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Investigating Adsorption Behaviour of Cobalt Vanadate Nanocomposites on Methylene Blue Dye

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(α, β)-CoV_3O_8/V_4O_7 nanocomposites have been successfully synthesized through a facile hydrothermal method at low temperature. The structural properties of these nanocomposites are characterized via Powder X-ray diffraction, Fourier Transform Infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), and X-ray energy dispersive spectroscopy (EDX) analysis. Synthesized nanocomposites were determined to have an approximate crystalline size of 3.72 nm, and SEM imaging exhibited aggregated irregular rectangular shaped nanocomposites. Adsorption kinetics and isotherms were examined, and the outcomes showed that the adsorption followed pseudo-second-order kinetic model and Langmuir isotherm. Adsorption of methylene blue dye was investigated using (α, β)-CoV_3O_8/V_4O_7 nanocomposites at varying concentrations of the dye. 20 µM aqueous solution of methylene blue was found to have a high adsorption efficiency of almost 95% in 5 minutes.

Keywords: Methylene blue; FTIR; Adsorption kinetics; Nanocomposites

1 Introduction

Dye effluent from industrial processes is a major source of water contamination and a contributor to the world's pollution crisis[1]. Dyes have multiple benefits, including textile, printing, food, and cosmetics[2,3]. Despite their numerous benefits, dyes have highly deleterious effects on the environment and human health. Methylene blue (MB) is a common cationic dye toxic to humans and the environment at high concentrations[4]. Dye removal, degradation, and toxicity reduction often use a combination of physical, chemical, biological, and thermal processes[5]. Metal oxide nanoparticles are utilized as a catalyst to improve nanotechnology-based methods for removing and treating hazardous cationic dyes. Transition metal oxides have drawn attention for a variety of applications due to their unique physiochemical characteristics. (α, β)-CoV_3O_8/V_4O_7 nanocomposites are mostly used photocatalytic degradation of cationic dyes whereas in this work these nanoparticles show adsorption properties of MB dye. Synthesis of nanocomposites via hydrothermal method is simple, low-cost and environment friendly. It produces aligned and ordered nanostructures. Adsorption is employed for removal of dye and there are several factors affecting this such as adsorbent dose, temperature and pH effect. Using analytical methods such as PXRD, SEM, and UV-Visible spectroscopy, the adsorption effectiveness for MB dye of hydrothermally produced (α, β)-CoV_3O_8/V_4O_7 nanocomposites is utilized for treatment of wastewater.

2 Materials and Methods

$Co(NO_3)_2.6H_2O$(>99% purity, Emsure Merck), VCl_3(>97% purity, TCI), PEG(Merck), and MB (Thermo Fisher Scientific) were procured. For the purpose of conducting experiments, 1000 µM MB stock solution was prepared and further diluted to achieve the desired µM levels. The hydrothermal approach was used to synthesize (α, β)-CoV_3O_8/V_4O_7 nanocomposites from $Co(NO_3)_2.6H_2O$ (0.50 M) and VCl_3 (0.30 M). Both of the aforesaid compounds were dissolved in a small amount of water before being with 50 ml of polyethylene glycol (PEG) as a solvent. To homogenize the mixture, agitate it for 15 minutes using a magnetic stirrer. The solution is then transferred to a Teflon vessel, packed in an autoclave, and placed in oven for 15 hours at 150 °C. Autoclave was cooled to room temperature before filtering and washing it 3-4 times with water to remove any

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impurities. The sample was dried at 120 °C for 12 hours, yielding a greenish-black powder.

3 Results and Discussion

3.1 X-ray diffraction

The PXRD pattern has been shown in Fig. 1. The synthesised nanocomposites exhibits orthorhombic phase, α-CoV_3O_8 with space group Ibam (72) and monoclinic phase, β-CoV_3O_8 with space group C2/m (12) are in agreement to JCPDS file No. 22-0598 and 22-0599 respectively[6]. The X-ray pattern has characteristic planes (001), (211), (222), (303), (040), (701), and (134)[7]. The high intensity peaks at (211), (222), and (303) corresponds to formation of α-CoV_3O_8[6]. The phase of V_4O_7 was found to be in primitive lattice with space group $P\bar{1}$(2) which corresponds to JCPDS file No.65-6448. This analysis confirms that (α, β)-CoV_3O_8/V_4O_7 nanocomposites were successfully formed via the hydrothermal method. Debye-Scherrer equation was utilized to determine the average crystalline size of nanocomposites from PXRD, which was 3.72 nm.

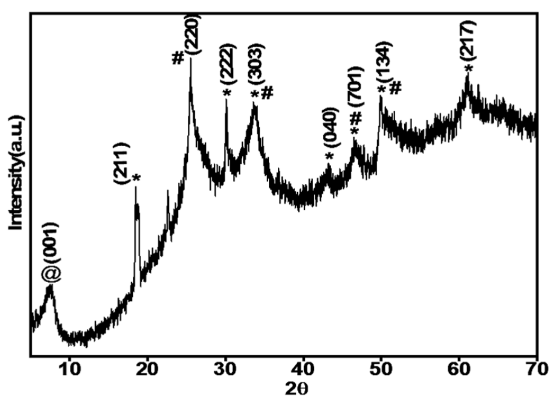

Fig. 1 — PXRD pattern of (α, β)-CoV_3O_8/V_4O_7nanocomposites, where (*) shows α-CoV_3O_8 phase, (#) describes β- CoV_3O_8 phase and (@) shows V_4O_7 phase.

3.2 SEM Analysis

The morphological studies of different sizes of sample particles have been characterized by SEM. Fig. 2(A), describes aggregated irregular rectangular shaped nanocomposites. Additionally, elemental composition and uniformity of Co, V and O in nanocomposites has been validated.

3.3 FTIR Studies

The FTIR analysis was obtained to analyse different stretching frequencies in (α, β)-CoV_3O_8/V_4O_7 nanocomposites which represents strong peaks at 1102 cm^{-1}, 990 cm^{-1} and 508 cm^{-1} in Fig. 3. Strong peak at 757 cm^{-1} represented stretching frequency of V-O and peak at 983 cm^{-1} describes stretching frequency of V=O bond[8]. The stretching frequency of Co-O is around 508 cm^{-1}. The stretching frequency at higher range around 500-700 cm^{-1} belongs to tetrahedral site of metal whereas range around 400 cm^{-1} depicts octahedral site of metal[9,10].

3.4 UV-Visible Spectroscopy

The nanocomposites completely adsorbed the dye, changing the solution from blue to transparent. 0.05 g of nanocomposites in 50 ml of aqueous dye solutions were evaluated with varied dye concentrations. Fig. 4, shows efficient adsorption of MB dye by (α, β)-CoV_3O_8/V_4O_7 nanocomposites, which resulted in nearly 95% adsorption within 5 minutes. This high rate of adsorption may be credited to the large surface area of aggregated irregular rectangular shaped nanocomposites, as confirmed through XRD and SEM results. The removal or adsorption efficiency (η) has been calculated using the Eq. 1:

$$\eta=[(C_o-C_t)/C_o]\times100=[(A_o-A_t)/A_o]\times100 \quad ... (1)$$

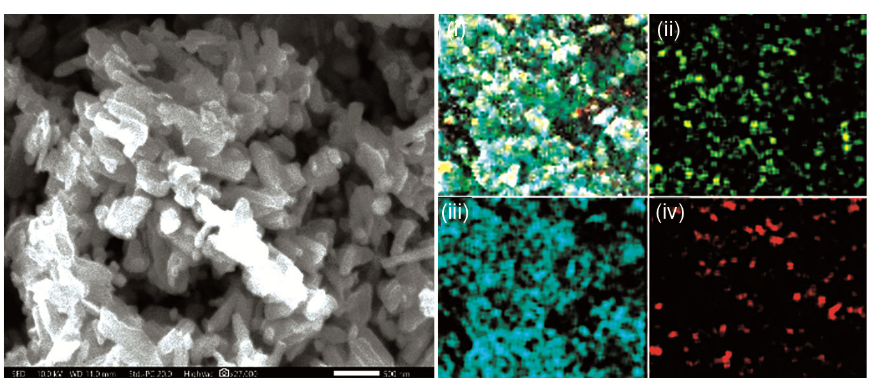

Fig. 2 — SEM image of (α, β)-CoV_3O_8/V_4O_7nanocomposites andelemental mapping of synthesized nanocomposites illustrates (i) (α, β)-CoV_3O_8/V_4O_7 nanocomposites, (ii) Co as green colour, (iii) V as blue colour, (iv) O as red colour.

Here, C_o and C_t are concentrations at t=0 and at time t, respectively. A_o and A_t correspond to initial absorbance and absorbance after time t[11].

3.5 Adsorption Kinetics

In order to determine the governing mechanism of adsorption processes, pseudo-first-order and pseudo-second-order kinetic models were used Fig. 5, illustrates that pseudo-first-order kinetic didn't fit well. In fact, the pseudo-second-order equation produced an excellent match to the experimental data, with regression coefficient of R^2 values over 0.99%.

3.6 Adsorption Isotherms

In this investigation, the Freundlich and Langmuir adsorption isotherms were implemented. The Freundlich isotherm is used for a heterogeneous surface energy system. The Langmuir isotherm follows up homogeneous surface energy system[12]. Fig. 6, depicts

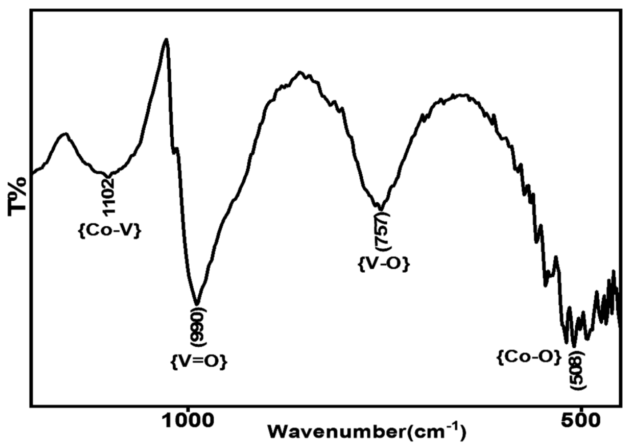

Fig. 3 — FTIR data of produced (α, β)-CoV_3O_8/V_4O_7nanocomposites.

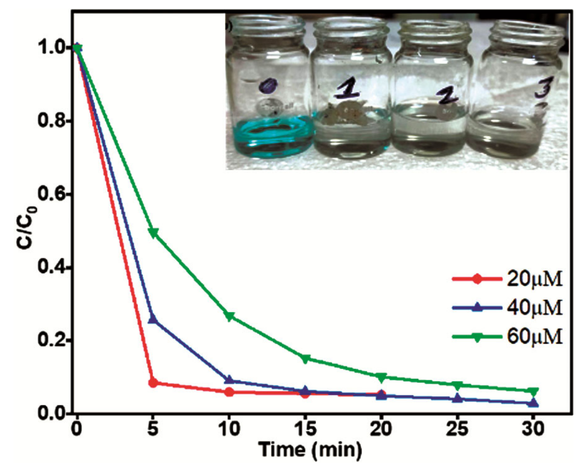

Fig. 4 — Adsorption of MB dye under various concentrations (red for 20µM, blue for 40µM, green for 60µM), inset image depicts complete decolorization of MB dye at different time intervals.

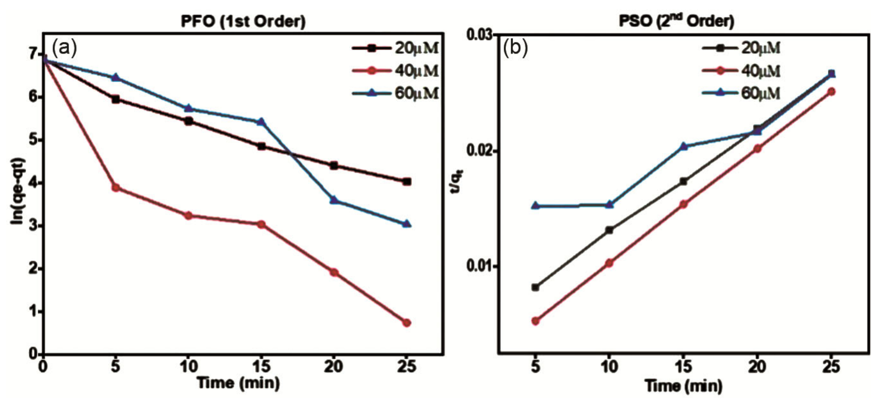

Fig. 5 — Plots of $\ln(q_e-q_t)$ v/s t and t/q_t v/s t depicts the pseudo-first order kinetics and pseudo-second order kinetics respectively.

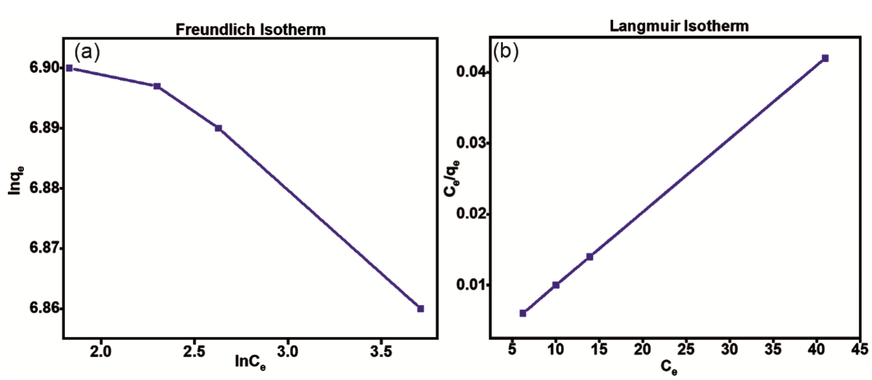

Fig. 6 — Plots of $\ln q_e$ v/s $\ln C_e$ and C_e/q_e v/s C_e describes Freundlich isotherm and Langmuir isotherm respectively.

that Langmuir isotherm fits better with R^2 value of 0.99% from experimental analysis.

4 Conclusion

This study is intended to demonstrate the Synthesis of (α, β)-CoV_3O_8/V_4O_7 nanocomposites. The aggregated irregular rectangular-shaped nanocomposites have found to be of average crystalline size 3.72 nm. Furthermore, UV-Visible based adsorption studies have proven the use of synthesized nanocomposites for the removal of MB dye from its equeous solution. At 20μM MB concentration, the adsorption efficacy of 95 % is obtained within 5 miniutes. The mechanism for adsorption includes electrostatic attraction, π-π interactions, as well as H-bonding interactions. The experimental data governs that it best fits pseudo-second-order kinetic model and Langmuir isotherm.

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