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Full Length Article

# Synthesis and characterization of coral-like hierarchical MgO incorporated fly ash composite for the effective adsorption of azo dye from aqueous solution

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ABSTRACT

In the present work, coral like hierarchical magnesium oxide (MgO) incorporated fly ash (FA) composite (FAMgO) synthesised by sol-gel method was evaluated for the adsorption of Reactive Black 5 (RB5) azo dye from aqueous solution. Adsorbent characterization using FE–SEM, XRD and FT-IR ascertained the formation of the FAMgO composite. Batch mode sorption studies were carried out for RB5 azo dye removal as a function of pH, FAMgO dose, initial dye concentration and temperature. The compliance of Langmuir isotherm model ($R^2 = 0.999$) corroborated the homogeneous nature of sorption of RB5 dye onto FAMgO with the sorption capacity ($Q_{max}$) of 48.78 mg $g^{-1}$. The regression coefficient value revealed the best fit of pseudo–second–order model with the $Q_e$ value of 29 mg $g^{-1}$. The thermodynamic parameters such as $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ suggested the spontaneous and endothermic nature of RB5 dye sorption onto FAMgO and suitable mechanism has been proposed.



## 1. Introduction

Water pollution is a rising issue of recent years due to swift industrialization throughout the world [1]. The water pollution caused by organic and heavy metals pollutants is of utmost importance because of their toxic and carcinogenic effects on living systems including human beings. Therefore there is an urgent need to remove these contaminants from water bodies. The dye containing wastewaters are produced from various industries such as textile, pulp and paper, plastic and leather which pose significant environmental issues and problems [2,3]. The industrial wastewater containing synthetic organic dyes may be toxic, carcinogenic, teratogenic and mutagenic in nature for human as well as aquatic ecosystem [4].

These synthetic dyes structured with one or more benzene rings undergo degradation at low rates and lead to degraded toxic products. As a consequence of this practical problem, effluents containing azo dyes ought to be treated before their discharge into water bodies.

Both the aesthetic and aquatic flora pollutions are caused due to dye effluents (dye concentration as low as 1 mg $L^{-1}$) which further diverted towards the formation of degraded by-products. The Reactive Black 5 (RB5) (Fig. 1) is of homo bi-functional nature and a member under the class of azo dyes. It contains the aromatic substituents (R, R') of the chromophoric group R—N=N—R' typically bear functional elements such as —OH and $-SO_3H$ [5]. During the dyeing process, the vinyl sulfone moieties of RB5 azo dye molecule get hydrolysed into 2–hydroxy ethyl sulfone groups which do not fix onto cellulose fibers and ultimately causes deleterious problems to water [6–9].

Several approaches including adsorption [10], coagulation [11], membrane-filtration [12], photo-catalysis [13], ozonation and oxidation [14] have been reported for the removal of dyes from wastewater. Each method has its own advantages and disadvantages like higher cost, sludge production and low regeneration capacity but adsorption being a conventional method is used

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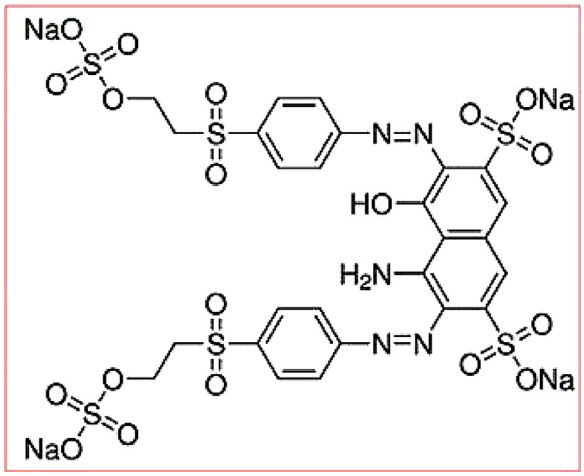


**Fig. 1.** Molecular structure of RB5 azo dye.

broadly as it is cost effective, eco-friendly and easy to use. Adsorbents like activated carbon [15,16], Pumice [17], Walnut activated carbon [17,18], Biomass FA [19], Peanut shell [20], Agro-industrial wastes [21] and naturally occurring materials [21] were of great interest in dye sorption. The advantages of functional materials like metal oxides have been received a lot of contemplation due to their applicability in dye sorption [22–25]. Among them, magnesium oxide (MgO) acts as a promising material for water application due to non-toxicity and chemical stability in nature [26,27].

The conspicuous contribution of MgO in dye removal was reported by early researchers [28,29]. Despite the problems associated with bare MgO such as rapid aggregation, poor adsorption and difficult to recover the materials, attempts have been made to immobilize it on some adsorbent materials without loss of materials. The commonly used materials are silica, alumina, activated carbon, zeolites, clays, modified clay materials, layered hydroxides and glass [30–32]. Apparently, amount contraction with selection of adsorption utilities is of vital importance.

Thermal power plant residue of fly ash (FA) has been considering as a solid waste. Currently 90% of coal based thermal power plants running across the world [33,34]. The worldwide annual production of FA is estimated to be around 600 million tons. It is estimated that only 20–30% of FA is utilized, while the remaining amount of 70–80% FA has to be stored in ponds or deposited in old mines and lead to the disastrous sequel as a source of air, water and soil pollution [35]. Therefore, extensive research is needed to find the way to utilize FA for useful applications.

Taking the above into consideration, the immobilization of MgO on the surface of FA and its application for the treatment process might be a good attempt to solve the problems concerned with pollution. Several researchers investigated the degradation ability of the ZnO, $TiO_2$ and Ag loaded FA catalysts under certain preparation and reaction conditions [36–40]. Interestingly, Jain et al. reported that MgO doped FA (MgFA) composite can be used as a highly active heterogeneous base catalyst for Claisen–Schmidt condensation reaction [41]. Based on the extensive literature survey we made, the present contribution using FAMgO is first of its kind on the sorption of dye with promising efficiency. The bi–faceted profile of FAMgO composite in environmental protection and waste utilization is supposed to be the appropriate solution in the current scenario. Therefore, a facile strategy was developed to fabricate unique coral–like hierarchical FAMgO composite using waste FA, $Mg(CH_3COO)_2.4H_2O$ and $CO(NH_2)_2$ as precursors. The MgO nanoparticles were in situ synthesized on the FA matrix, characterized and applied for the removal of RB5 azo dye from water.

## 2. Experimental

### 2.1. Materials and reagents

Fly ash (FA) was procured from Neyveli thermal power station (Tamil Nadu, India). Chemicals such as magnesium acetate ($Mg(CH_3COO)_2.4H_2O$) and urea ($CO(NH_2)_2$) were purchased from Nice Chemicals Private Limited, India. Sodium hydroxide (NaOH) and anionic RB5 azo dye (Fig. 1) were received from SD Fine Chemicals, Mumbai, India. All the chemicals used in the study are of analar (AR) grade.

### 2.2. Synthesis of hierarchical MgO incorporated fly ash composite (FAMgO)

In an autoclave contained titanium vessel of 2 L capacity, exactly 5 g of FA was taken in 500 g of distilled water and stirred (500 rpm) at 120 °C for 2 h to do activation. Then the activated FA was cooled to room temperature, filtered, washed and dried at 105 °C for 2 h. The coral – like hierarchical MgO incorporated FA composite was prepared as follows. Separately dissolve 1 g (0.017 mol in 40 mL) of urea and 1.5 g (0.007 mol in 50 mL) of magnesium acetate in distilled water. These two solutions were mixed and stirred at 500 rpm for 30 min. Later, activated FA of 0.1 g was added to the above mixed solution and shaken for 5 h at ambient temperature. The resulted sol-gel was maintained at 130 °C for 12 h followed by annealing at 200 °C for 2 h. The finally obtained solid was abbreviated as FAMgO composite.

### 2.3. Characterizations

The surface morphologies of the untreated FA, treated FA and FAMgO composite were observed using field-emission scanning electron microscopy (FE-SEM) along with Energy–dispersive X-ray Analysis (EDAX). The structure and phase composition of the FA and FAMgO samples were obtained with a Panalytical X'PertPro X-ray diffractometer (XRD, Phillips, Holland) with Cu Kα (λ = 1.540 Å) radiation over Bragg angles ranging from 10° to 80°. Fourier-transform infrared (FT-IR) spectral analysis for the samples was carried out using an IRAffinity-1S, IR Shimadzu, Japan.

### 2.4. Adsorption procedures

The adsorption experiments were carried out at various pH, temperature and RB5 azo dye concentrations. The batch mode technique was carried out by stirring with an optimized amount of the FAMgO in 0.1 L of the synthetic dye solution. The absorbance of the supernatant obtained was measured using a UV–Vis Spectrometer (UV–Vis1800, Shimadzu, Japan) at the wavelength (λ = 598 nm) corresponding to the maximum absorbance of the RB5 azo dye solution. The residual dye concentration was determined using the calibration curve carried out with a range of known RB5 azo dye concentrations. The adsorption capacity of the dye by used material was calculated using the following expression:

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Where $Q_t$ (mg $g^{-1}$) is the amount adsorbed at time t (min), $C_0$ and $C_t$ (mg $L^{-1}$) are the initial and at time (t) dye concentration, respectively. V is the volume of solution (L) and m is the quantity of used adsorbent (g).

The pH for the solutions were adjusted using HCl and NaOH solutions of 0.1 M. The effects of pH (2–10), FAMgO dose (0.05–0.25 g), initial dye concentration (10–100 mg $L^{-1}$), solution temperature (30–60 °C) and stirring speed (50–250 rpm) were studied. The basic surface contents of FAMgO were determined

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