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## Photo Degradation of Reactive Dye Acid Red 1 under UV-C Radiation Using Fly Ash from Different Thermal Power Plants

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Abstract: A comprehensive study was carried out on two different fly ashes used as a catalyst for the degradation of Acid Red 1 using ultraviolet rays. These fly ashes are collected from different thermal power stations located at various places in India and having different chemical compositions. One fly ashes is from lignite-based thermal power plant and the other is from the coal-based power plant. One fly ash is classified as Class C and other is not conforming to ASTM C618 classification. X-Ray Fluorescence (XRF) analysis was used to identify the chemical composition of fly ashes and SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, MgO, SO<sub>3</sub> and TiO<sub>2</sub> were found to be the major elements present it in different proportions. Various analysis were carried out on all the fly ashes like Scanning Electron Microscopy (SEM) to identify the microphysical properties, Energy Dispersive X-ray spectroscopy (EDS) to quantify the elements present in the catalyst and X-Ray Diffraction (XRD) to identify the catalyst phase analysis. The radical generated during the reaction was identified by Electron paramagnetic resonance spectroscopy (EPR). The parameters such as initial pH of the dye solution, catalyst dosage and initial dye concentration which influence the dye degradation efficiency were studied and optimised. In 60 minutes duration, the dye degradation efficiency at optimum parametric values of pH 2.5, initial dye concentration of 10 mg/L and catalyst dosage of 1.0 g/L using various fly ashes, i.e., Salam Power Plant (SPP), and Neyveli Lignite Thermal Power plant (NLTP) were found to be 40% and 95% respectively. The contribution of adsorption alone was 18% at the above mentioned optimum parametric values. Among the above four fly ashes NLTP fly ashes proved to be most efficient.

Keywords: Dye degradation, Photocatalyst, Acid Red 1, fly ash, UV-C irradiation

#### 1. Introduction

The thermal power stations in India burn Coal or Lignite in the production of thermal energy. The byproducts of the thermal power stations are fly ash, slag ash and bottom ash. The component of these three was up to 45 % for the Coal or Lignite extracted from Indian terrain. In India, according to 2014 - 15 statistics, nearly 73.24 million tonnes (42.37 %) of fly ash generated from thermal power stations are unutilized (CEA *report 2014*). To store such a huge quantity of fly ash, large areas of valuable land is required. If not properly disposed of, it poses threat to the environment. Fly ash used in many areas such as the manufacture of structural elements, construction industry and agriculture, but its utilisation in wastewater treatment is reportedly less.

Dyes used in many industries such as textile, food, paper, pharmaceutical and plastic. India accounts for nearly 16% of world's production of dyestuff and dye intermediates. Dyes and pigments share in total chemicals produced in India for the year 2013-14 was about 5% and expected to increase to 8% in coming five years (*MCF report 2014*). Dyes are of different types, among which reactive, organic, dispersive and azo dyes are major ones. Reactive dyes used for

dyeing cellulose fibres (cotton) and cotton utilisation are about 40% of total world textile production. Out of 236,070 MT of dyes produced in India during 2013-14, reactive dyes share was 95,330 MT (40.38%) (MCF report 2014). These reactive dyes are harmful and toxic to living beings when left untreated.

Degradation of dyes can be carried out by many processes significant among them are adsorption, coagulation, filtration, reverse osmosis and advanced oxidation processes. Amongst, advanced oxidation processes were proved to be effective as it converts the pollutants into inert materials whereas others convert them from one phase to other without completely removing. In advanced oxidation processes, Fenton and photoFenton processes are being used vividly in the dye degradation.

Many studies reported using fly ash and its derivatives as an adsorbent for the removal of dyes (Dafeng Zheng and Piaui Pi, 2010, Indra D. Mall et al., 2006, Chunhui Fan et. al., 2011, Xu, HuanYan, et al., 2014), in the removal of heavy metals (Mohan S, Gandhimathi R, 2009), in combined adsorption and heavy metal removal processes (Maria Visa et. al., 1998), and in the removal of phenols (T. Viraraghavan, Flor de Maria Alfaro, 1998). Few



studies were also carried out on dye degradation in the process of combined adsorbent and photocatalysis using fly ash doped with a photoreactive element  $TiO_2$  (Yu, Yeon-tae, 2004). Some studies were also carried out in degradation of dyes using fly ash and  $H_2O_2$  in the presence of ultrasonication (Song, 2009). Fly ash doped with  $TiO_2$  was proved to be effectively used in removal of organic pollutants (Prem Singh Saud, Bishweshwar Pant, et al., 2015). A recent research on fly ash class C was proved to be effective when used alone in the degradation of dye by combined adsorption and photocatalysis and also proved that it can be reused (Giribabu P. V. S. and Swaminathan G, 2015).

In the present study, an effort was made to optimise the various influencing parameters like pH, initial dye concentration and catalyst dosage in the degradation of a reactive dye Acid Red 1 using two different types of fly ashes obtained from various thermal power plants using coal or lignite from different mines as their raw material. A comparison of dye degradation efficiencies was made among the two fly ashes, when tested as a photocatalyst in a combined adsorption and photodegradation process and corresponding kinetic coefficients were worked out.

#### 2. Materials and Methods

Ultrapure distilled water used for all experiments was taken from LaboStar TWS UV7 model Siemens water purifier. Acid Red 1, a reactive dye, was procured from Sigma Aldrich, USA. It is highly water soluble and its molecular weight, empirical formula and Colour index number are 509.42, C<sub>18</sub>H<sub>13</sub>N<sub>3</sub>Na<sub>2</sub>O<sub>8</sub>S<sub>2</sub> and 18050 respectively. The highest peak observed at a wavelength of 532 nm in the absorption spectrum of the dye. Concentrated H<sub>2</sub>SO<sub>4</sub> and NaOH of analytical grade were purchased from Merck. The catalysts fly ash was procured from different thermal power plants in India i.e Neyveli Lignite Thermal Power plant (NLTP) and Salem Power Plant (SPP) located in Tamilnadu state. Phillips UV-C tube light, 4w was used as a light source which emits UV-C rays at 254 nm wavelength. Remi magnetic stirrer having speed and temperature control facilities was used for stirring the dye solution continuously. Henna HI 98107 handheld pH meter was used to measure the pH of the dye solution.

### 2.1 Ultraviolet light experimental setup

A cubical wooden box of 50 cm side was used to conduct UV experiments. Proper arrangements were made to house a magnetic stirrer inside the box and provisions of electrical supply through small holes were made to both magnetic stirrer and UV light. All the UV light experiments were conducted at ambient room temperature in the laboratory.

#### 2.2 Dye Degradation studies using UV-C light

All experiments with UV-C light were carried out with a 200ml dye solution in a 250ml glass beaker.

Initial Dye Concentration (IDC) of 10 mg/L was used in all experiments except in the variation of IDC studies. Required dosage of catalyst was added to the dye solution, according to research plan and pH of the solution was adjusted using standard H<sub>2</sub>SO<sub>4</sub> and NaOH solutions. The beaker containing the dye solution was placed on the magnetic stirrer and UV light housed in quartz tube was inserted into the solution and power was switched on. Samples of 5ml each was withdrawn at the stipulated time intervals for further analysis. Samples were centrifuged at 10000 rpm for 10 minutes to settle down the catalyst present in it, and the absorbance of the clear solution was measured at 532 nm using a spectrophotometer. Percentage of dye degradation is calculated from the following equation.

Percentage degradation =  $[1-(C/C_0)] \times 100$ 

Where Co was initial concentration and C is concentration of dye at time t.

In the present study, the dye degradation efficiency in the process of combined adsorption and photocatalysis were reported. The dye removal efficiency through adsorption alone was studied separately and was found to be 18% at optimum conditions after 60 minutes for both the fly ashes.

#### 2.3 Catalyst Characterisation

X-Ray Fluorescence (XRF) analysis of fly ash was carried out using Horiba XGT 5200 machine to analyse for chemical composition. X-Ray Diffraction (XRD) analysis was done using Rigaku, D/Max, Ultima III machine, to identify the catalyst phase analysis. The XRD analysis was carried out at 0.02 step size for 20° to 80° scan range and 10° / minute scan speed. Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray spectroscopy (EDS) was done using VEGA3 SB – Easy Probe. Lambda 750, PerkinElmer UV / VIS / NIR Spectrophotometer was used to find out the absorbance spectrum of the dye solution. The Bruker EMX plus instrument was used for EPR spectrum analysis of the dye solution at different times of reaction.

#### 3. Results and discussion

### 3.1 X- Ray Diffraction (XRD) analysis

To know the phase analysis of the catalysts and various elements present in it, XRD analysis carried out for all the two samples of fly ashes and the result are shown in Fig. 1. The major elements observed were CaO,  $Fe_2O_3$ ,  $SiO_2$ ,  $Al_2O_3$ ,  $SO_3$ , MgO and  $TiO_2$  in different proportions in different fly ashes and were marked at their respective peaks. In case of NLTP fly ash calcium oxide and iron oxide peaks are more after silica peaks; whereas in SPP fly ash result calcium peaks are predominate. All these results were in compliance with the XRF results shown in Table 1.



Fig. 1. XRD patterns of the different fly ashes used in the present study

# **3.2** Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS)

The samples were analysed using SEM and EDS and the corresponding images are shown in Fig. 2. NLTP fly ash images shows a clear spherical particles and SPP fly ash show more linear shaped particles and were identified as calcium particles (Barbara G. Kutchko, Ann G. Kim, 2006). The EDS result of SPP also reveals that the calcium oxide concentration was more compared to other oxides.

#### 3.3 Preliminary experimentation

Raw fly ashes were washed several times with ultrapure water and finally dried, and its chemical compositions were analysed. To quantify the more appropriate concentration of elemental oxides present in fly ash, X-ray fluorescence (XRF) analysis of the same sample at multiple points were carried out and the mean values are tabulated in Table 1. As per the XRF result, fly ash contained as many as 20 elements and was heterogeneous in nature. The major elements present in it were SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, MgO and TiO<sub>2</sub>. As per ASTM C618, if the sum of the percentage of elements SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> present in fly ash is equal to more than 50 %, it is classified as fly ash class C, and if the same is more than 70 %, it is classified as Class F fly ash. As per Indian standard IS 3812 (Part 1): 2013, if the concentration of CaO is more than 10%, it is classified as Calcareous fly ash. From the chemical composition of the two different types of fly ashes obtained from the XRF analysis, as per ASTM C618, Neyveli Lignite Thermal Power Plant, NLTP (63.6%)) were categorised as class C and SPP (47.8%) is having slightly less than 50% and was not conforming to any category.

 
 Table 1. The mean elemental composition of different fly ashes from XRF analysis

Elemental Oxide	NLTP	SPP
SiO <sub>2</sub>	26.479	33.61
A12O <sub>3</sub>	22.551	12.528
CaO	19.075	41.034
Fe <sub>2</sub> O <sub>3</sub>	14.543	1.605
SO <sub>3</sub>	9.317	2.779

MgO	2.923	5.357
TiO <sub>2</sub>	2.492	1.047
Na <sub>2</sub> O	1.958	0
SrO	0.162	0.067
ZrO <sub>2</sub>	0.148	0.054
PdO	0.095	0
$P_2O_5$	0.063	0.395
MnO <sub>2</sub>	0.047	1.032
$Y_2O_3$	0.044	0.009
ZnO	0.031	0.005
$Cr_2O_3$	0.028	0.012
K <sub>2</sub> O	0.019	0.465
NiO	0.009	0
Cl	0.008	0.001
CuO	0.006	0



Fig. 2. SEM images of various fly ashes used in the present study



#### 3.4 Dye Degradation Mechanism

The composition of fly ash reveals that it was a heterogeneous material and study of the reactions developed during dye degradation using fly ash as a photocatalyst in the presence of UV-C light is very complicated. Among the major elements present in fly ash, oxides of silica, alumina and sulphur are the elements which are said not to participate in dye degradation processes and are treated to be inert in this process. In the presence of UV-C light, the elements present in the fly ash TiO<sub>2</sub>, CaO (Song et. al., 2009) will produce a pair of electrons and holes. The positive- hole of  $TiO_2$  in reaction with water molecule produce hydrogen gas and hydroxyl radical (Wen-Shiuh Kuo and Wen-Yu chen, 2012), whereas the negative electron reacts with hydrogen molecule and produce superoxide anion. These superoxide anions in further reaction produce hydrogen peroxide. The Ferric Oxide ( $Fe_2O_3$ ) present in the fly ash then reacts with the hydrogen peroxide (Madhusudhana N et. al., 2010) and initiate the Fenton reactions which produce hydroxyl radicals required for the dye degradation.



Fig. 3. EPR spectra of FA at different time intervals during experimental process

To validate the presence of hydroxyl radicals, Electron Paramagnetic Response (EPR) spectrum analysis was carried out at different times (2, 5, 15 & 40 minutes) during the experimental run and the corresponding result were shown in Fig. 3. The result reveals that the presence of high hydroxyl radical concentration (at g-factor value 2.2) at the beginning of the reactions and the concentration was gradually decreases with time.

# **3.5 Dye Degradation Experiments for Optimising the Influencing Parameters**

#### 3.5.1 Optimum dosage of Catalyst

To optimise the dosage of different fly ashes, experiments were conducted on the degradation of acid red 1 dye with 10 mg/L initial dye concentration. Earlier studies on acid red 1 dye (N.K. Daud and B.H. Hameed, 2011) proves that the dye was more efficient in photocatalysis at pH 2.5 and hence, that pH value

was used initially for obtaining optimum dosage of the catalyst. Five different dosage values starting from 0.50 mg/L to 1.5 mg/L at an interval of 0.25 mg/L were chosen, and the results are shown in Fig. 4. From the result, it may be inferred that for NLTP fly ash 1.0 mg/L dosage is optimum and the further increase in dosage results has low impact in dye removal efficiency. Whereas, SPP shows considerable improvement in dye removal efficiency from 1.0 mg/L to 1.25 mg/L. However, for comparing the performance of two fly ashes a particular dosage has to be taken and in this case 1.0 mg/L was chosen. The reason for decreasing performance with increased dosage at 1.5 mg/L may be due to obstruction to the penetration of light as the number of fly ash particles present in the solution were increasing with increase in dosage. in acidic range only. From the results, it was observed that for NLTP fly ash the efficiency in dye degradation at pH values between 2.0 to 3.5 were not much varied. The maximum efficiency found at pH 2.5, and at 4.0 the efficiencies were reduced considerably. In the case of SPP, the degradation efficiencies are almost same at pH 2.0 and 2.5 and from there it was considerably reducing at a nearly constant rate. Hence, an optimum pH value of 2.5 is taken for further study.



Fig 4. Dye degradation efficiencies for different dosages of fly ashes used in the present study (pH 2.5;IDC 10 mg/l)

### 3.5.2 Optimization of pH dye solution

The performances of fly ashes in the degradation of dye at various pH values 2, 2.5, 3, 3.5, 4 was tested and the result was shown in the fig 5(a).

Previous studies (N.K. Daud and B.H Hameed, 2011) reported that reactive dye acid red 1 was effectively degrade in acid pH values, hence the variation of ph values were carried out in that range only.

#### 3.5.3 Variation of initial dye concentration (IDC)

An IDC of 10 mg/L used in all the experiments. A study was done to know the performance of the catalyst at other initial dye concentrations, i.e., at 5 mg/L, 15 mg/L, 20 mg/L and 30 mg/L also and the result obtained are shown in Fig. 5(b). The result

reveals that for the initial dye concentrations less than the assumed 10 mg/L concentration, with the same dosage of catalyst, were having increased by 4 % and 65% respectively for NLTP and SPP. The increase in efficiency in dye removal was due to reducing the IDC by 50 % and using the same dosage required for 10 mg/L. For the IDC values more than the assumed value, the dye degradation efficiencies were gone on reducing with the increase in IDC value. A 50% increase in IDC results in the reduction dye degradation efficiencies by 8 % and 6% respectively for NLTP and SPP. For 100% increase in IDC, values resulted in reduced efficiencies by 38 % and 20% respectively for NLTP and SPP. The reduction of dye removal efficiencies of 48 % and 30% respectively for NLTP and SPP observed when IDC values increased by 200%. The reduction in efficiency was due to the less quantity of catalyst was goes on reducing with the increase in IDC as the dosage taken optimum for assumed 10 mg/L IDC value.



Fig. 5 Dye degradation efficiencies with a) variation of pH (IDC10 mg/L; catalyst dosage 1.0 g/L) b) variation of IDC (Catalyst dosage 1.0 g/L; pH 2.5)

# **3.6** Comparison of dye degradation efficiencies of different fly ashes

The dye degradation efficiencies of different fly ashes at the optimum parameters are shown in Fig. 6. The result reveals that the efficiency was more in the case of NLTP (95%) followed by SPP (31%). From the mean composition of fly ashes and the mechanism of dye degradation mentioned above, if the concentration of calcium oxide and Ferric Oxide is more or less equal, better dye degradation efficiencies were noticed as in the case of NLTP. The degradation efficiency was less in the case of SPP, the reason being even though more calcium is available, the ferric oxide available is very less.



Fig. 6 Comparison of dye degradation efficiencies of different fly ashes used in the study (Catalyst dosage 1.0 g/L; pH 2.5; IDC 10 mg/L)

#### 3.7 Kinetic coefficients for rate of dye degradation

The equation used to determine the kinetic coefficients for dye degradation curves  $\ln (C_0/C) = k_1 t$ , where  $C_0 = initial$  dye concentration,

C = concentration of the dye at any time t, and  $k_1$  = apparent dye degradation rate constant. The apparent rate constants, Standard Error and R-Square values were shown in Table 4 for dye degradation using UV-C light by various fly ashes. The r-squared values obtained for all the fly ashes are of good agreement to suggest a pseudo-first order model. The result shows that the NLTP fly ash shows better rate constant followed by SPP.

Table 4. Kinetic coefficients for Pseudo First Order

Experimental method	K Value	Standard Error	R- Square
NLTP	0.05322	0.000501	0.9996
SPP	0.00667	0.000668	0.9519

#### 4. Conclusions

Two different fly ash from different sources of mines and different power plants in India (NLTP and SPP) procured and tested for physical and chemical properties and found that they are heterogeneous material in nature having particles of sizes varying from 300  $\mu$ m to less than 38  $\mu$ m. According to ASTM C618 standards based on chemical composition, NLTP were classified as class C and SPP was not conforming to any category.

The efficiency in removal of dye through adsorption alone was found to be 18% for both the fly ashes.

During the experimental process, dye solution was analysed for EPR spectra and result confirmed that hydroxyl radicals were present during the early stages of the reaction. Fly ash containing considerable amounts of CaO and  $Fe_2O_3$  along with a small quantity of TiO<sub>2</sub>, which plays a vital role in dye degradation by photocatalysis.

Among different fly ashes, NLTP degrades the dye effectively (95%) compared to SPP (31%).

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