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# CATALYTIC INFLUENCE OF IRON LOADED SBA-15 FOR THE PHOTODEGRADATION OF CONGO RED DYE

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## ABSTRACT

A series of iron loaded SBA-15 was prepared by simple impregnation method using ferric nitrate as a metal precursor and tetra ethyl orthosilicate as a silica source. The metal loaded SBA-15 was confirmed by various characterization techniques such as x-ray diffraction (XRD), $N_2$ sorption studies, scanning electron microscope (SEM) and transmission electron microscope (TEM). The results of XRD, nitrogen sorption and TEM indicate the formation of highly ordered hexagonal structures of mesoporous materials. Photodegradation of congo red (CR) were studied using Fe/SBA-15 under direct sunlight and analyzed the samples by UV visible spectrophotometer. The degradation efficiency of CR was observed within 90 min and the optimization studies were also done systematically.

**KEY WORDS:** mesoporous materials, SBA-15, congo red, photodegradation, advanced oxidation process.

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# INTRODUCTION

Dyes are widely used in industries such as textiles, leather, printing, food, and plastics, etc.[1,2] Conventional methods for the removal of dyes from wastewater include adsorption onto solid substrates, chemical coagulation, oxidation, filtration and biological treatment. Advanced oxidation processes (AOPs) constitute a promising technology for the treatment of wastewaters containing non-easily removable organic compounds. The commonly used photocatalytic materials are $TiO_2$ based composites, they have certain drawbacks like utilization of Ultra-Violet region due to large band gab (3.2 eV) which has limited its role as photocatalyst. The mesoporous materials have large surface area, good sorption capacity and uniform pore size with this exceptional properties it has large potential application in the chemical industry and adsorption processes for remove environmental pollutants from water and petroleum refinery industry.[3] Heterogeneous photocatalysis is one of the attractive and highly effective methods to degrade the toxic and non-biodegradable organic compounds which are pollutant to the environment. Moreover the photocatalytic efficiency is also increase by decreasing the electron-hole recombination, facilitating the interfacial charge transfer from the surface of the photocatalyst to the substrate.[4] In this work, we have synthesized a highly ordered Fe substituted mesoporous SBA-15 material by simple wet impregnation method. The synthesized material was characterized by x-ray diffraction (XRD), Nitrogen sorption studies, scanning electron microscope (SEM) and transmission electron microscope (TEM). The photocatalytic activity of the SBA-15 was tested towards the degradation of congo red (CR) dye under direct sunlight.

# MATERIALS AND METHODS

Tetraethylorthosilicate (TEOS) and tri-block copolymer poly (ethylene glycol)- blockpoly(propylene glycol)-blockpoly(ethylene glycol) (Pluronic P123, molecular weight = 5,800, $EO_{20}PO_{70}EO_{20}$) (Aldrich) were used as silica source and structure directing agent, respectively.

### *Synthesis of Fe-SBA-15 mesoporous molecular sieve*

Mesoporous siliceous SBA-15 was prepared employing the optimized procedure as described elsewhere.[5,6] In a typical synthesis, 4 g amphilic triblock copolymer (Pluronic P123) in 30 ml water was stirred for 4 h. Thereafter, 120 g hydrochloric acid solution (2 M) was added to it and the gel was stirred for another 2h. Then, 9g TEOS was added to it and continued the stirring for 24 h at 40 ºC. The mixture was finally heated in an autoclave at 100 ºC for 48h. The solid product thus obtained was filtered, dried at 100 ºC and then calcined at 550 ºC in air to expel the template. About 1g of calcined SBA-15 was treated with required amount of 1M iron nitrate solution with different percentage loading 10, 20 and 30 wt%. The mixture is stirred at room temperature for 3h in ethanol which followed by filtration and drying at 80 ºC. Then the obtained solid products were calcined at 550 ºC for 3h.

### *Photodegradation Experiment*

The photocatalytic activity measurements were conducted by degradation of congo red under direct sun light according to our previous report.[7] In a typical reaction, 50 mL of 0.8 g/L congo red solution was added to 30 mg of Fe/SBA-15 (20 wt %) and placed in dark room for 30 min to attain adsorption equilibrium between dye and photocatalyst. Further degradation studies were performed under direct sunlight at given irradiation time intervals, from the suspension solution about 2mL were collected and centrifuged to separate the photocatalyst particles.[8] The centrifugation was used to monitor the colour removal of CR by determining its absorbance at $\lambda_{max}$=619 nm using Shimadzu UV-3600 Model.

### *Photocatalytic Activity of Fe/SBA-15 Catalysts*

The effect of the catalyst concentration on congo red dye degradation under direct sun light was studied by keeping dye concentration (0.1g/L) constant and varying only catalyst concentration of the Fe/SBA-15 (20%) between 0.01 to 0.04g and the obtained results were analyzed with spectrophotometric method to know the percentage removal of congo red. From the result 0.02g of catalyst concentration Fe/SBA-15 (20%) achieved the maximum removal of CR and it was chosen for further studies.

### *pH*

Photocatalytic degradation of Congo Red (CR) was studied by varying the pH of the CR aqueous solution in the range of 1-10 (using diluted NaOH or HCl solution) with keeping constant of 0.020g/L fixed initial dye concentrations and catalyst dosage 0.020g for period of 90 min. The degradation efficiency was calculated using initial concentration and residual concentration of CR by spectrophotometric method. The optimized pH of 3 was used to perform the further reaction condition.

### *$H_2O_2$ concentration variation*

The experiment was performed by varying $H_2O_2$ concentration from 0.1mL to 0.5mL and keeping constant the catalyst concentration (0.020 g) at pH 3. The maximum degradation efficiency was obtained at 0.3mL of $H_2O_2$ concentration. The optimized condition was used to study the effect of initial dye concentration.

### Initial dye concentration

To optimize the condition of the initial dye concentration, the experiment was performed at suitable time intervals at room temperature while the samples were stirred continuously by varying the initial CR concentration ($C_o$) from 0.10g/L to 0.5g/L and keeping constant parameters such as 0.02g of catalyst, 0.3mL of $H_2O_2$ concentration at pH 3.

# RESULTS AND DISCUSSION

### *XRD pattern of SBA-15 and Fe/SBA-15*

Figure 1 illustrate the powder XRD patterns of SBA-15 and Fe/SBA-15 (10%, 20% and 30 wt%) samples which clearly shows three well-resolved sharp diffraction peaks are indexed to the (100), (110), and (200) planes, indicating hexagonal symmetry with the *p6mm* space group.[5,6] The distinct peaks in the XRD patterns of

Fe/SBA-15 samples illustrate, the ordered hexagonal porous framework were retained even after impregnating iron cation on the SBA-15 silica matrix.

***$N_2$ sorption studies of the catalysts***

Another primary technique used to measure the physical properties is $N_2$ Physisorption. Figure 2 shows the $N_2$ sorption studies of SBA-15 and Fe/SBA-15. The samples exhibited type IV isotherms, according to IUPAC classification, featuring a narrow step due to capillary condensation of $N_2$ in the primary mesopores.[9] Filling of the mesopores of the SBA-15 with iron materials having a sharp capillary condensation step in the range of 0.65-0.90,[10] which was reflected as a steep increase in the isotherm. Both the BET surface area and pore volume dropped after iron loaded (Table 1). This may be caused by a partial blockage of the SBA- 15 pores by iron particles or a partial collapse of the mesoporous structure during the procedure of impregnation and recalcination or from the condensation of silanol groups on the surface.

***SEM and TEM analysis of Fe/SBA-15 catalysts***

The SEM image of Fe/SBA-15 sample shown in Figure 3 clearly indicates the morphology of the materials and also rod or rope like shape with uniform size. It is well known that this kind of morphology have been investigated in detail elsewhere.[11,5] Figure 4 illustrates the TEM image of Fe/SBA-15 sample which show the hexagonal array of uniform channels with the honeycomb appearance of SBA-15 materials.[5]

***Influence of catalyst concentration***

Figure 5 show the influence of the catalyst concentration on CR degradation under direct sun light was investigated by employing different concentrations of the Fe/SBA-15 (20%), varying from 0.01 to 0.04g at 0.1g/L dye concentration. The results showed that on increasing the amount of catalyst from 0.01 to 0.02 g increases colour removal from 85% to 95% for a reaction time of 90 minutes. As the catalyst amount continues to be increased to 0.02 g, the degradation rate increases to 95% because the increase in catalyst amount provides more active sites for CR, leading to a increase in the hydroxyl radical responsible for the degradation of CR. Further increasing the catalyst from 0.02 to 0.04 g there will be small decrease in decolorization. It is due to the fact that at higher amount, the vacant sites are consumed by the intermediate products formed during the reaction which retards the degradation property of the substrate lead to unnoticeable decreased or retained degradation property of the catalyst. When increasing weight of catalyst there would have been scattering effect of light and thereby reduction in light penetration through the solution. Therefore we concluded that the optimum weight of CNTs catalyst to be 0.02g for effective photodegradation.[12]

***Influence of pH on photodegradation***

Figure 6 shows the degradation of dye by varying the pH. The degradation efficiency of dye increases with increasing pH from 1 to 3 and decreases slightly when pH is above 3. The lower decolourization obtained at pH 1 is probably due to the hydroxyl scavenging by the $H^+$ ions (13) At pH 5 and above the degradation is found to be good but lesser than the acidic pH 3 which is coincide with previous investigation.[14]

***Influence of $H_2O_2$ concentration***

Figure 7 shows the photocatalytic effect of $H_2O_2$ concentration. The results reveals that the photocatalytic degradation efficiency increases with $H_2O_2$ dose from 0.1mL to 0.3mL it might be due to the increase in hydroxyl radical.[15] Further increase in $H_2O_2$ dosage, the degradation efficiency decreases this may be due to the fact that auto decomposition of $H_2O_2$ and the excess formation of peroxyl radical ($HOO^{\cdot}$) radicals which has much less oxidation capabilities than ($HO^{\cdot}$) there by reduces the rate of degradation of dyes.[16]

***Influence of initial dye concentration***

Figure 8 shows the influence of initial dye concentration. Higher degradation of CR dye was achieved for dye concentration of 0.10 g/L and had significantly decreased when the concentration was increased from 0.10g/L to 0.5g/L. The reason behind it when the concentration of the dye was increased still the hydroxyl radical concentration remained steady for all dye molecules resulted in reduced rate fall.[17] So increase in dye concentration resulted in competition for active sites, causes variation in proportion of color deduction. This might also due to the factor like reduced penetrability of photons into dye solution i.e (higher dye concentration might serve as the inner filter shunting the photons away from the catalyst surface). Thus these factors lead to decreased OH radical production and lesser degradation.[18]

**Table 1**
***Textural properties of the catalysts***

| Catalysts | $d_{100}$ (nm) | Unit cell-$a_0$ (nm) | Surface area ($m^2g^{-1}$) | Pore diameter (nm) | Pore Volume ($cm^3g^{-1}$) |
|---|---|---|---|---|---|
| SBA-15 | 9.80 | 11.05 | 685 | 6.8 | 0.95 |
| Fe-SBA-15 (10 wt %) | 9.60 | 10.75 | 580 | 6.5 | 0.85 |
| Fe-SBA-15 (20 wt %) | 9.20 | 10.60 | 546 | 6.5 | 0.82 |
| Fe-SBA-15 (30 wt %) | 8.89 | 10.30 | 484 | 6.4 | 0.65 |

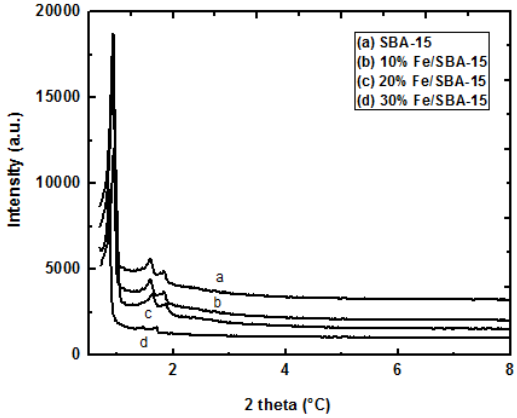


**Figure 1**
***XRD Pattern of SBA-15 Catalyst***

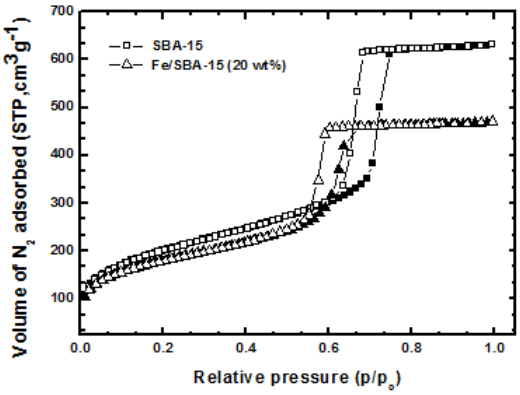


**Figure 2**
***$N_2$ physisorption studies***

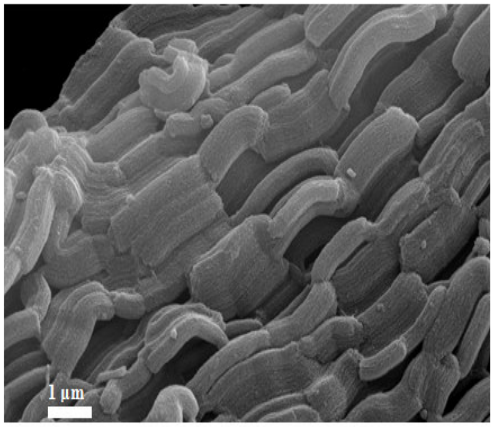


**Figure 3**
***SEM image of Fe/SBA-15 catalyst***

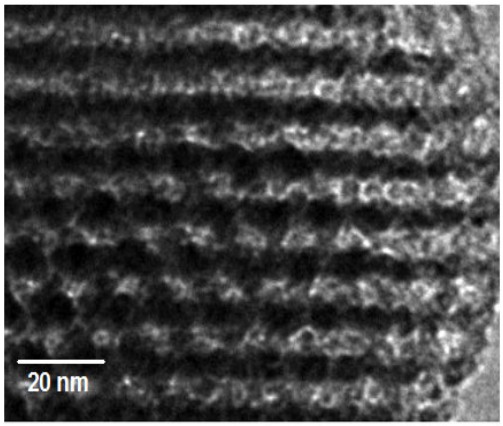


**Figure 4**
***SEM image of Fe/SBA-15 catalyst***

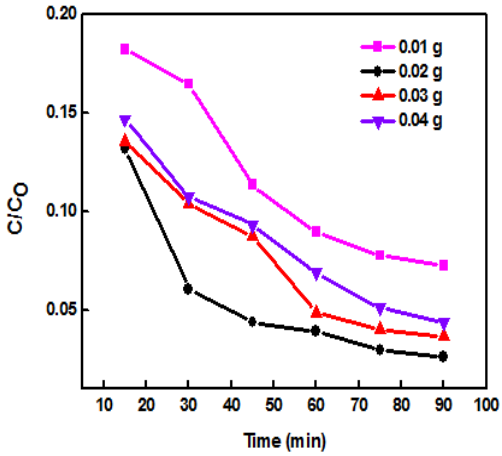


**Figure 5**
***Effect of catalyst concentration***

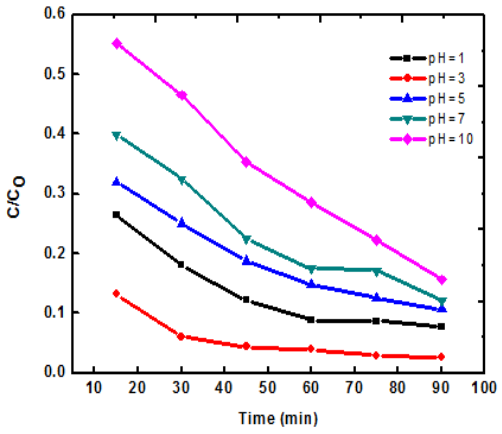


**Figure 6**
***Effect of pH on photodegradation***

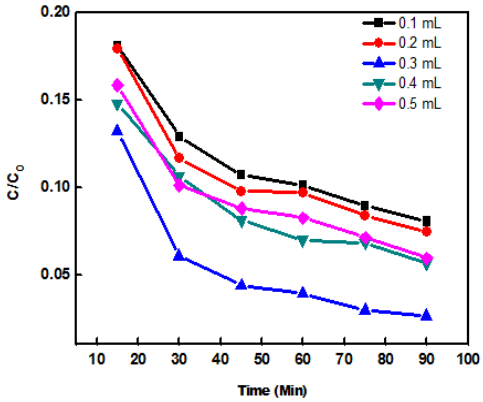


**Figure 7**
***Effect of $H_2O_2$ Concentration***

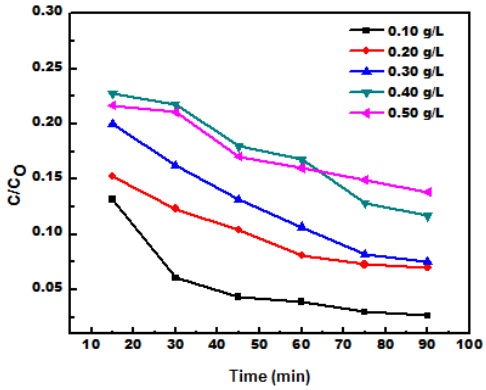


**Figure 8**
***Effect of initial dye concentration on degradation studies***

## CONCLUSION

Highly ordered iron substituted mesoporous SBA-15 was synthesised by simple impregnation techniques. The obtained mesoporous materials were confirmed by XRD, $N_2$ sorption studies, SEM and TEM. The XRD pattern clearly confirms the three well-resolved sharp diffraction peaks indicating hexagonal symmetry with the *p6mm* space group. The mesoporous nature, morphology and hexagonal array with honey comb appearance of SBA-15 materials were analyzed by SEM and TEM, respectively. The photodegration study of CR was investigated using Fe/SBA-15 under direct sunlight. By varying the parameters such as catalyst weight, $H_2O_2$, dye concentration and pH, we found that the efficiency of Fe/SBA-15 (20 wt%) for the removal of CR is 95 % at pH=3 with 0.02 g/L of catalyst and 0.3 mL of $H_2O_2$ under direct sunlight. This results proves that Fe/SBA-15 catalysts are efficient photocatalyst for the removal of organic pollutant.

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## CONFLICT OF INTEREST

Conflict of interest declared none.

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