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# Synergetic degradation of reactive dye Acid Red 1 by cobalt-doped lignite fly ash

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## ABSTRACT

Degradation studies on a reactive dye Acid Red 1 are carried out by lignite fly ash (LFA) and cobalt-doped over LFA under UV-C radiation. In India, disposal of fly ash is a major problem. As fly ash is an inert material containing small quantities of photoreactive, inorganic oxides like $TiO_2$, CaO and $Fe_2O_3$, this paper makes an effort to use it to overcome the degradation of dye and disposal of the fly ash problem. The chemical composition of LFA is analysed by X-ray fluorescence. Scanning electron microscopy with energy dispersive X-ray spectroscopy and X-ray diffraction are carried out to characterise the physical and photophysical properties of the catalyst. The optimum parameters affecting the dye degradation are found for LFA and cobalt-doped LFA under UV-C light. The kinetic coefficients for both catalysts are also determined. Cobalt-doped LFA proved the most effective, followed by LFA, and the corresponding efficiencies are 99 and 95%, respectively, at the end of 60 min. The reuse of cobalt-doped fly ash and fly ash are also tested, and it is found that the efficiency for the first reuse is 93 and 88%, respectively, at the end of 60 min.

*Keywords:* Dye degradation; Acid Red 1; Photocatalyst; Lignite fly ash; Cobalt-doped lignite fly ash

## 1. Introduction

The major contribution to power generation in India is from coal- or lignite-based thermal power plants. The ash content in coal available in India is about 45% and 10–15% in imported coals. The generation of a large quantity of ash from coal- or lignite-based thermal power stations requires a large area of valuable land for its disposal. This open disposal leads to air and water pollution. Steps have been taken by the Government of India to use it as an alternative source for cement and subsoil but the targets are yet to be achieved. Of the 164 million tons of fly ash produced in 2012–2013, only 100 million tons were reused as per the report of the Central Electricity Authority, Government of India [1]. Many industries are starting to utilise this fly ash in making useful products like cement, fly ash bricks, fly ash concrete and precast elements, but their utilisation in waste water treatment is still in the early stages. In the present study, an attempt has been made to utilise lignite fly ash (LFA) in the treatment of wastewater containing a reactive dye, Acid Red 1.

The textile industries produce large quantities of wastewater containing reactive dyes and chemicals. They are lethal to living organisms due to the oxygen

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depletion they create. Their presence affects the light penetration in water [2]. Treatment of effluents is therefore required before it is discharged into the natural environment. Degradation of dyes is usually done by physical and chemical methods which include adsorption, reverse osmosis, coagulation and filtration. But these methods have shortfalls like high regeneration cost and also require post-treatment processes. These methods transform the pollutant from one phase to another, without making it inert, thereby necessitating further treatment. Biological methods are also used for dye degradation, but they suffer a limitation as all the chemicals are not readily biodegradable. Advanced oxidation processes proved to be the better alternative compared to other processes and it is used in the present study.

A few studies were done using fly ash as adsorbent only on AO II, AR, BG [3] and Crystal Violet and Basic Fuchsin [4] dyes, adsorption along with heavy metal removal like cadmium, copper and nickel simultaneously [5,6]. Some studies on the combination of sonication and photocatalysis [7,8], and a few studies on the combination of photocatalysis and adsorption studies were also carried out by some researchers using $TiO_2$ nanofibre-coated fly ash [9,10], fly ash-based geo-polymers [11] and tungsten oxide with fly ash [12]. The results show that the degradation of MB and Bemacid Blau N-TF (BB) and Bemacid Rot N-TF (BR) from Bezema dyes is always more in adsorption assisted by photocatalysis. The majority of researchers have focused on class-F fly ash (bituminous fly ash) only. In the present investigation, an attempt has been made to use LFA (fly ash produced from the burning of lignite or sub-bituminous coal) of class-C in dye degradation.

## 2. Materials and experimental methods

### 2.1. Fly ash

Fly ash used in this study was procured from the Neyveli lignite thermal power plant, Neyveli, Tamilnadu state in India. Fly ash is a heterogeneous material and its chemical composition depends on the quality of coal or lignite used in the thermal power plants and the conditions in which they are burnt. To ascertain the appropriate chemical composition of LFA used in this study, X-ray fluorescence (XRF) analysis was carried out at 10 different points in the same sample and the mean value was reported in Table 1 along with the minimum and maximum values. If sum of the elemental composition of $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ is greater than or equal to 50%, the fly ash was classified as class-C and if the same was more than 70%, it was classified as class-F according to ASTM C618. The sum of the above elemental composition in the LFA is 63.573% from the result shown in Table 1, and hence it was classified as class-C as per ASTM C618. As per Indian standard IS

Table 1
XRF result of LFA

| Elements in oxide form | Mean concentration (%) | Range (%) |
|---|---|---|
| $SiO_2$ | 26.479 | 22.696–30.841 |
| $Al_2O_3$ | 22.551 | 20.845–25.277 |
| CaO | 19.075 | 16.898–22.452 |
| $Fe_2O_3$ | 14.543 | 10.944–18.761 |
| $SO_3$ | 9.317 | 8.971–9.987 |
| MgO | 2.923 | 2.686–3.334 |
| $TiO_2$ | 2.492 | 2.158–2.668 |
| $Na_2O$ | 1.958 | 1.571–2.632 |
| SrO | 0.162 | 0.122–0.232 |
| $ZrO_2$ | 0.148 | 0.063–0.205 |
| PdO | 0.095 | 0.052–0.149 |
| $P_2O_5$ | 0.063 | 0.000–0.181 |
| $MnO_2$ | 0.047 | 0.039–0.056 |
| $Y_2O_3$ | 0.044 | 0.034–0.064 |
| ZnO | 0.031 | 0.03–0.033 |
| $Cr_2O_3$ | 0.028 | 0.01–0.045 |
| $K_2O$ | 0.019 | 0.007–0.038 |
| NiO | 0.009 | 0.005–0.013 |
| Cl | 0.008 | 0.000–0.023 |
| CuO | 0.006 | 0.005–0.008 |

3812 (Part 1): 2013, if the concentration of CaO is more than 10%, it is called calcareous fly ash.

## 2.2. Dye solution

A reactive dye, Acid Red 1 (Amido Naphthol Red G, Azophloxine) was purchased from Sigma Aldrich, USA and the structure is as shown in Fig. 1. The empirical formula (Hill Notation) of the dye is $C_{18}H_{13}N_3Na_2O_8S_2$ and the molecular weight is 509.42. It contains 60% dye and an absorption frequency of $\lambda_{max}$ at 506 and 532 nm. The colour index number is 18,050.

## 2.3. Chemicals and reagents

Concentrated $H_2SO_4$ and NaOH of Merck brand with AR grade were used for the pH adjustment. For catalyst preparation, cobalt(II) nitrate hexa hydrate of Merck AR grade was used.

## 2.4. Catalyst preparation

Cobalt doping over the fly ash was done by the incipient impregnation method [13]. For the preparation of CoLFA1, 0.05 gm of Co is added to 100 ml of double-distilled water and stirred till it is fully dissolved. Then 5 gm of LFA is added to the solution. The mixer is now kept in an orbital shaker at 80°C till the water evaporates fully and the sample is kept in a Muffle furnace for 4 h at 600°C. Four different concentrations of cobalt with 1, 2, 3 and 4% w/w were added to fly ash and are denoted by CoLFA1, CoLFA2, CoLFA3 and CoLFA4, respectively.

## 2.5. Characterisation

The phase analysis of the catalyst was investigated by X-ray diffraction (XRD) (Model: Rigaku, D/MAX, Ultima III, Japan) at a scan speed of 10°/min and step size of 0.02 for a scan range of 10–80°. The peaks obtained were compared with the data from the Joint Committee on Powder Diffraction Standards. Scanning electron microscopy (SEM) images with EDS were taken from VEGA3 SB—Easy Probe. PerkinElmer UV/vis/NIR Spectrometer, Lambda 750 was used to measure the absorbance of dye at 532 nm.

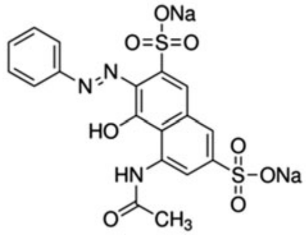

Fig. 1. Structure of reactive dye Acid Red 1.

## 2.6. Experimental set-up

All experiments with UV-C light were done in a closed wooden box, with cube-shaped sides of 50 cm as shown in Fig. 2. A Phillips brand UV-C light of 4 W was used, which emits rays at a frequency of 254 nm. A Remi brand magnetic stirrer was used to control the speed and temperature.

## 2.7. Degradation studies under UV light

Degradation studies on Acid Red 1 dye were carried out in a 250-ml glass beaker and the sample volume was 200 ml. Initial dye concentration used for all experiments was 10 mg/L except during the variation of initial dye concentration experiments. After mixing the required dosage of catalyst, initial pH of the dye solution was adjusted to the opted value. UV-C light in a quartz tube was inserted into the solution and switched on. The solution was continuously stirred at 300 rpm with a magnetic stirrer. Samples were taken at stipulated time intervals (15, 30, 45 and 60 min), centrifuged in a centrifuge at 10,000 rpm for 10 min and the clear solution was tested in UV spectrometer at 532 nm wavelength. All experiments were carried out at room temperature (25 ± 2°C). Dye degradation efficiencies were calculated by the following formula:

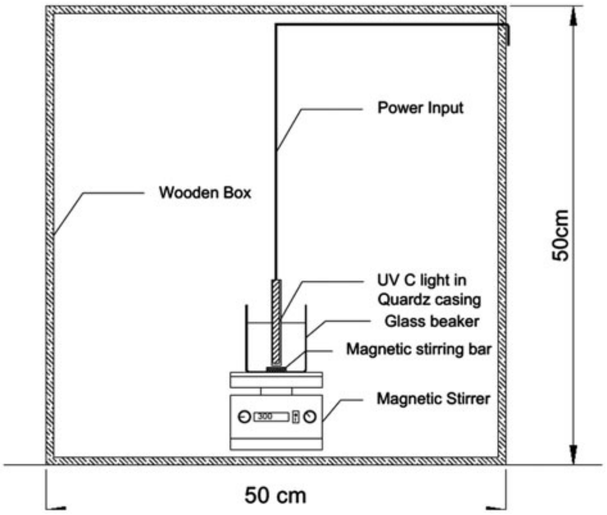

Fig. 2. Experimental set-up.

$$\text{Percentage dye degradation} = (1 - (C/C_0)) \times 100 \qquad (1)$$

where $C$ is the concentration of the dye at any time "$t$" and $C_0$ is the initial concentration of the dye.

## 3. Results and discussion

### 3.1. XRD patterns

The XRD patterns of LFA, CoLFA3 and single reused CoLFA3 named as CoLFA3R are given in Fig. 3, showing that the major components of all the three materials matched. The major components of LFA were mullite and quartz. From CoLFA3 and CoLFA3R XRD pattern, the presence of cobalt oxide at 2$\theta$ value 50.15° was observed. The enhancement of intensity of cobalt in the CoLFA3 and CoLFA3R was observed compared to LFA through XRD analysis.

### 3.2. SEM and EDS images

SEM image of LFA, CoLFA3 and CoLFA3R, and SEM images of LFA are shown in Fig. 4(a) and (b). It may be inferred and visualised that LFA particles are of different sizes ranging from 0 to 300 μm and are almost spherical in shape. The surface of LFA appears to be smooth. Fig. 5(a) and (b) shows the CoLFA3 images. It is clearly seen that the round crystal structure of the fly ash particles was not distorted and was uniformly coated with cobalt. From the EDS report, an increase in the concentration of cobalt from 0.26 to 3.27% by weight was found which was confirmed by the XRD results. From Fig. 6(a) and (b), it was inferred that some adsorption of dye took place on the surface of the catalyst and the catalyst's physical properties like structure were not changed. The coating of cobalt still existed.

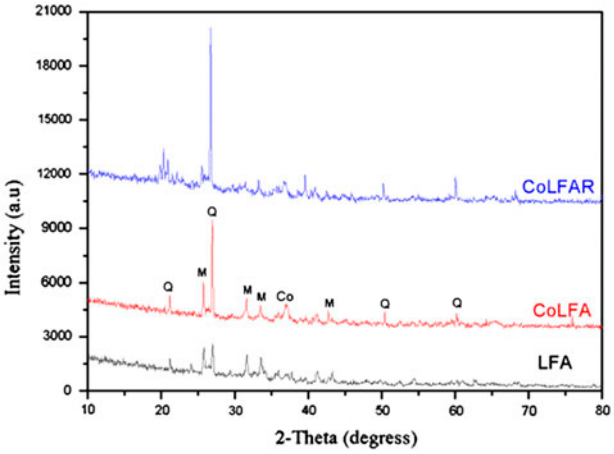

Fig. 3. XRD of pattern of LFA, CoLFA3 and CoLFA3R.

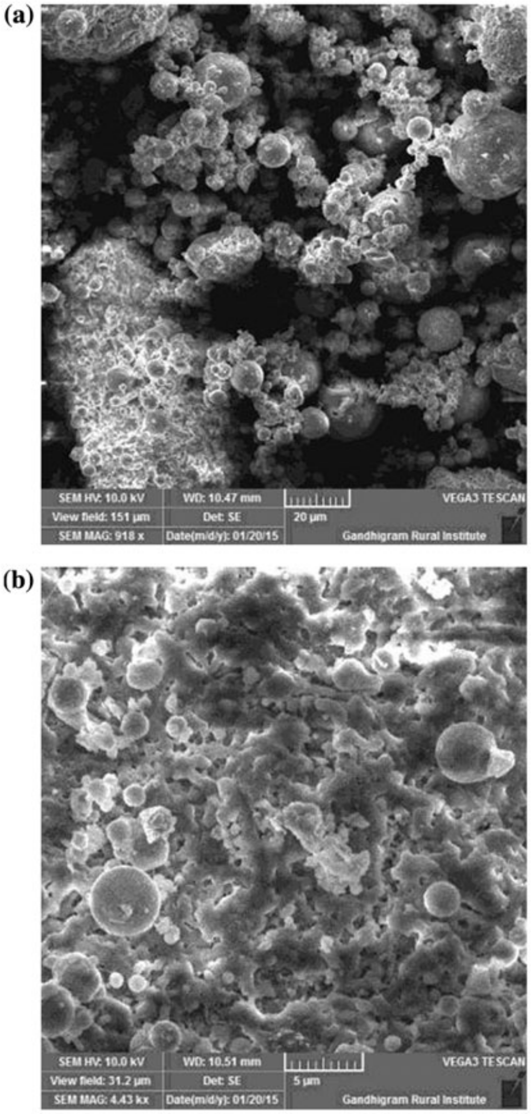

Fig. 4. (a) and (b): SEM images of LFA.

### 3.3. Preliminary experimentation with LFA

Dye degradation experiments were conducted using fly ash with an assumed dosage of 1.0 g/L to degrade the reactive dye Acid Red 1 and without pH adjustments. A removal efficiency of 11% was observed without UV-C light and it was 17% with UV-C light, after 60 min exposure.

### 3.4. Effect of pH on Acid Red 1 degradation by LFA

With the assumed dosage of 1.0 g/L of LFA, the degradation studies were undertaken at other pH

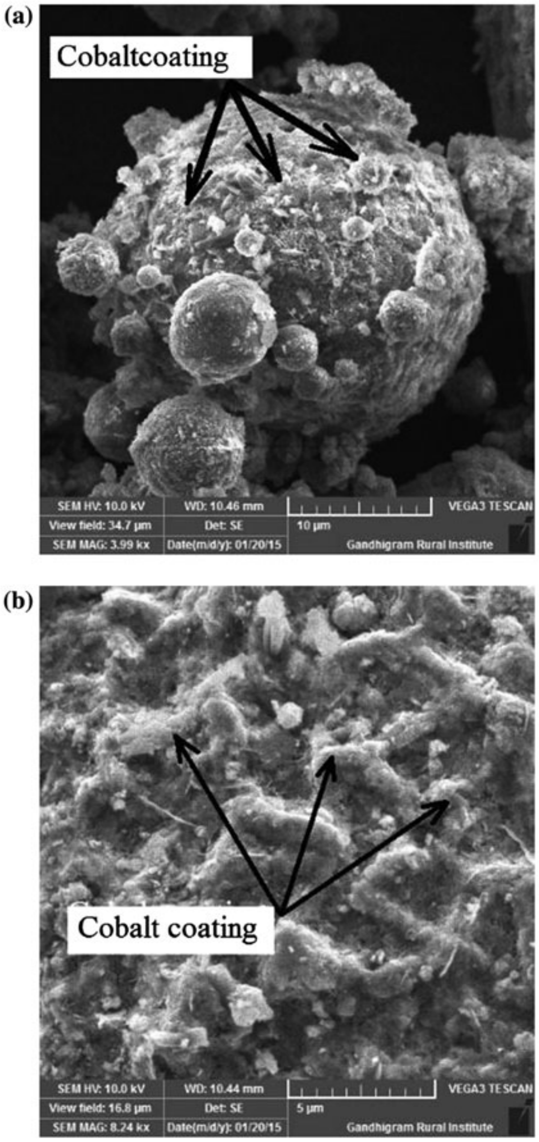

Fig. 5. (a) and (b): SEM images of CoLFA3.

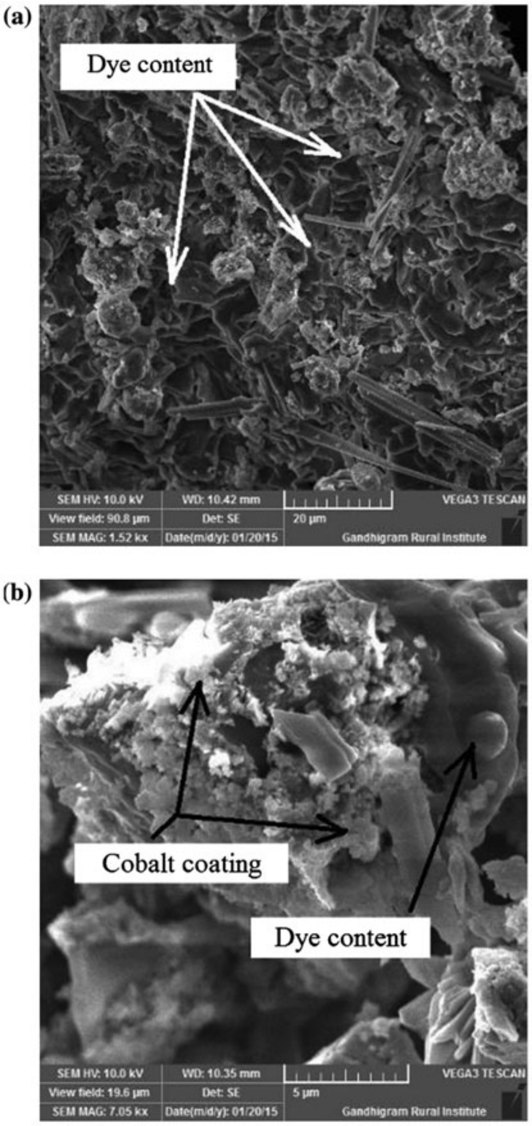

Fig. 6. (a) and (b): SEM images of CoLFA3R.

values (2, 2.5, 3, 3.5 and 4) and the results are shown in Fig. 7. The solution's pH affects the degradation efficiencies considerably. From the experimental result, for the solution with initial pH more than 3.5, considerable reduction in the efficiency was observed. Whereas it shows better efficiencies if the solution pH was in between 2.0 and 3.5. Optimum efficiency was observed at pH 2.5, which was concurrent with previous studies on Acid Red 1 dye [14].

### 3.5. *Effect of variation of LFA (0.25–1.5 g/L) on degradation of Acid Red 1*

Experiments were conducted for various dosages of the raw LFA on dye degradation, varying the dosage from 0.25 to 1.5 g/L in an interval of 0.25 g/L keeping the initial concentration of the dye at 10 mg/L, and at pH at 2.5 as shown in Fig. 8. At lower concentrations, the dye removal efficiency was less because the required quantity of photoreactive elements was not present; thereby, the amount of OH radicals produced was also less. The variation of dye degradation shows that 1.0 g/L dosage was slightly less than that of 1.25 g/L, but was not considerable. Hence, a dosage of 1.0 g/L was taken as an optimum dosage of LFA. LFA in the above-said conditions degrades 95% in 60 min. It was observed that the degradation due to adsorption (when the experiment was carried out without UV light and in darkness) is only 18% and the remaining

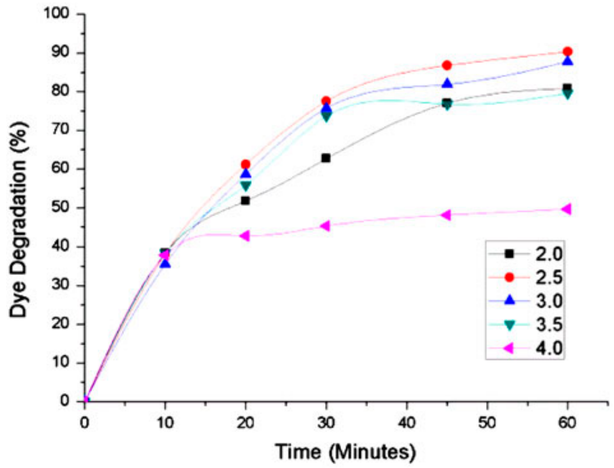

Fig. 7. Dye degradation percentages for only fly ash with UV-C light at different pH values (IDC = 10 mg/L; dosage of catalyst = 1.0 g/L).

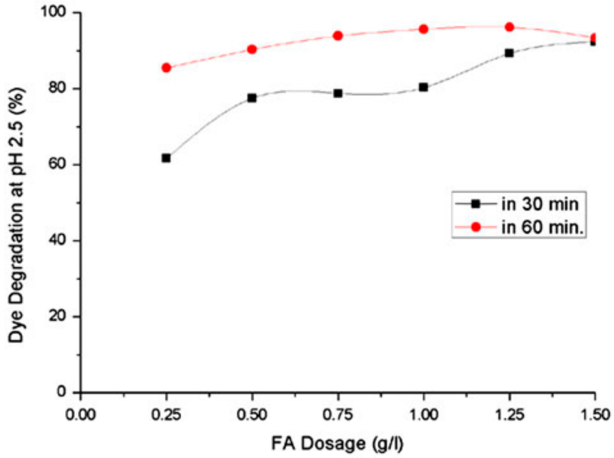

Fig. 8. Dye degradation percentages for different dosages of fly ash with UV-C light at (IDC = 10 mg/L; pH 2.5).

77% degradation is credited to photocatalytic activity as shown in Fig. 9.

Initially, for dosage up to 1.0 g/L, considerable improvement in efficiency was observed for 60 min compared to 30 min exposure, but for the dosages 1.25 g/L and above the difference is not significant.

### 3.6. Effect of gradation of LFA on dye degradation

Sieve analysis was done for the fly ash to know the particle size distribution over a set of sieves ranging from 0 to 300 μm and the results are given in Table 2. It was observed that all the LFA passed through 300-μm sieve. Five different sieves of 150, 75, 63, 45 and 35 μm were used to get six different size fractions and the corresponding dye degradation efficiencies are shown in Fig. 10. The dye degradation efficiency of size fractions above 150 μm was less when compared to other size fractions, as the surface area of the fly ash containing larger size fractions was less compared to smaller size fractions for a given weight. Due to the lesser surface area, the rate of reaction was also less compared to smaller size fractions. The weight of the particle increased with size. It was observed during the experiment that larger size fraction particles settled down at the bottom of the container, instead of floating in the solution, leading to an ineffective participation in the reaction with the dye solution.

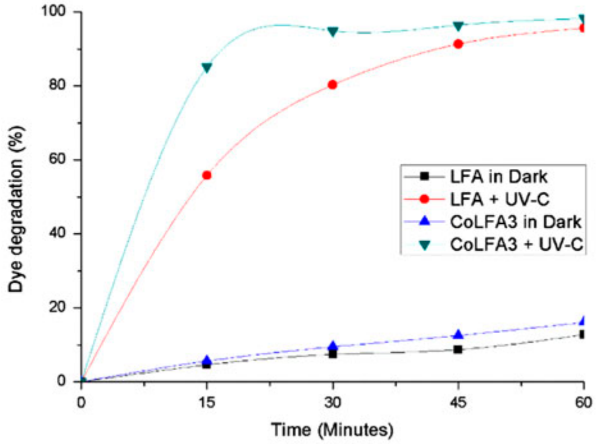

Fig. 9. Dye degradation percentages for LFA and CoLFA3 in dark and under UV-C light (IDC = 10 mg/L; pH 2.5).

### 3.7. Variation of cobalt dosage on LFA (1–4%)

Studies were done with doping of cobalt with a variation of 1–4% by weight over LFA. The results of dye removal efficiency of CoLFA under the same conditions as that for LFA are shown in Fig. 11. For comparison, LFA degradation was also shown in the graph. From Fig. 11, it was found CoLFA3 degrades 98.3% under similar conditions as that of LFA. By doping of cobalt over LFA, degradation rates in

Table 2
Particle size distribution of LFA

| Sieve size in μm | 150 | 75 | 63 | 45 | 38 | PAN |
|---|---|---|---|---|---|---|
| Weight retained (%) | 34.88 | 56.7 | 1.76 | 3.4 | 2.3 | 0.96 |

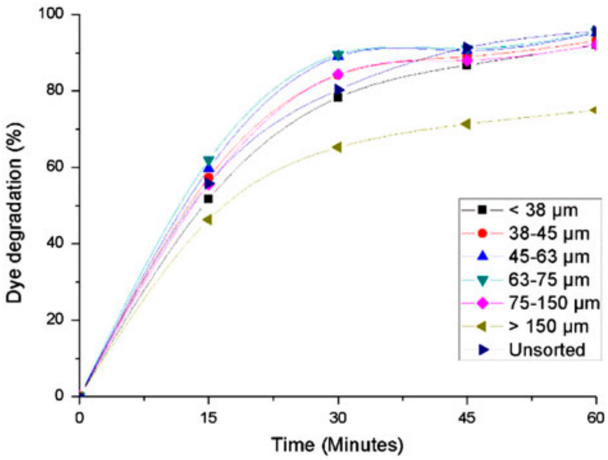

Fig. 10. Dye degradation efficiencies of different size fractions of LFA (IDC = 10 mg/L; pH 2.5; dosage = 1.0 g/L).

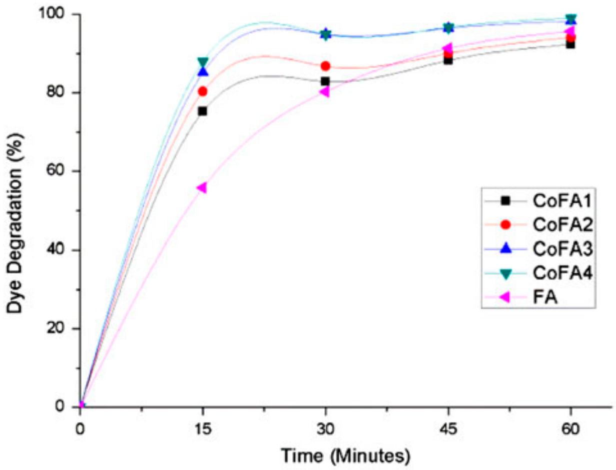

Fig. 11. Dye degradation percentages for only LFA and cobalt-doped LFA (IDC = 10 mg/L; pH 2.5; dosage of catalyst = 1.0 g/L).

the first 15 min increased by 50% compared to that of LFA and the difference was narrowed with an increase in the reaction time. At 60 min of exposure, the improvement observed was only about 4%.

### 3.8. Effect of single reuse of LFA and CoLFA3

An attempt was made to reuse the used catalyst for once more. The catalyst which was used in the earlier experiments was used again after oven drying. The same set of experiments was carried out and the removal efficiency of 88 and 93% was observed for LFA and CoLFA3, respectively, as shown in Fig. 12.

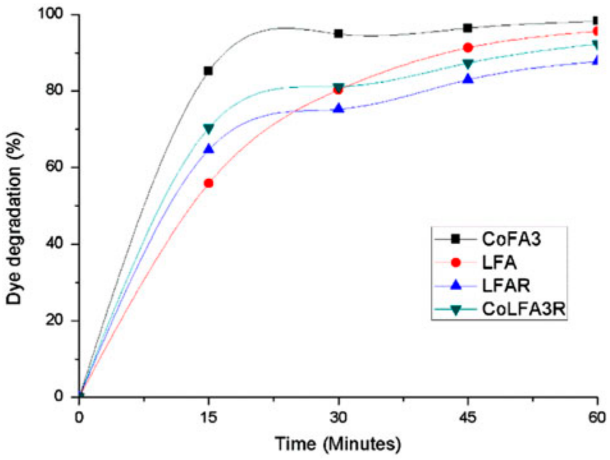

Fig. 12. Dye degradation efficiencies of LFA, CoLFA3 and corresponding single reuse efficiencies (IDC = 10 mg/L; pH 2.5; dosage of catalyst = 1.0 g/L).

### 3.9. Kinetic coefficients

The experimental results were used in the determination of kinetic coefficients assuming a pseudo-first-order reaction.

AR1 dye degradation curves by LFA and CoLFA3 catalysts were simulated as:

$$\ln(C/C_0) = k_1 t \tag{2}$$

where $C_0$ was the initial concentration, $C$ is the concentration of dye at time $t$ and $k_1$ is the apparent rate constant.

Table 3 shows the apparent rate constants, standard error and $R^2$ values for LFA and CoLFA3 and the corresponding graphs are shown in Fig. 13. The degradation pattern of the Acid Red 1 dye by UV-C radiation fits a mono-exponential curve, suggesting that a pseudo-first-order homogeneous reaction model can be considered to describe the kinetic behaviour.

Table 3
Kinetic coefficients for pseudo-first-order

| Catalyst | *K*-value | Standard error | $R^2$ |
|---|---|---|---|
| LFA | 0.05319 | 4.97683E−4 | 0.99956 |
| CoLFA3 | 0.07542 | 0.00711 | 0.95707 |

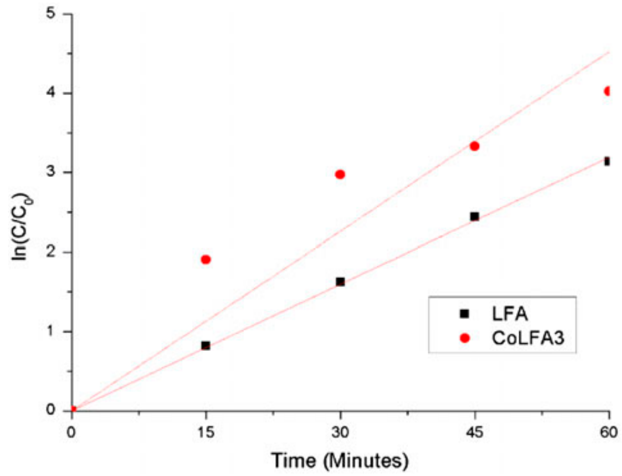

Fig. 13. Pseudo-first-order linear regression result of degradation of AR1 by LFA and CoLFA3.

## 4. Conclusion

(1) The fly ash class-C was studied as a photocatalyst and a carrier for cobalt in the degradation studies of a reactive dye Acid Red 1. It was found suitable for the purpose.

(2) Characterisation studies on raw LFA, CoLFA3 and CoLFA3R revealed that cobalt is effectively coated over LFA and maintained its crystalline structure.

(3) The studies in the dark with LFA and CoLFA3 show lower adsorption levels and maximum removal efficiency was 18% only after 60 min of exposure.

(4) With the assistance of UV-C light, degradation of dye by LFA, CoLFA3, LFAR and CoLFA3R was found to be 95, 99, 88 and 93%, respectively, after 60 min exposure.

(5) Gradation effect of LFA was studied and particles with size more than 150 μm were proved less efficient in dye degradation when compared to other lower size fractions.

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