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Photo-Catalytically Enhanced Removal of Extremely Toxic Acid Red Dye from Water

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Abstract

Acid dyes are toxic pollutants and known to be carcinogenic and harmful to organisms even at very low concentrations. Strict legislation governing the release of these harmful chemicals demands the development of a variety of effective techniques for removing organic contaminants from wastewater. The present study was undertaken to remove acid red dye using a hybrid material composite of Li/TiO_2 - waste powder of marble (WPM) industry which acts as both photocatalyst and adsorbent. The effect of various operational parameters including pH, dose, initial dye concentration, and time was optimized during the present study. The adsorbent material used was found very effective in dye removal.

Keywords: acid red dye, adsorption, photocatalysis, pH, dose

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1. Introduction

Composites of different raw waste have been prepared, which are used as adsorbent in wastewater treatment. For instance nanocomposites of graphene oxide were employed to remove methylene dye 100%, 92% of rhodamine, and 77% of methyl orange [1]. Similarly, the alginate nanocomposite of magnetite ferrite nanoparticles were effectively produced and then used to remove dyes (basic: blue 41, blue 9, red 18) [2]. Furthermore, fly ash has been employed as an adsorbent to remove various dyes [3-4]. Some of adsorbents like silicon polymers, bentonite, kaolin, graphene oxide, activated charcoal, and their modified nanocomposites are commonly used for textile dye removal due to high adsorption capacity, higher stability, and almost uniform structure. There are many advantages of using nanoscale adsorbents as they have unique chemical and physical properties, surface structure, unique size, and intraparticle interaction. Nanomaterials are efficient as adsorbents because of their low temperature modification, large surface area, short intraparticle diffusion distance, many sorption sites, surface chemistry, and variable pore size [5]. The present study was undertaken to remove acid red dye using a hybrid material composite Li/TiO_2 – waste powder of marble (WPM) industry which acts as both photocatalyst and the adsorbent. The effect of various operational parameters was optimized.

2. Materials and Methods

2.1. Preparation of materials

Analytical grade chemicals were used during the present study. The wavelength of maximum absorption for acid red was studied from 330 to 1000 nm. Waste powder of marble (WPM) industry is one of the most abundantly available wastes. This material was calcinized at 700 ˚C for 4h. Li impregnated TiO_2 was prepared by suspending 10g of TiO_2 (nanoform) in 20 ml of distilled water by constant stirring followed by dropwise addition of $LiNO_3$ (e.g., 0.1g for 1% doping). After stirring for 4h magnetically, the slurry was dried to complete dryness at 120 ˚C. The dried Li/TiO_2 powder was activated by heating at 600 °C for 2h [6-7]. The experiment of composite material containing photocatalyst were conducted under sunlight.

2.2. Optimization studies

To optimize various experimental parameters, effect of pH (5, 6, 7, 8, and 9), dose (0.5, 1, 2, 3, 4 g/L), initial metal concentration (5, 10, 15, 25, and 50 mg/L), temperature (30, 40, 50, 60, and 70 ˚C) and contact time interval (15, 30, 60, 120, and 240 minutes). Sample solutions were shaken at 200 rpm and filter through syringe filter (0.45μm). Absorbance of all samples was determined at λ_{max} of acid red dye.

2.3. Characterization studies

Fourier transform infrared (FTIR) spectroscopic analysis was obtained using Agilent technologies, FTIR spectrometer from 4000 to 650 cm^{-1} [7-8].

3. Results and discussions

3.1. Screening of composites

Acid dye removal was studied using Li/TiO_2 - WPM. Li/TiO_2 were prepared by doping of Li with TiO_2 was highly active photocatalysts and had strong dye adsorption ability (Fig. 1). In Li/TiO_2, the concentration of Li varied from 2 to 10 %.

After preparing these different concentrations, these all were mixed with calcinized form of white stone (WPM) to prepare hybrid composite materials. It can be concluded from results that 8% Li/TiO_2-WPM composite have shown for acid red dye removal. On increasing doping percentage further, aid red dye removal decreased. This might be due to decrease in photoactivity of Li/TiO_2-WPM composite. This shows that at higher Li percentages in composite materials decreased band gap and resulted in lower dye removal efficiencies.

3.3. Effect of pH

Popularity of TiO_2 as a photocatalyst for controlling and environmental pollution is increasing every day [9-10]. It is a semiconductor having a band gap of ~3.1 eV and unable to absorb in visible region (400–700 nm). Doping with metal ions in TiO_2 is required to make it functional [11-13]. The introduction of metal into crystal structure of TiO_2 is required to narrow band gap energy to make an effective photocatalyst in the visible region [10]. TiO_2 surface is amphoteric in nature and can develop both negative or positive charge [14]. This is the reason a pH variation can affect dye adsorption onto TiO_2 surfaces [15]. The studied range of pH varied from 5 to 9 to determine acid red dye removal efficiency. pH 7 was found to be the most effective pH for dye removal. Li/TiO_2-WPM composite removed dye using photodegradation and adsorption process. The removal of acid red dyes is retarded in acidic solutions (pH $\leq$ 5), by the presence of high concentrations of protons, resulting in reduced dye removal efficiency. On the other hand, in alkaline medium (pH $\geq$ 9), photodegradation and adsorption of dyes is reduced by the presence of hydroxyl ions (Fig. 2). Li/TiO_2-WPM composite dye removal at 7 is quite beneficial as it does not require drastic changes in pH for dye removal.

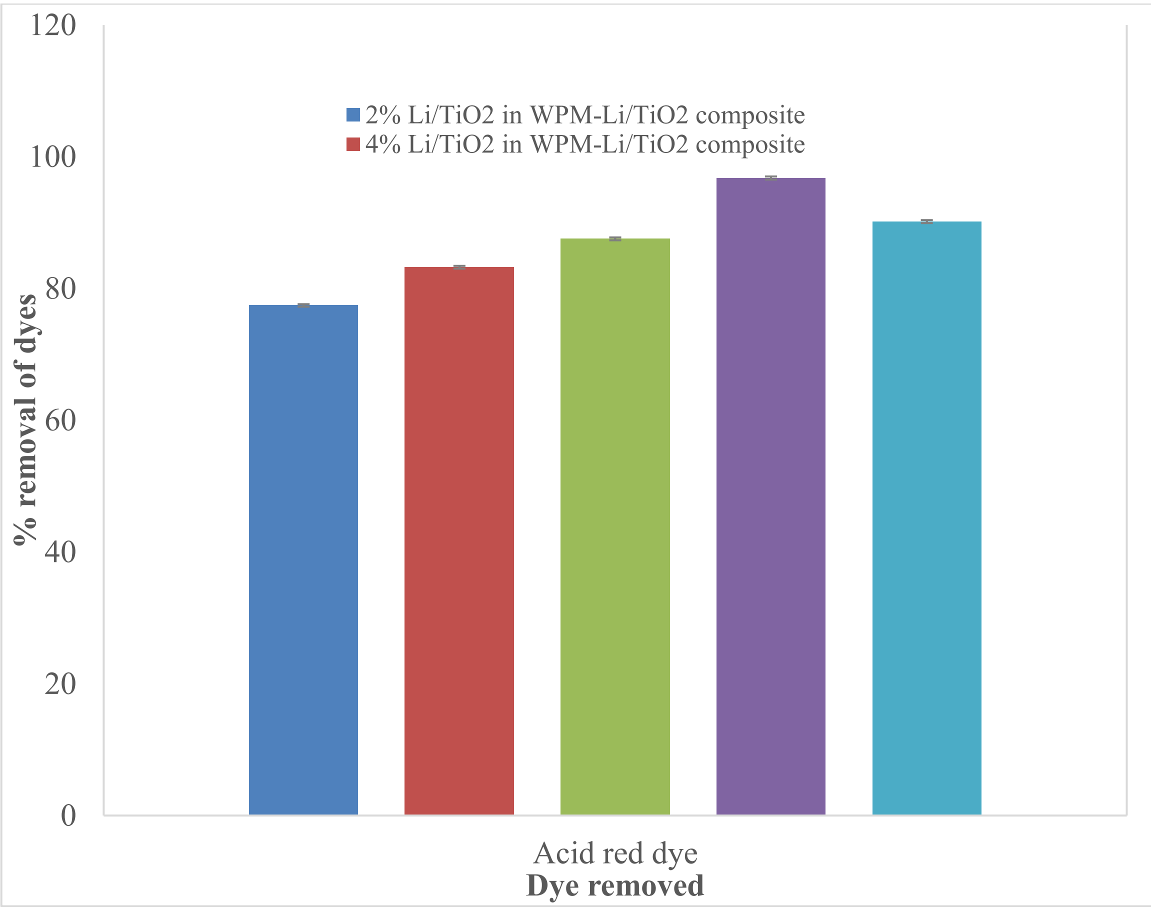


Fig. 1: The effect of doping percentage of photocatalyst for acid red dye removal

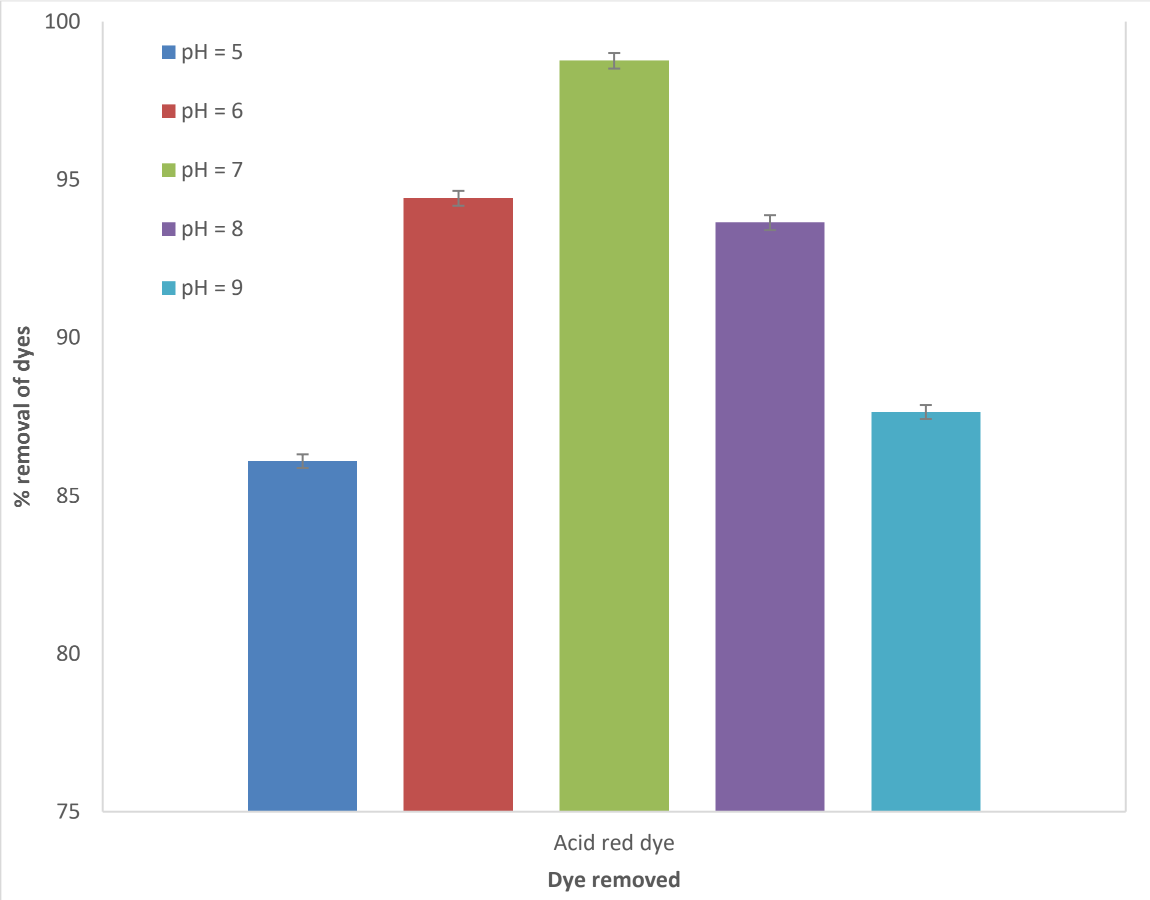


Fig. 2: The effect of pH for acid red dye removal using 8% Li/TiO_2

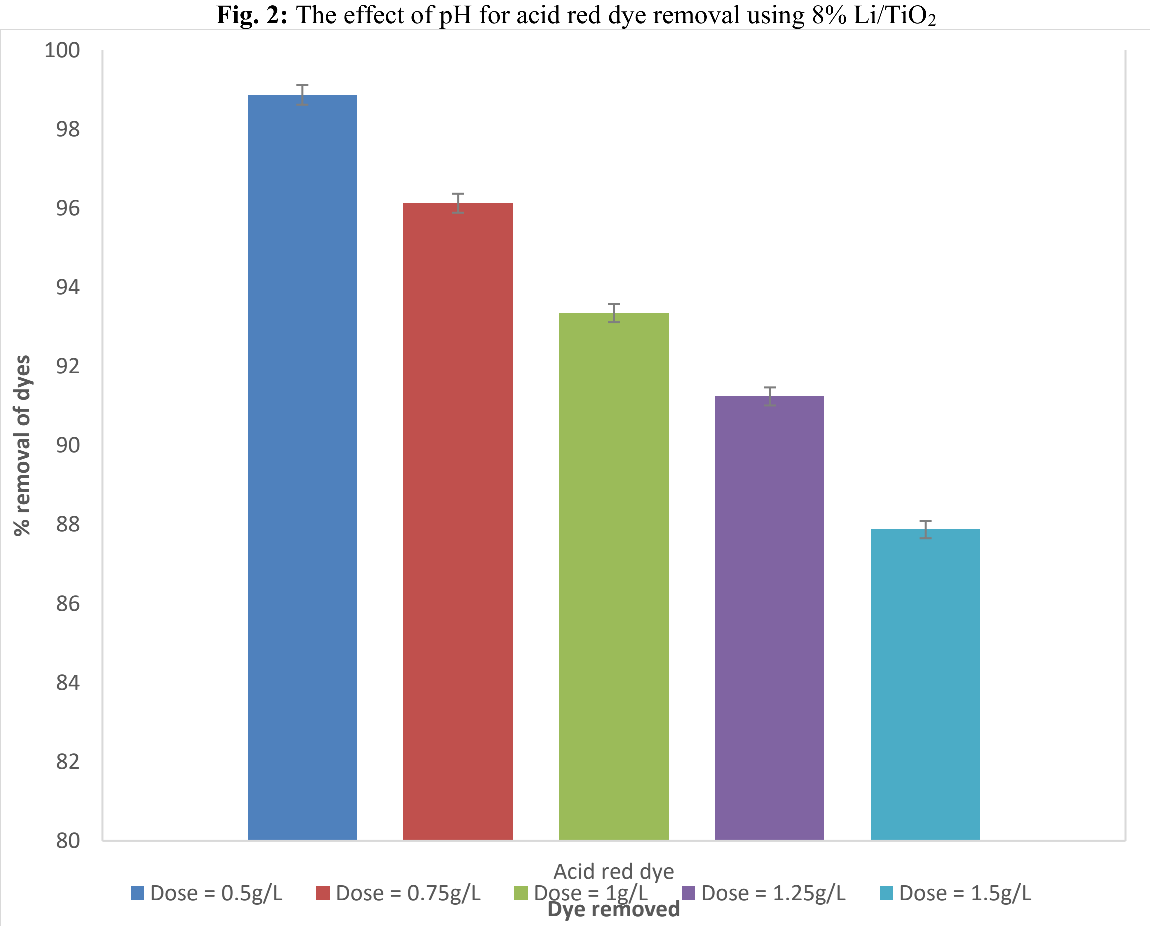


Fig. 3: The effect of dose for acid red dye removal using 8% Li/TiO_2

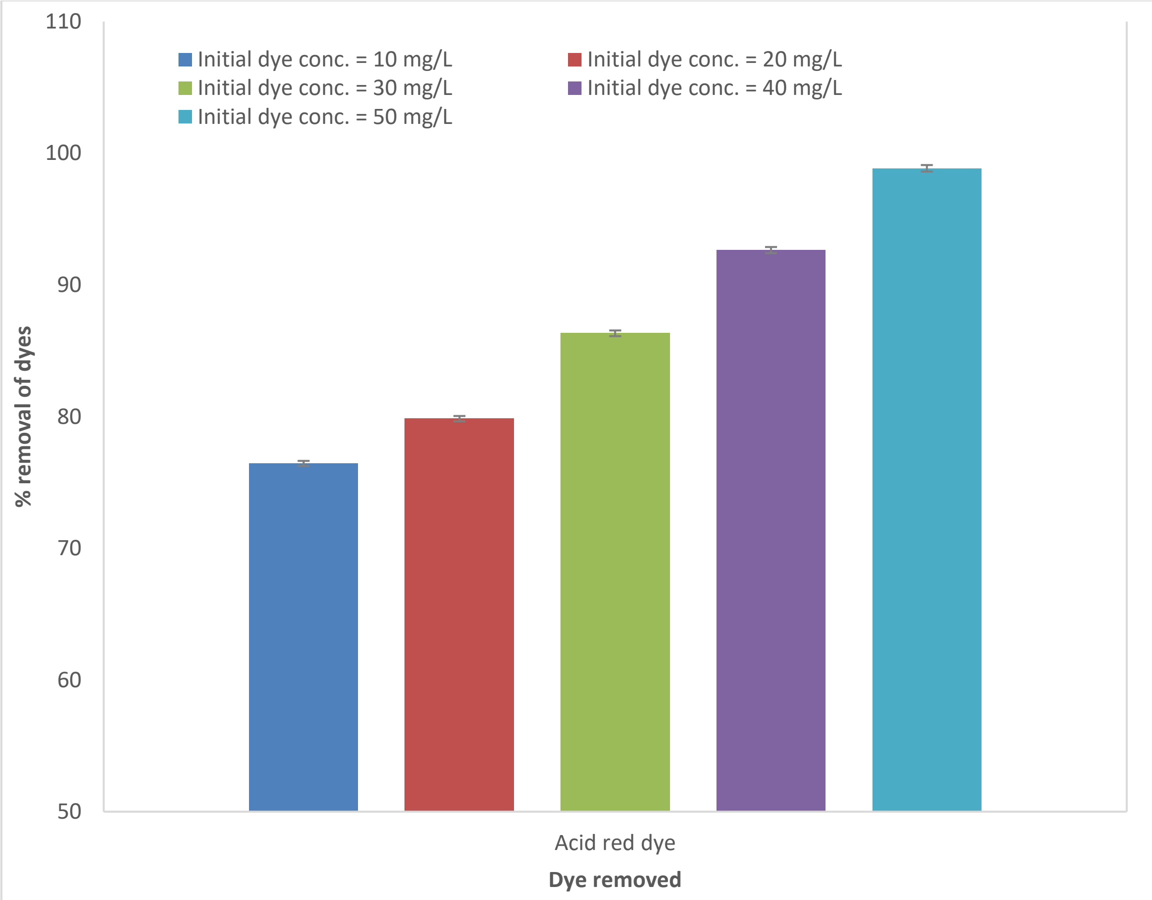


Fig. 4: The effect of initial dye concentration for acid red dye removal using 8% Li/TiO_2

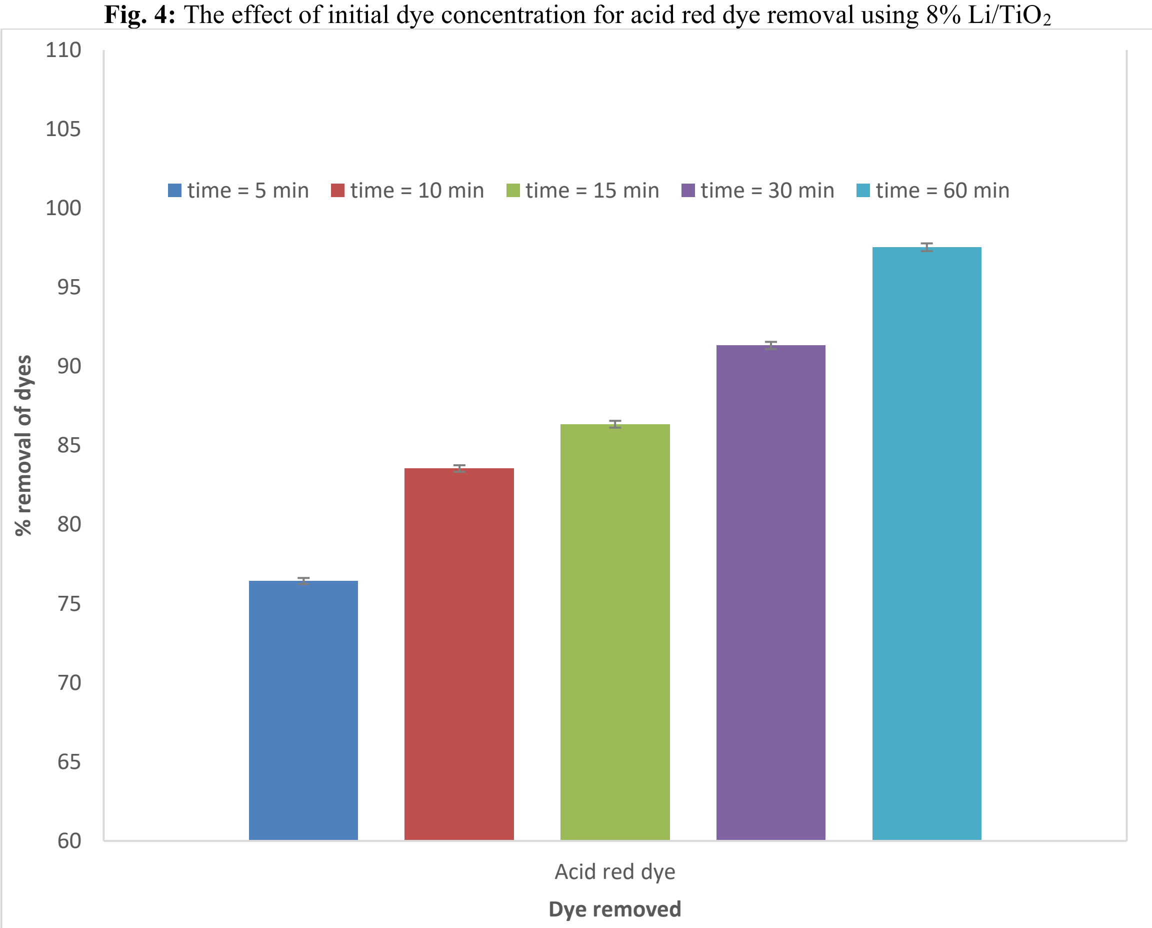
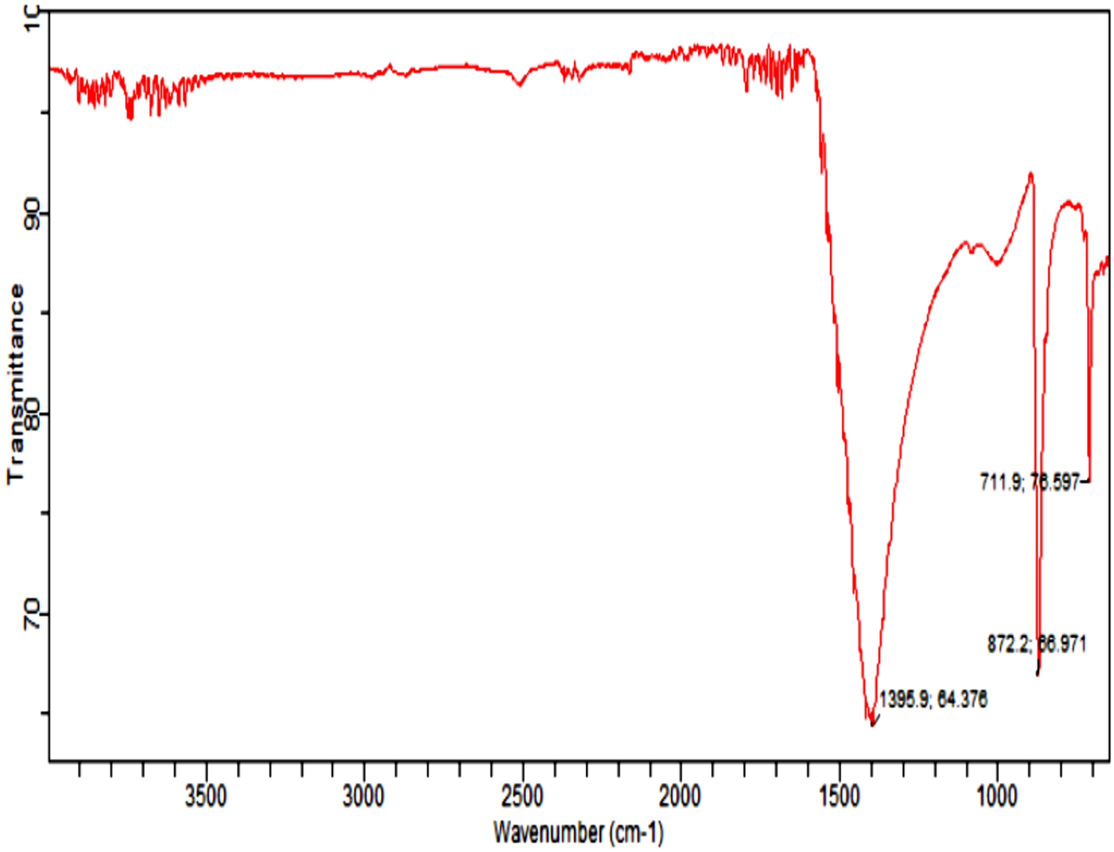


Fig. 5: The effect of time for acid red dye removal using 8% Li/TiO_2



b

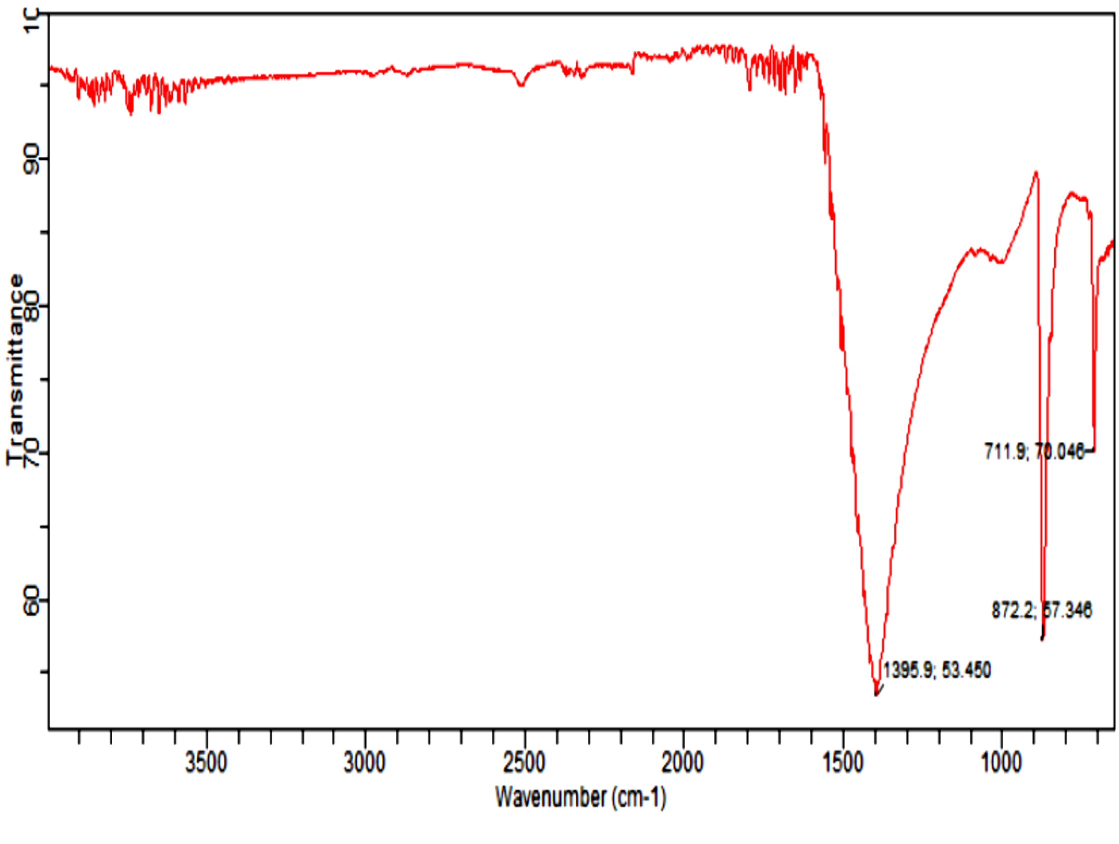


Fig. 6: FTIR spectra of Li/TiO_2 composite with WPM (a) pure form (b) loaded with acid red dye.

3.4. Effect of dose

The effect of dose was studied from 0.5 to 1.5 g/L at 50 ppm initial dye concentration for the removal of acid red dye (Fig. 3). Acid red dye uptake capacity was maximum at the dose of 0.5g/L. This means that this material can be utilized at very low concentrations to remove dye from large volumes of water. Acid red uptake capacity decreased further on increasing dosage [16].

3.5. Effect of initial dye concentration

The effect of initial dye concentration on dye removal using Li/TiO_2-WPM composite (Fig. 4) was studied at 10, 20, 30, 40 and 50 mg/L. The acid red removal efficiency of Li/TiO_2-WPM composite was found to be maximum at 50 mg/L. At higher concentrations of dye, the chances of interaction between dye and Li/TiO_2-WPM composite molecules increase which results in better uptake capacities as compared to lower concentrations. Thus, there will be more dye removal at elevated concentration till composite surface becomes saturated [17].

3.6. Effect of contact time

The effect of contact time for the removal of acid red dye using Li/TiO_2- WPM composite is presented in Fig. 5. These results clearly suggest that Li/TiO_2-WPM composite can effectively remove acid red dye in 60 min which is a very short time for toxic acid red dye removal. The short contact time is very important to remove dyes from huge quantities of dye contaminated waters discharged daily basis [17-18].

3.7. Characterization studies

FTIR spectra of white stone powder (a) pure form (b) loaded with acid red dye is shown in Fig. 6. Comparing pure form of WPM with acid red dyes shows intensity changes in three regions 1200-900 cm^{-1} (Si–O stretching vibrations), 1800-1500 cm^{-1} (carbonyl stretching vibrations) and 3900-3500 cm^{-1} (-OH stretching region)[19]. The presences of above described functional groups in the stones powders provides effective adsorption sites for dye contaminants [20].

4. Conclusions

In conclusion, the results of this comprehensive study show that novel 8% Li/TiO_2 -WPM composite was very effective in removal of acid red dyes in only 60 minutes of contact time. Future studies required for scaleup utilizations.

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