



## Research article

# Iron impregnated biochars as heterogeneous Fenton catalyst for the degradation of acid red 1 dye

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## ABSTRACT

In the present work, Acid Red 1 (AR1) dye degradation by two heterogeneous Fenton catalysts, namely iron loaded rice husk biochar (Fe-RHB) and coir pith biochar (Fe-CPB) are studied. Biochar prepared from RHB and CPB were sonicated in the presence of ferric nitrate for the synthesis of Fe-RHB and Fe-CPB by incipient impregnation method. Effect of operational parameters such as pH, the dosage of catalyst, H<sub>2</sub>O<sub>2</sub> concentration and temperature were examined. Characterization of the synthesized Fenton catalyst, Fe-RHB and Fe-CPB were analysed by SEM, EDS, XRD and XPS techniques. In Fe-RHB Fenton system, maximum dye removal efficiency of 97.6% and TOC removal efficiency of 84.2% were obtained at pH 3 for 50 mg L<sup>-1</sup> of AR1 concentration, with 16 mM of H<sub>2</sub>O<sub>2</sub> and 5 g L<sup>-1</sup> of catalyst dosage within 120 min reaction time. Similarly, for Fe-CPB, maximum dye removal efficiency of 99.1% and TOC removal efficiency of 86.7% were obtained with 16 mM of H<sub>2</sub>O<sub>2</sub> and 4 g L<sup>-1</sup> of dosage for 50 mg L<sup>-1</sup> of initial dye concentration at pH 3. The prepared catalysts can be reused for successive cycles as the catalyst materials are highly stable and have very less iron leaching property.

## 1. Introduction

Textile dyeing industry is one of the major industries that consume large volumes of water for various operations and it discharges enormous quantity of wastewater to the environment. In many instances, the dye containing wastewater discharged without any effective treatment caused various environmental issues. There are instances where wastewater-containing dyes were discharged into natural surroundings without effective treatment strategies. Due to their structural complexities and nature, most of the synthetic dyes are highly toxic and resistant to natural/biological degradation (Zheng et al., 2007). In India, 60,000 MT of dyes are produced from different dyestuff industry which is approximately 6.6% of total colorants used all over the globe (Teli, 2008). About 10–15% of the used dye enters the aquatic environment through the wastewater discharged from various dye industry (Singh and Arora, 2011) and 12% of the dyes produced enter water bodies during its production and subsequent coloration process (Sandhya et al., 2005). The nature of textile wastewater is highly complex due to its high composition variability and colour intensity, thereby posing difficulties in treating it effectively. The typical characteristics of textile wastewater include, total dissolved solids (TDS),

total Kjeldahl nitrogen, biochemical oxygen demand (BOD), chemical oxygen demand (COD) and BOD/COD ratio which are in the range of 2900 to 3100 mg L<sup>-1</sup>, 70 to 80 mg L<sup>-1</sup>, 80 to 6, 000 mg L<sup>-1</sup>, 150 to 12,000 mg L<sup>-1</sup> and 0.25, respectively. The above characteristics confirm the presence of persistent organic pollutant in high concentration that has the potential to damage aquatic life severely (Oller et al., 2011). High colour intensity of the untreated/partially treated effluents, obstructs the light penetration thus affects the photosynthetic activity of plants and other organisms (Nagel-hassemer et al., 2011). Moreover, most of the commercial dyes available for dyeing activity are highly toxic and carcinogenic in nature (Nidheesh et al., 2018, 2013).

The commonly adopted methods for the treatment of textile wastewater involve chemical precipitation, adsorption, membrane process, coagulation and flocculation, and biological treatment (Nagel-hassemer et al., 2011). Some of the treatment processes such as reverse osmosis, nano filtration and multiple effect evaporators are effective but quite expensive, whereas the conventional treatment methods are non-destructive, comparatively less effective, and time-consuming (Cuiping et al., 2012; Rache et al., 2014). Considering the merits and demerits of the treatment processes available for the purification of dye-containing wastewater, it is a matter of great concern to develop a novel and cost-

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effective technique. Advanced oxidation processes (AOPs), a promising treatment process involves highly reactive oxidizing radicals and capable of degrading different organic contaminants present in wastewater as well as ordinary water (Nagel-hassemer et al., 2011; Romero et al., 2010). AOP has been receiving great considerations since the principal oxidizing agents responsible for the destruction of target contaminants are highly active reactive oxygen species such as hydroxyl/sulphate/peroxide radicals. Fenton's oxidation is catalysis based simple advanced oxidation processes, which could treat wide variety of pollutants effectively with low costs in comparison to other AOPs. Fenton reaction involves in the generation of hydroxyl radicals through the catalytic decomposition of hydrogen peroxide in presence of ferrous iron (Eq. (1)) and the reaction is based on the electron transfer reactions between  $H_2O_2$  and ferrous ions (Barbusiński and Majewski, 2003). Eqs. (2) and (3) show the regeneration of ferrous ion in the presence of hydrogen peroxide and hydroperoxyl radical and these reactions can be considered as an advantage for the Fenton's process in terms of further degradation by ferrous ions. In addition to the requirement of large amounts of iron concentration for the reaction process, the other drawback of Fenton's process includes the requirement of an additional step such as separation and treatment of the iron sludge generated at the end of the treatment process eventually increases the overall operational cost. Heterogeneous solid Fenton catalysts were recommended by different studies to overcome the disadvantages of homogenous Fenton based processes. In heterogeneous Fenton's process, solid iron catalysts have the capability to generate hydroxyl radicals from hydrogen peroxide in wide range of pH and also prevents the generation of iron sludge (Laiju et al., 2014; Nidheesh et al., 2014). Various heterogeneous catalysts such as iron oxides, iron loaded materials, soils etc. were reported by various researchers for the effective treatment process. (Bec et al., 2014; Duarte et al., 2009; Hassan and Hameed, 2011a; Nogueira et al., 2014; Rusevova et al., 2012; Yao et al., 2013). However, the preparation and utilization of environmental friendly and low-cost heterogeneous Fenton catalyst is very important to make the treatment more affordable (Litter and Slodowicz, 2017; Park et al., 2018).

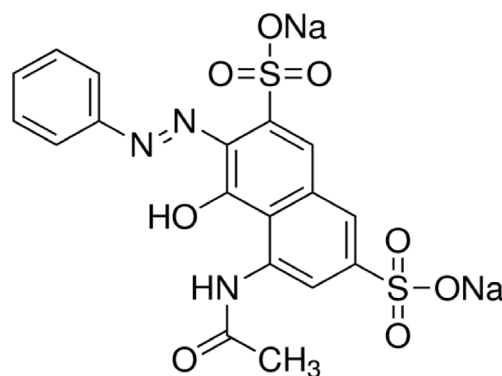


Biochar is a porous carbon-rich product synthesized by thermochemical conversion of organic material in the presence of oxygen limited condition (Ahmad et al., 2014). Many studies have been reported on the usage of biochar for soil improvement, waste management and energy production but limited studies were done on biochar application on water and wastewater treatment (Mohan et al., 2014; Tan et al., 2016). The objective of our present study is the synthesis of iron impregnated biochar from agricultural waste such as rice husk and coir pith, which exhibit high catalytic degradation ability for the degradation of dye, Acid Red 1 (AR1). AR1 is an azo dye with molecular formula  $C_8H_{13}N_3Na_2O_8S_2$ , molecular weight  $509.42 \text{ g mol}^{-1}$ , and red in colour. The structure of AR1 is given as Scheme 1. The presence of dye in water is highly noticeable and objectionable even in less than  $1 \text{ mg L}^{-1}$  concentration. The AR1 dye can be toxic and mutagenic at high concentration (Daud et al., 2010; Hassan and Hameed, 2011b). Experiments were performed under different conditions to understand the effect of dosage, pH, temperature and hydrogen peroxide concentration on the optimum dye removal efficiency.

## 2. Materials and methods

### 2.1. Materials

All the chemicals used were of AR grade and were purchased from Merck. The pH of the solution was adjusted using  $1N H_2SO_4$  and  $1N NaOH$ . Rice husk was obtained from rice mill located in Kollam, Kerala,



Scheme 1. Molecular structure of AR1.

India and coir pith was collected from coir industry located in Kollam, Kerala, India.

### 2.2. Preparation of iron loaded heterogeneous catalyst

Collected rice husk and coir pith were washed with distilled water three to four times for removing the impurities such as dust and then sun dried. Both the materials were kept in hot air oven and dried at  $105^\circ C$  for 24 h to remove the moisture content. They were then kept in a muffle furnace at  $700^\circ C$  for 5 h. The collected powder of both rice husk and coir pith were treated with  $1.0 M$  nitric acid for 24 h to remove metallic impurities. Filtered samples were washed thoroughly with deionized water until the pH values of 6.1 and 6.4 for RHB and CPB, respectively were obtained. The rice husk biochar (RHB) and coir pith biochar (CPB) were dried in an oven at  $110^\circ C$  overnight. The RHB and CPB were grounded and sieved to the size of  $300 \mu m$ . The iron loaded RHB and CPB catalyst, here referred as Fe-RHB and Fe-CPB respectively were prepared by the incipient impregnation method (Fig. S1). RHB or CPB of about 10 g was added to a solution containing 5 g Fe  $(NO_3)_3 \cdot 9H_2O$  dissolved in 50 mL distilled water and was continuously agitated in sonicator (bath type) for 30 min. The mixture was washed in distilled water and oven dried at  $105^\circ C$  for one day, followed by calcination at  $500^\circ C$  for 4 h in a muffle furnace.

### 2.3. Characterization of prepared catalysts

The surface morphology of RHB, CPB, Fe-RHB, and Fe-CPB was done by FE-SEM (Field Emission Scanning Electron Microscopy, Make: Carl-Zeiss, Model: Carl-Zeiss ultra plus) analysis system with magnification range of  $25x-1000kx$  fitted with EDAX (Energy-Dispersive X-ray analysis) for determining the chemical composition and elemental analysis of biochars and iron impregnated biochars. X-ray powder diffraction (XRD) analysis was conducted with a Bruker X-ray diffractometer (Make: Bruker, Model: D8-Advance) with X-ray source of  $2.2 \text{ kW}$  Cu anode at a step angle of  $0.01^\circ$  and measurement started at  $2\theta = 10^\circ$  and ended at  $90^\circ$ . In order to examine chemical composition and electronic state of iron precipitated, XPS (X-Ray Photoelectron Spectroscopy) analysis was done using X-ray beam induced secondary electron imaging and measurements were taken with a monochromatic Al  $K\alpha$  radiation source of  $1486.6 \text{ eV}$  with a step size of  $0.05 \text{ eV}$  using Physical Electronics, model PHI 5000 Versa Probe III. The average depth of analysis using PHI 5000 Versa probe III was done at approximately  $5 \text{ nm}$ .

### 2.4. Experimental procedure

Batch experimental runs were carried out in a  $500 \text{ mL}$  glass beaker placed on a hot plate magnetic stirrer with an agitation of  $150 \text{ rpm}$  for  $120 \text{ min}$ . The working volume of  $200 \text{ mL}$  AR1 solution at the

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