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## Heterogeneous Fenton degradation of oxalic acid by using silica supported iron catalysts prepared from raw rice husk



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#### ARTICLE INFO

### ABSTRACT

Keywords: Advanced oxidation processes (AOPs) Heterogeneous process Catalytic degradation Raw rice husk RHSi-xFe catalyst Supported catalyst Iron impregnated catalyst (RHSi-Fe) prepared from raw rice husk was used in the degradation of aqueous oxalic acid at acidic pH. The prepared catalyst was characterized using various analytical techniques. X-ray diffraction (XRD) and Energy dispersive X-ray (EDX) analysis were employed to characterize the catalyst which consistently confirmed the presence of silica as a major constituent in amorphous form. Scanning Electron Microscope (SEM)/EDX results indicated that the metal was present as agglomerates and the Fe ions were not homogeneously distributed in RHSi-Fe catalyst. Presence of Si–O–Fe bond was also evident from the FTIR analysis. Percentage degradations of oxalic acid were 20.18 and 59.06 corresponding to the homogeneous (Fe(III)) and heterogeneous (RHSi-10Fe) catalytic degradations, respectively. Influence of different reaction operating parameters like iron loading to silica matrix, mass of prepared solid catalyst, initial concentration of substrate (oxalic acid), oxidant (hydrogen peroxide) and reusability of the catalyst on degradation of oxalic acid. Oxalic acid degradation in 60 min. 1 g/L of RHSi-10Fe dosage was found to be optimum for effective degradation of oxalic acid. Oxalic acid degradation was improved by increasing temperature from room temperature (303 K) to 343 K. About 69.71% of oxalic acid was degraded within 60 min at a temperature of 343 K. The present study finally helps to get a biogenic catalyst which act as a heterogeneous catalyst on degradation of oxalic acid.

#### 1. Introduction

The attention towards wastewater treatment is gaining much importance and environmental regulations regarding water pollution have become more stringent. So there is a strong need of proper treatment facility for the treatment of wastewater. In this context, the implementation of Advanced Oxidation Processes (AOPs) can give effective and technological solution. One of the establishments in the field of practical application of AOPs is the company Chemviron Carbon, USA. The reference list of Chemviron Carbon consists of more than 50 fullscale installations of UV, UV/H<sub>2</sub>O<sub>2</sub>, or O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> systems worldwide [1]. There have been some studies that offer helpful solutions in implementing AOPs. For instance, doping TiO2 with non-metallic elements could possibly boost the photo-catalytic activity [2] and implementation of ultrasonic treatment could support the production of hydroxyl radicals [3]. Likewise, there are also heterogeneous AOPs where we can use solid catalyst. In this study, immobilized catalyst prepared from raw rice husk was used for the degradation of oxalic acid. Oxalic acid, the organic pollutant is commonly found in wastewater. It is mainly present in wastewater coming out from textiles,

metal treatments, pharmaceuticals and pulp and paper industries. It causes severe irritation to skin, nose, eyes and respiratory tract [4]. In the body, oxalic acid also combines with metals ions such as  $Ca^{2+}$ ,  $Fe^{2+}$  and  $Mg^{2+}$  to deposit crystals of the corresponding oxalates, which can irritate the kidneys [5].

Literature survey shows some attempts have been made to oxidize oxalic acid ( $C_2O_4H_4$ ) by using different process. Photo-catalytically active thin TiO<sub>2</sub> films were produced by dip-coating by means of an alkoxy precursor onto a transparent conducting electrode substrate and by thermal oxidation of titanium metal. Later on, these films were used to study the photo-electro catalytic degradation of oxalic acid and 4-chlorophenol (4-CP) under near monochromatic UV light source. In the course of oxalic acid degradation, CO<sub>2</sub> formation accounted for up to 100% of the total organic carbon degradation [6]. A complete kinetic model was developed for the photo-oxidation of oxalic acid in a fluidized bed of TiO<sub>2</sub>/quartz sand composite, in a UV-fully illuminated photoreactor and was correlated with the experimental results [7]. There is one review paper presenting the application of platinum catalysts in bubble column reactor for catalytic wet air oxidation (CWAO) of oxalic acid [5]. For the degradation of oxalic acid, ozonation is most

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commonly used [8,9]. Ozone being unsafe, it is essential to build up environmentally friendly catalytic process that is valuable, cost-effective, and energy-efficient. There is no available literature for degradation of oxalic acid by heterogeneous immobilized catalyst. In this work, immobilized solid catalyst from raw rice husk was prepared by modified alkali extraction process with sol-gel technique and the same was used for the degradation of the oxalic acid. Catalytic degradation lowers the operational costs in comparison with the homogeneous and heterogeneous processes without the use of catalyst. Some homogeneous catalysts exhibit better performances for different AOPs. But, the metal ions in the treated water become a problem, which further enquires a costly separation process to remove. Hence, the development of catalytic degradation processes using different types of heterogeneous catalysts has been attempted. The use of heterogeneous catalysts makes the process more attractive by achieving high efficiency for degradation of organic compounds at a lower temperature and pressure [10-13]. Raw rice husk (RRH) is a waste produced from the rice processing industry. Burning of RRH waste can solve the problem, but it leads to another environmental problems. It is very difficult to degrade biologically and it is a slow process. Therefore, utilization of RRH as an alternative source of silica has gained more interest nowadays [14].

The catalytic performance of an immobilized catalyst from RRH was evaluated on catalytic degradation of a Xanthenes dye, Rhodamine B. In their work, the catalyst was loaded with about 3 wt.% of iron and the effects of different reaction parameters such as initial concentrations of dye and oxidant (H<sub>2</sub>O<sub>2</sub>), catalyst dosage, pH and temperature were studied. Almost complete decolorization was achieved in 10 min at pH 3 [15]. Utilization of silica from RRH for the immobilization of transition metals has been reviewed in the article [16]. Silicon precursor was obtained in the form of sodium silicate. Sodium silicate was obtained by direct silica extraction via alkali extraction method. Transition metals were immobilized into the silica matrix via the sol-gel technique. All the catalysts show good physical and catalytic potential in degradation of various organic compounds and dyes found in waste water. Tin material (Sn) could also be incorporated into the silica matrix by simple sol-gel technique using rice husk ash as a source of silica [17]. The photocatalytic activity of silica-tin material was observed in the degradation of methylene blue under UV-irradiation. The experimental results showed the silica-tin nanotubes exhibit high photocatalytic activity compared to pure rice husk silica. A series of iron immobilized silica catalyst with (5-20) wt.% Fe3+ was prepared via simple solvent extraction and sol-gel method. These solid catalysts were used for the oxidation of phenol employing hydrogen peroxide. Oxidation of phenol by RHSi-10Fe gave 95.2% degradation at 343 K [14]. The purpose of this research is to develop environmental friendly advanced oxidation process using immobilized solid catalyst which can effectively reduce the concentration of aqueous organic pollutants (oxalic acid) in wastewater. In this work, silica supported iron catalyst having different weight percentage of iron loading has been prepared. The present work is intended to prepare and characterize the catalyst to evaluate the efficiency of the process. Prepared immobilized catalyst was characterized for its suitability to heterogeneous AOPs. The study was undertaken with the objectives of investigating the parameters viz. iron loading to silica matrix, mass of prepared solid catalyst, initial concentration of substrate (oxalic acid) and oxidant (hydrogen peroxide) on degradation efficiency of the process.

#### 2. Experimental

#### 2.1. Materials

Analytical reagent grade ferric nitrate extra pure non-hydrate, Fe  $(NO_3)_3$ ·9H<sub>2</sub>O (98.0%) was obtained from LOBA Chemie, analytical grade oxalic acid dihydrate (MERCK, 99.0%), hydrogen peroxide (30 wt.%) was purchased from MERCK and used as received. Raw rice husk was obtained from a local rice mill in Raipur, Chhattisgarh, India.

All the other chemicals were of analytical grade and used without further purification.

#### 2.2. Catalyst preparation from raw rice husk

The method used for the acid washing of raw rice husk and the extraction of the sodium silicate from acid washed rice husk was similar to the reported literature [15]. 70 gm of dried rice hull was acid washed with 1 l of 1.0 mol/L HNO<sub>3</sub> under stirring for 48 h to remove the metal impurities in a batch reactor. The rice hull was then filtered and washed thoroughly with plenty of demineralized water until the pH of the wash-out was near a range of 7 (neutral). The acid treated rice hull residue was then dried at 383 K in a hot air oven. The rice husk finally obtained was of light weight and considerable amount of inorganic material was removed by leaching. The dried residue was then stirred in 1 l of 1.0 M NaOH for 24 h in an isothermal batch reactor. The resulting dark brown suspension was filtered through ashless filter paper (Whatman-41 grade) in order to obtain the sodium silicate solution. Finally, the residue left on the filter paper was scrapped off and the prepared sodium silicate solution was collected into 500 or 1000 ml of beaker for further process of metal loading. Prepared sodium silicate solution will act as the silica precursor for further process. For the synthesis of RHSi-Fe catalyst, 3.0 M HNO<sub>3</sub> and appropriate mass of Fe  $(NO_3)_3$ ·9H<sub>2</sub>O to obtain 5, 10 and 15 wt.% of Fe<sup>3+</sup> was added drop-wise into the already prepared sodium silicate solution under stirring. The drop-wise addition was continued until the suspension become pH 3.0 (acidic). The resulting gel solution was aged in the mother liquor for 24 h at room temperature without disturbing. The gel was then recovered through filtration by using ashless filter paper (Whatman-41 grade). The gel after washing was dried in a hot air oven at 383 K for 24 h to obtain RHSi-Fe having 5, 10 and 15 wt.% of iron loading. The dried sample of prepared catalyst (RHSi-xFe) was ground to fine powder using mortar and pestle and stored in a safe and dry place or in any plastic bottle for its application part.

#### 2.3. Characterization of the prepared catalyst

The study of physicochemical properties of metal incorporated catalysts is a challenging task and many analytical methods were applied to characterize the catalysts. In order to analyze the crystallinity of RHSi-xFe, X–ray diffraction (XRD) analysis was carried out. The X–ray source was Cu K-alpha radiation ( $\lambda = 0.1542$  nm). The diffractogram was recorded in the 20 range 10–80°. Fourier Transform Infrared (FTIR) spectroscopy was conducted to study the functional groups of the RHSi-Fe and the FTIR spectra of metal incorporated (RHSi-Fe) catalyst was recorded with a Fourier Transform Infra–Red unit of Bruker, model alpha, laser class 1. All measurements were done with a cell equipped with potassium bromide (KBr) windows. The morphologies of RHSi-Fe were analyzed using high resolution images obtained from scanning electron microscope (SEM). A detailed analysis of RHSi-Fe has been performed by energy dispersive X-ray analysis (EDX) to get the amount of each species in prepared catalysts.

#### 2.4. Fenton-like degradation of oxalic acid

1000 ppm of oxalic acid solution was prepared using demineralized (DM) water collected from the Millipore by dissolving 1000 mg of oxalic acid to 1 l of water. Stoichiometric amount of prepared catalyst was added to the solution. Oxalic acid and catalyst was then stirred magnetically at around 400–500 rpm for 60 min at room temp. 10 ml of aliquot was withdrawn to determine initial concentration of oxalic acid, (termed as 'C<sub>o</sub>') before the addition of hydrogen peroxide in the solution. The oxidant (0.98 mM of hydrogen peroxide (30% w/v)) was added to the solution to start the reaction. This time was recorded as a starting time of the reaction. At certain reaction intervals, again 10 ml of the aliquot withdrawn and concentration of oxalic acid (here termed

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