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# Synthesis of porous adsorbent using microwave assisted combustion method and dye removal

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A B S T R A C T

Zinc aluminum hydroxide (ZAH) as a porous adsorbent was synthesized using microwave assisted combustion method and its dye removal ability from single and binary systems was studied. The ZAH characteristics were investigated using XRD, FTIR, and SEM. Acid Blue 92(AB92), Acid Red 14 (AR14), and Direct Red 23 (DR23) were used. The effect of ZAH dosage and initial dye concentration on dye removal was investigated. Adsorption isotherm and kinetic was evaluated. The capacity of ZAH to remove AB92, AR14, and DR23 was 95 mg/g, 84 mg/g and 75 mg/g, respectively. Dye removal fitted with the Langmuir model and pseudo-second order kinetics.



## 1. Introduction

Dyes are released into wastewater from several industries such as textile, paper and plastic. Textile industry uses dyes for dyeing of goods. However, the first known use of a dye was much later, being nearly 4000 years ago, when indigo was found in the wrappings of mummies in Egyptian tombs. Till the late nineteenth century, all the dyes were more or less natural with main sources like plants, insects and mollusks, and were generally prepared on small scale. It was only after 1856 that with Perkin's historic discovery of the first synthetic dye, mauveine, that dyes were synthesized on a large scale. About 15% of the total world dyes production is lost during textile dyeing which is released in textile effluents. Several methods were used to remove dyes from wastewater. Adsorption process as one of the effective treatment methods is used to remove dyes from wastewater. Several adsorbents are synthesized and used [1–11]. The synthesis of adsorbents by conventional methods is more complex and high cost. Thus, the synthesis of materials by a low cost and simple method is an important task.

Synthesis and modification of materials using microwave radiation has attracted considerable attention as a green technology. Microwave radiation has both electrical and magnetic properties. The radiation of material by microwave results in vibration of molecules by induced or permanent dipoles. The quantity of microwave energy absorbed by the materials determines the intensity of vibration. The size, shape and polarizability of the molecules, as well as, extent of intermolecular bonding of the materials are main factors on the intensity of vibration [12].

A literature review showed that anionic dye removal ability of zinc aluminum hydroxide (ZAH) as a porous adsorbent from binary (bin.) system was not studied in details. In this paper, ZAH was synthesized using microwave assisted combustion method and characterized. The dye adsorption capacity of ZAH from single (sin.) and binary (bin.) systems was studied. Acid Blue 92(AB92), Acid Red 14 (AR14), and Direct Red 23 (DR23) were used as anionic dyes. The isotherm of dye removal and kinetics were investigated.

## 2. Experimental

### 2.1. Materials

Acid Blue 92(AB92), Acid Red 14 (AR14), and Direct Red 23 (DR23) were achieved from Ciba and applied. Fig. 1 shows the structure of dyes. The other materials were obtained from Merck.

### 2.2. Synthesis of ZAH

Microwave assisted combustion synthesis method was used to synthesis of porous adsorbent (ZAH). Microwave assisted combustion synthesis of oxide materials was introduced by Patil et al. [13] which is well-known as propellant chemistry. In this method, oxidizer to fuel ratio ($\Psi$) is calculated as an effective parameter. The oxidizer to fuel ration ($O/F$) is calculated by dividing the ratio of $\sum$(coefficient of metal nitrate elements) × (valence) to $-\sum$(coefficient of fuel elements) × (valence). Nitrogen in combustion is ineffective and role of this specie of compound on combustion reaction is negligible so the valence number of $N$ is equal to zero. In this study, urea as a suitable fuel was selected. Stoichiometric reaction of metal nitrates and urea fuel is shown as follows:

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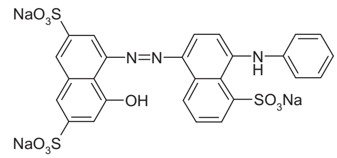
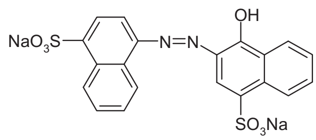
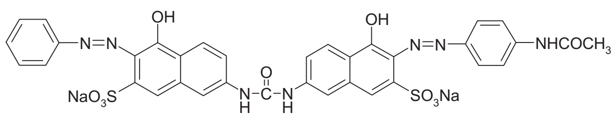



AB92




AR14




DR23

**Fig. 1.** The chemical structure of dyes.

$$Zn(NO_3)_2 + 2Al(NO_3)_3 + \Psi CH_4N_2O \rightarrow ZnAl_2O_4 + \Psi CO_2 + 2\Psi H_2O + 1.6\Psi N_2 \quad (1)$$

The $\Psi$ value which is determined by *O*/*F* ratio of propellant chemistry was equal to 6.67.

The combustion synthesis of aluminate structure has different steps. In first step, mix solution of 0.26 M zinc nitrate and 0.52 M aluminum nitrate was prepared. Second step was addition of ammonium chloride (0.18 g) to the metal nitrate solution. The main role of $NH_4Cl$ is enhancement of exhaust gases and improvement of sponge-like structure of products. Next step was addition of urea with respect to the calculated *O*/*F* ratio (0.35 mol, 2.11 g). Fourth step before combustion reaction was the conversion of solution to the viscose gel. The formation of well distribution of metal in an organic structure is the main goal of gelation. For this purpose, solution was gradually heated at 70 °C until the gelation process was completed. The gel complex of metal nitrates and urea fuel was transferred to the microwave oven and combustion process was quickly happened less than 3 min with the power of 900 W. The intense ignition under microwave irradiation leads to straight formation of porous structure of zinc aluminum hydroxide.

### 2.3. Physicochemical characterization of ZAH

The synthesized ZAH was characterized using X-ray diffraction (XRD) (PW1800 Philips), Fourier transformation infra-red (FTIR) (Perkin–Elmer) and Scanning electron microscope (SEM) (UK 1455VP Leo).

### 2.4. Adsorption studies

The dye removal using ZAH was done by mixing of adsorbent in 250 mL of dye solution (50 mg/L) in jars. The solution samples were taken from sample point during the dye removal process at certain time intervals and centrifuged. The residual concentration of dyes in supernatant solution was measured at the maximum wavelength ($\lambda_{max}$) of dyes. The $\lambda_{max}$ of AB92, AR14, and DR23 was 580 nm, 517 nm and 504 nm, respectively (Fig. 2). Perkin–Elmer Lambda 25 UV–VIS spectrophotometer was used to measure of dye absorbance in samples. The dye removal data were verified with the adsorption isotherm and kinetics.

The effect of ZAH dosage on dye adsorption from single and binary systems was studied by contacting 250 mL of dye solution (50 mg/L) at room temperature (25 °C) for 60 min.

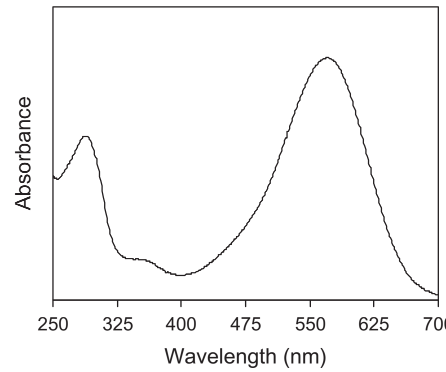
The effect of initial dye concentration on dye adsorption was investigated by contacting 250 mL of dye solution with ZAH at room temperature (25 °C) for 60 min.

Dye concentrations in a binary system of components *A* and *B* at wavelengths of $\lambda_1$ and $\lambda_2$, respectively, to give optical densities of $d_1$ and $d_2$ were measured as follows [14]:

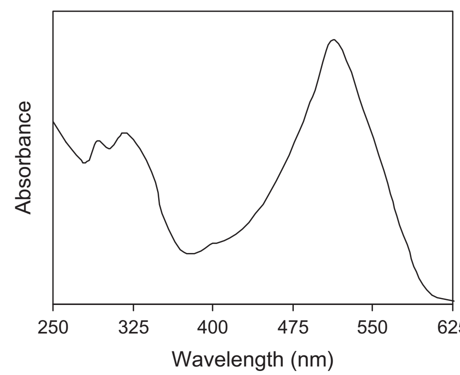
$$d_1 = k_{A1}C_A + k_{B1}C_B \quad (1)$$

$$d_2 = k_{A2}C_A + k_{B2}C_B \quad (2)$$

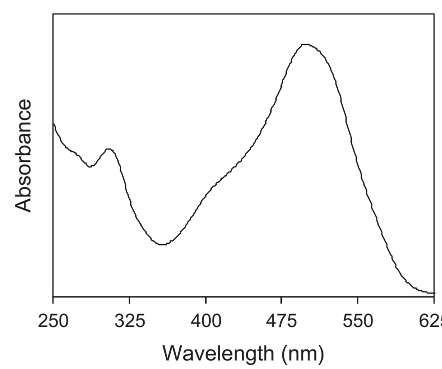
$$C_A = (k_{B2}d_1 - k_{B1}d_2)/(k_{A1}k_{B2} - k_{A2}k_{B1}) \quad (3)$$




AB92




AR14




DR23

**Fig. 2.** UV–VIS spectrum of dyes.

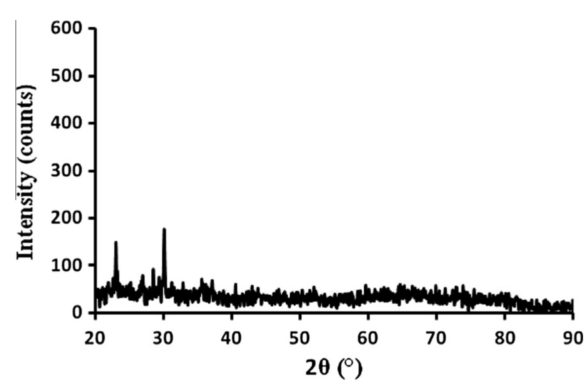



**Fig. 3.** X-ray diffraction pattern of ZAH.