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Nickel Cobaltite Nanomaterial as an Adsorbent for Removal of Methylene Blue from Wastewater

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Abstract

In recent years, perovskites have become effective adsorbents for removing contaminants from wastewater. They have attracted widespread attention as excellent adsorbents because of their unique physical and chemical properties. By solution combustion method, nickel cobaltite perovskite powder was synthesized and characterized by X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM). An in-depth study of the effects of different adsorption parameters, such as dye concentration, solution pH, amount of photocatalyst, and exposure time, on the amount of methylene blue dye removal, was described in this paper. Also, it reports an overview of the research related to methylene blue removal and its limitations.

Keywords: *Adsorbent, Methylene blue, Nickel cobaltite, Nanophoto catalyst, Perovskite*

1.0 Introduction

The much needed water is getting polluted due to various developmental activities, resulting in potable water scarcity. Industrial wastewater containing hazardous and toxic organic molecules poses a significant threat to the life of living organisms and the environment. Dyes constitute the largest group of compounds responsible for water pollution worldwide. These dyes are inevitably released as wastewater from textile, leather, pulp, printing, paper, cosmetic, food, and pharmaceutical industries. Among them, the textile industry accounts for two-thirds of the total dyestuff market. Textile industries lose approximately 10-15% of the dye in the effluent during the dyeing process[1,2,3]. The presence of dyes in the receiving water bodies is not only aesthetically unbearable but also harmful due to their carcinogenic and mutagenic properties[4,5,6,7,8]. The presence of dyes increases, which increases the chemical oxygen demand (COD), biological oxygen demand (BOD), and other toxic chemical compounds in aquatic ecosystems, also leading to a reduction in sunlight penetration. This decreases photosynthetic activity and has acute toxic effects on aquatic living organisms and the environment[9,10,11]. Furthermore, they add a dark colour to water and make it toxic.

One of the very water-soluble dark green powders that produce a blue solution in water is methylene blue (MB). It is a formal derivative of phenothiazine with the molecular formula ($C_{16}H_{18}N_3SCl$). It is generally, utilized for medical purposes, tanning, printing, leather, and cotton dyeing[12]. Although this dye is not particularly hazardous to humans, eye and skin irritation may result from it[13,14]. The side effects of MB include headache, high blood pressure, nausea, vomiting, diarrhoea, mental confusion, abdominal pain, gastritis, excessive perspiration, and breathing difficulties[14]. As a result, the removal of such dyes from wastewater effluents is essential. In order to cope up with the problems caused by the MB and other dyes in the environment, several conventionally practicing biological, physical and chemical

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techniques have been used to purify the water. However, each technique has its limitations. Out of these techniques, some are time-consuming, expensive, and produce high sludge. Therefore, an eco-friendly and economically viable technique to be developed to remove dyes from the contaminated water. In recent years adsorption has gathered much attention and proven to be a more effective and efficient technique because of its simplicity, economic viability, ease of operation, and availability of a wide range of adsorbents.

Solid activated carbon powder has a high surface area and high adsorption coefficient making it the most popular adsorption material. The problem with it is that it is expensive, produces a significant amount of solid residues, and isn't easy to desorb dye molecules from it, so reusing it is not an option. So researchers have been focused on the development of cheap and effective adsorbents. In this regard, several metal oxides, natural and agricultural by-products, have been utilized as adsorbents to remove MB from contaminated water. Metal oxides and perovskites, especially those in nano and micro size, have a high surface area and structures that lead to surface cavities. Metal oxides and perovskites have shown high adsorption capacity to remove dye molecules from effluents. These materials adsorbed with dyes can be removed from the effluent through filtration and recovered easily after subjecting them to dye removal methods such as heat treatment or hot air blowing and they can be reused.

In the present work, functionalized nickel cobaltite perovskite nanomaterial has been tested for the purification of water contaminated by highly loaded MB dye. The effect of different operational parameters on the removal of dye was studied, and it has been observed that the proposed material efficiently and effectively purifies the water and makes it suitable for reusability in the same process. The proposed adsorbent is easy to synthesize, does not require a complex experimental set up, and is a viable adsorbent for removing MB dye. The adsorption experiment was studied as a function of pH, adsorbent dose, contact time, and concentration for maximum adsorption.

2.0 Material and Methods

2.1 Materials and Chemicals

The nickel cobaltite ($NiCo_2O_4$) perovskite nanoparticles were prepared with analytical grade chemicals such as cobalt nitrate ($Co(NO_3)_2.6H_2O$) (99% A.R.), ammonia (NH_3) (30% A.R.), were obtained from S D Fine-chem Limited, Mumbai, India. Nickel nitrate ($Ni(NO_3)_2.6H_2O$) (98% A.R.), was obtained from Loba Chemie Pvt. Ltd. Mumbai, India, and citric acid ($C_6H_8O_7$) (98% A.R.) was obtained from Avra Synthesis Pvt. Ltd. Hyderabad, India. Furthermore, these are used as received without any further purification. Commercially available MB dye was obtained from Panamá Biochemicals, Bangalore. Furthermore, it was used as received without any further purification. Double distilled water was utilized for all the experimental work. By adding dilute 0.1 M HCl (35.4%) or 0.1 M NaOH solutions to the experimental solutions, the pH of the experimental solutions was adjusted using a pH meter. The concentration of the dye in the solutions was measured at an optimized wavelength (665 nm) using a UV-Vis spectrophotometer.

2.2 Preparation of adsorbate

In this investigation, MB is used as a model dye adsorbate. MB has the chemical formula $C_{16}H_{18}N_3SCl{\cdot}3H_2O$, and its molecular weight is 319.85g. It was utilized without being purified. 1g of MB dye was dissolved in 1L double distilled water to make the stock solution. To attain the necessary concentration, the experimental solutions were made by diluting the stock solution with double distilled water. By adding dilute 0.1 M HCl or 0.1 M NaOH solutions to the experimental solutions, the pH of the experimental solutions was adjusted.

2.3 Synthesis of Nickel Cobaltite Perovskite Nanoparticles

In order to prepare nickel cobaltite nanoparticles, nickel nitrate, cobalt nitrate, and citric acid (as fuel) were used in the solution combustion method. In a silica crucible, nickel nitrate, cobalt nitrate, and citric acid were first dissolved in a 2:2:3 molar ratio using the smallest amount of water. The crucible was introduced to the preheated muffle furnace (at 100^{o}C), then increase the muffle furnace temperature from 100^{o}C to 300^{o}C. The solution boils and dehydrates, then decomposes with the emission of a certain amount of gases; it swells and forms a foam, which erupts with a flame. After combustion, a voluminous and foamy nickel cobaltite was obtained. After the complete combustion, the crucible was taken out and allowed to cool.

2.4 Adsorption Experiments

Adsorption experiments were performed to optimize several adsorption parameters like pH, adsorbent (nickel cobaltite) concentration, contact time, and adsorbate (MB dye) concentration. An initially known amount of nickel cobaltite was added to a fixed volume of MB dye solution to optimize adsorption parameters. The solutions were kept under direct sunlight for 30 min, and nickel cobaltite-MB was separated from the solution through centrifugation at around 8000 rpm for 5 min. The concentration of the supernatant solution was then measured using a UV-Vis spectrophotometer. In order to determine the maximum uptake of the dye by nickel cobaltite, an entire set of experiments were performed at varying pH (3-11), adsorbent dose (25-150mg), time interval (10-40 min), and dye concentration (20-150 mg L^{-1}) at room temperature (23-28°C). The percentage removal of MB by nickel cobaltite in the adsorption experiment was calculated using Eqs.1

$$(\%R) = \frac{(Ai–At)\ 100}{Ai} \quad \text{... (1)}$$

Where A_i is the absorbance of the initial MB solution; A_t is the absorbance of the solution after illumination at the time 't' for MB solution.

2.5 Characterization

X-ray diffraction (XRD) pattern of nickel cobaltite was obtained for phase analysis by X-ray diffractometer using Cu-Ká radiation. The average crystallite size of pure nickel cobaltite was calculated using Debye Scherer's

$$D = K\lambda / (\beta \text{ cas } \theta) \quad \text{... (2)}$$

Where K is the shape factor (0.9), λ is the wavelength of emitted X-rays (0.15418 nm), λ is full width at half maximum of the corresponding XRD peak, which was estimated by using XRD standard reference material (silicon powder), θ is the angle of incidence of an X-ray beam, D is the size of particles. The shape and size of nickel cobaltite were characterized by Scanning electron microscopy (SEM).

3.0 Results and Discussion

3.1 Powder X-ray Diffraction (PXRD)

The powder x-ray diffraction(PXRD) analyzer revealed phase components and crystalline structural information of the adsorbent sample.

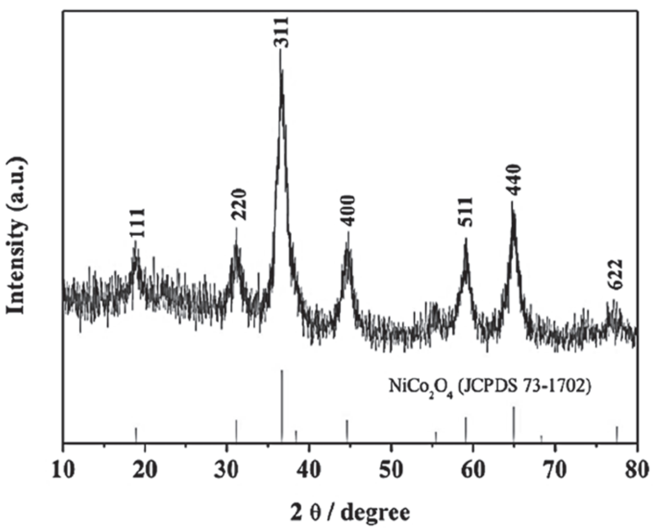

Figure 1: XRD pattern of nickel cobaltite sample

The PXRD pattern of the nickel cobaltite was presented in Figure 1, and all the diffraction peaks located at 2θ of 18.9°, 31.1°, 36.7°, 38.4°, 44.6°, 55.4°, 59.0°, and 64.9° could be indexed to (111), (220), (311), (222), (400), (422), (511) and (440) planes. These obtained PXRD diffractograms are ideally suited to the standard pattern for nickel cobaltite (JCPDS card No. 73-1702) with cubic spinel structure, and no residues or other phases were detected. The results indicate that high-purity nickel cobaltite perovskite nanoparticles were successfully synthesized.

3.2 Scanning Electron Microscopy (SEM) analysis

In the present study morphology of a powdered sample of nickel cobaltite was characterized by the SEM technique. The SEM images of prepared nickel cobaltite nanoparticles (Figure 2) exhibited an irregular, dense crystals-like appearance with many nano flakes-like surfaces forming the porous nanostructure. The results indicate that high-

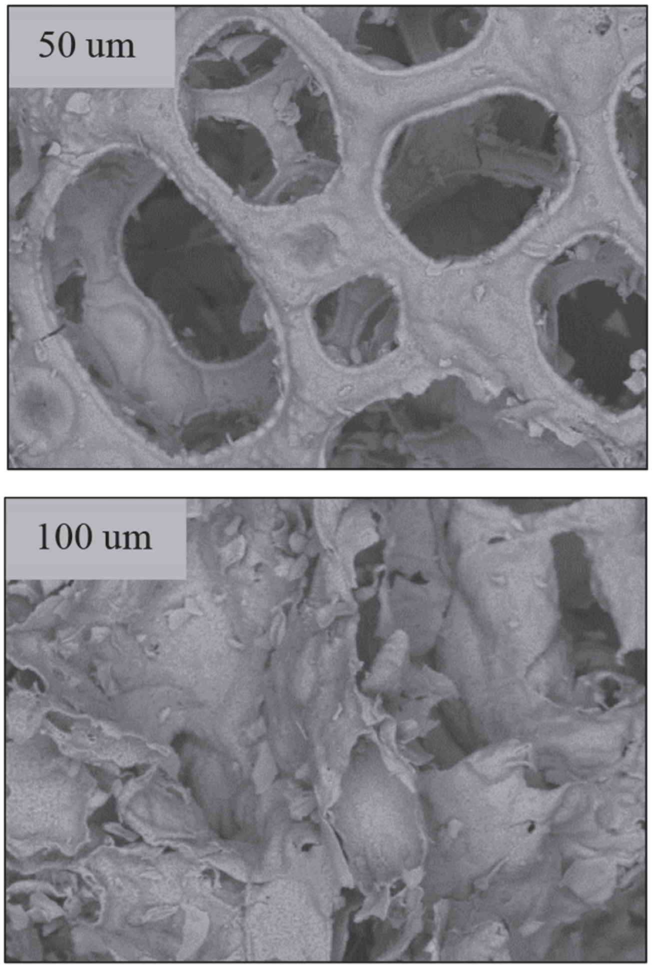

Figure 2: SEM images of nickel cobaltite with different magnifications

performance nickel cobaltite perovskite nanoparticles with large surface area and highly porous structure were successfully synthesized.

3.3 Optimization of Adsorption Parameters

Optimization of adsorption parameters of MB dye using $NiCo_2O_4$ as an adsorbent, we studied the effect of several factors on the adsorption process, including adsorbent concentration, contact time, adsorbate concentration, and solution pH.

3.3.1 Optimization of contact time

Contact time was optimized by adjusting it from 0 to 40 min at an optimal adsorbent dose for the same volume and dye concentration as shown in Figure 3. It was observed that the per cent removal of MB by nickel cobaltite increased with the increasing contact time. The reason for this is that additional time permits the adsorbent to interact with the dye for a longer amount of time. At 30 min, the highest dye elimination was observed, after which it became constant. To achieve maximum absorption, nickel cobaltite, and dye should be in contact for 30 min.

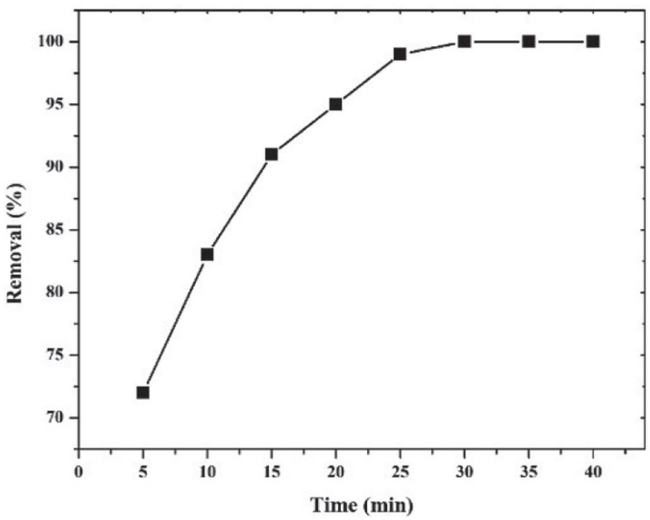

Figure 3: Effect of contact time on per cent removal of MB

3.3.2 Optimization of pH

In order to optimize the pH of the dye solution, the pH of a 50mL MB dye solution was varied from 3 to 11, and the per cent removal of MB by nickel cobaltite was investigated. 50mg nickel cobaltite was added to each solution. The removal effectiveness of MB by nickel cobaltite is nearly 100 per cent across the whole pH range (3-11), as shown in Figure 4. Based on the adsorption data, it can be inferred that the suggested nanomaterial effectively removes MB dye throughout a wide pH range. It has also been discovered that when nickel cobaltite was added to the test solution, the pH of the solution immediately adjusts to the 7 ± 0.5 pH range.

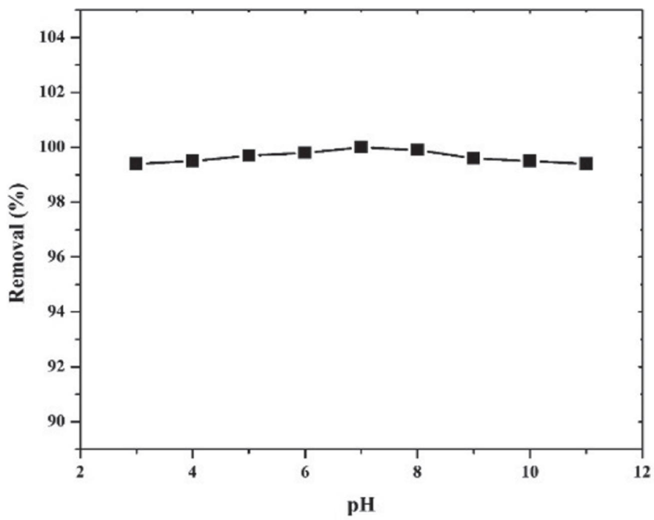

Figure 4: Effect of pH on per cent removal of MB

3.3.3 Optimization of adsorbent concentration

In order to optimize the nickel cobaltite concentration, the nickel cobaltite concentration was varied from 5 mg to 25 mg per 50 mL of MB dye. The results are shown in Figure 5, which reveals that the per cent removal of MB increases with the increasing nickel cobaltite concentration. The reason is that nickel cobaltite has a higher adsorption capacity because the number of sites available on a nickel cobaltite surface increases as the adsorbent concentration increases. At 10 mg, the maximum percentage removal of MB has been observed. As the adsorbent concentration increased, the turbidity of the solution was observed.

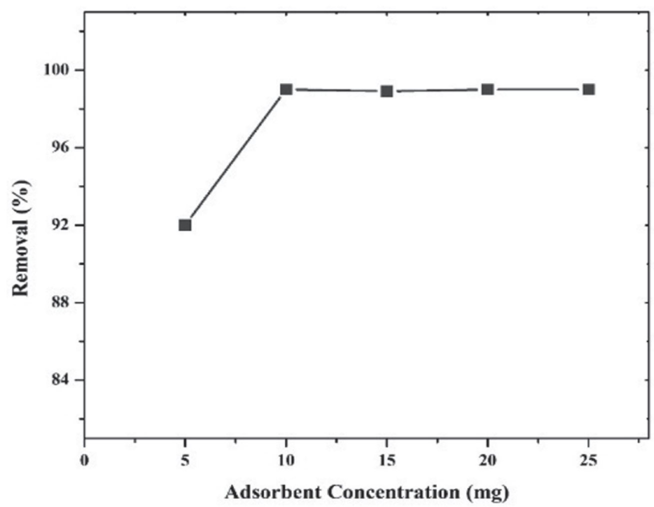

Figure 5: Effect of adsorbent concentration on per cent removal of MB

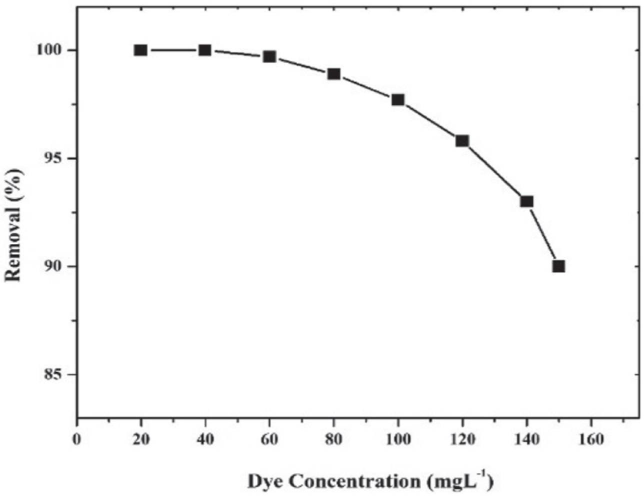

Figure 6: Effect of dye concentration on per cent removal of MB

3.3.4 Optimization of adsorbate concentration

To achieve the maximum adsorption capacity of nickel cobaltite, the MB dye concentration was optimized. To optimize the concentration of MB dye solution, we assessed its per cent removal at different initial concentrations (20-150 mg L^{-1}) at a suitable adsorbent dose and time. The results are displayed in Figure 6, which shows that as the dye concentration increases, the per cent removal of MB dye decreases. This decrease is due to the saturation of active sites of nickel cobaltite after the adsorption of a certain concentration of MB.

4.0 Conclusion

We have successfully prepared nickel cobaltite nanoparticles with the perovskite-type structure using an eco-friendly approach. Various spectral and microscopic techniques were used to examine the structure and morphology of the nanoparticle. The experiment of decolorizing MB confirmed that the proposed material was easily synthesized and has shown excellent adsorption properties for MB dye from contaminated water at room temperature. The experiment was directed by varying adsorption parameters like pH, adsorbent dose, contact time, and dye concentration. It can be concluded that the nickel cobaltite nanoparticle is an effective catalyst for removing organic contaminants from industrial wastewater.

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