11]. However, the generation of iron sludge and incomplete mineralization of organic pollutants are the major drawbacks of this process [12]. Further, lower efficiency of photon utilization restricts its industrial applications [13].

Among advanced oxidation processes, another method that has been extensively explored is TiO_2 photocatalysis for the transformation of large variety of non-biodegradable pollutants into inorganic species [14–16]. The use of TiO_2 suspensions offers more desirable degradation efficiency due to better mass transfer applications and more effective illumination of the catalyst surface. The main pitfall of using suspended catalyst is its separation from the aqueous solution after treatment which becomes a hurdle towards its commercial applications [17]. Therefore, a viable solution to the preceding problem is immobilization of TiO_2 over some suitable inert support materials

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in a manner so as to avail sufficient amount of surface area to attain an effectual photodecomposition of the pollutants [18,19]. An extensive literature is available on the fixed-bed photocatalytic degradation of different organic pollutants using several types of support materials like cellulose fibre cloth [20], SBA-15 [21], cement beads [22], pebbles [23], silica gel beads [24], glass spheres [25], glass plate [26], cement slabs [27]. Although effective durability of the supports has been quoted in these studies but the increase in treatment time has always been a concern due to mass transfer limitations. Moreover, the successful implementation of photocatalytic systems has not been accomplished yet because of certain operational implications as well as high energy costs. These implications can be handled by modifying the process along with proper optimization of all the operating parameters which subsequently give way to their field-scale applications [28].

To enhance the degradation efficiency and reduce the time of photocatalytic reaction, many efforts have been devoted and reported in literature for increasing the concentration of hydroxyl radicals prevailing in the photocatalytic process. Addition of oxidants like H_2O_2, $S_2O_8^{2-}$, IO_4^-, ClO_4^- have already been proven effective for improving the reaction rate [29,30]. There are recent reports where coupling of the two processes (photocatalysis and photo-Fenton) have been cited for achieving higher degradation efficiency [28]. Although successful yet the viability of the process for commercial or field-scale utilization is still debatable. Most of the reported studies [31,32] deal with the cases where both the catalyst are in suspension form thus restricting the practical applicability of the technique due to the separation of catalyst post-treatment. None of the studies have been reported with complete immobilization of both catalysts (iron source and TiO_2) for the degradation of pollutants. Moreover treatment time for the degradation of the target pollutant was on higher side in these reported studies.

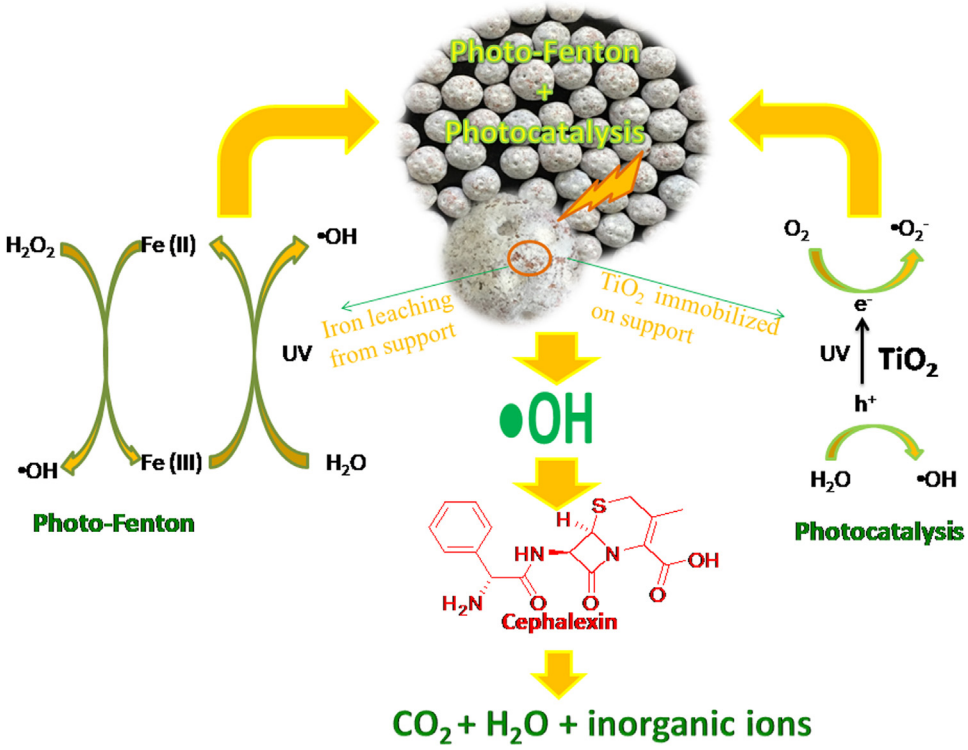
An effective utilization of waste FS and FA in dual process (photo-Fenton and photocatalysis) has been done to incorporate the synergistic effects of both processes so as to boost the degradation efficiency with reduction in treatment time for the removal of organic pollutants from water (Scheme 1). This is the first reported study of the dual effect with in-situ iron leaching besides giving value addition to waste. The model pollutant selected for the current research work is a cephalosporin β-lactamic antibiotic, Cephalexin (CEX) which is most commonly used to treat several urinary and respiratory tract infections. Cephalexin exhibits only 10% biotransformation rate leading to the fact that rest 90% is excreted out in urine unchanged [33]. The evidence of non-biodegradability of CEX can be revealed from its ubiquitous presence in various aquatic environments such as coastal water [34], municipal wastewater [35] and treated effluent from industry [36].

In the present investigation, the degradation of CEX using supported TiO_2 incorporating the dual effect has been demonstrated in batch experiments. TiO_2 was immobilized on various types of spherical beads comprising of appropriate portions of clay, FS and FA. These beads were assessed and checked for their efficacy and durability for the degradation of CEX. The various operating parameters like number of beads, size of beads, addition of oxidant, buffer, Area/Volume of reactor were optimized for best degradation of the pollutant. Further, mineralization of the pollutant was confirmed by reduction in COD along with monitoring of sulphate, nitrate and nitrite ions generation while intermediates formed were analyzed through GC–MS. The tentative degradation pathway for CEX has also been proposed.

2. Experimental

2.1. Chemicals and reagents

Cephalexin (CEX), (6R,7R)-7-[(2R)-2-amino-2-phenylacetamido]-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid was procured as a capsule under brand name, 'Phexin' from local drugstore, Patiala (India). CEX was used as collected without any further modification. Degussa P25 TiO_2, used



Scheme 1. Dual effect of photo-Fenton and photocatalysis for the degradation of CEX.