Article

Novel Starch-Modified NiCrMn-LDH-Based Composite for Photocatalytic Degradation of Reactive Orange 13

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Abstract: Water pollution has become a great challenge today. To address this problem regarding wastewater treatment by removing toxic synthetic dyes from wastewater, this research focused on the synthesis of a novel starch-modified NiCrMn-layered double hydroxide composite through the coprecipitation method and applied it as a photocatalyst for the degradation of reactive orange 13 dye. The synthesized photocatalyst was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), point of zero charges (PZC), dynamic light scattering (DLS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and Zeta potential techniques. These techniques revealed different characteristics of photocatalysts, like surface and structural properties. According to BET analysis, the final composite had $2.5 \times 10^2$ m$^2$/g BET-specific surface area with a 45.56 nm pore radius value, and the overall composite found as mesoporous. Similarly, in DLS analysis, bare NiCrMn-LDH had 404 nm hydrodynamic size, which increased for the final starch composite up to 667 nm. Zeta potential value changed from $-14.56$ mV to 0.95 mV after the incorporation of starch with NiCrMn-LDH. They confirmed the incorporation of starch with trimetallic NiCrMn-layered double hydroxide (2:1:2). Starch association improved the properties of the photocatalyst like surface area. Different parameters like pH value, initial dye concentration, photocatalyst dose, hydrogen peroxide concentration, effect of sacrificial reagent, and effect of inorganic anions were studied for degradation of RO13. Overall, the photocatalysis process for RO13 followed pseudo-first-order kinetics. Photocatalytic degradation reactions for reactive orange 13 were conducted with an initial dye concentration of 10 mg/L, photocatalyst dosage of 20 mg/50 mL, and pH value at 3 in the presence of sunlight, resulting in an impressive degradation removal rate of 86.68%. This remarkable degradation ability of the photocatalyst for reactive orange 13 proves this composite was highly efficient.

Keywords: orange 13 dye; photocatalysis; LDH; starch; hydrogen peroxide; degradation kinetics
1. Introduction

Water is the utmost vital substance on Earth’s surface. The physical and chemical characteristics of water pose significant considerations regarding water security, water provisioning, and water purification techniques [1]. One of the most pressing environmental issues resulting from industrial development is water contamination, which poses significant risks to both human health and ecosystems [2–4]. Water treatment has captivated considerable attention over the past few decades because of pollutants that induce detrimental impacts on aquatic environments. Nevertheless, given the swift pace of industrialization and population expansion, the water quality of conventionally processed discharges is steadily deteriorating [5]. The expansion of industries has led to the extensive degradation of various aquatic ecosystems worldwide [6]. Among a broad array of water contaminants, dyes have garnered considerable interest owing to their negative impacts on human well-being and the environment [7–10].

Industries across the globe utilize over 10,000 distinct colorants, and the yearly production of various dyes and pigments exceeds 700,000 tons. Around 10–15% of these colorants are released into water sources during manufacturing or other uses [2,11–13]. Dyes exhibit excellent light stability and are not biodegradable; they possess resistance to anaerobic digestion and stand out as one of the most formidable components to eliminate from industrial wastewater [14]. Azo dyes are artificial colorants characterized by intricate structures comprising substituted aromatic rings connected by at least one azo group (–N=N–) [15,16]. These dyes find wide applications in various industries such as textile, leather, cosmetics, paper, and food, contributing to approximately 50–60% of the total global dye production [17,18]. The textile sector stands as the largest consumer of azo dyes; regrettably, approximately 10–15% of these dyes are discharged through effluents [19,20]. The untreated release of dyes poses significant environmental and health issues due to their toxicity, alteration of water pH, the elevation of biological and chemical oxygen demand, and the induction of intense coloration, thereby potentially hindering photosynthesis [21–23].

Therefore, the application of this treatment is crucial to safeguard human health, plant health, and the environment [24]. Hence, through numerous degrees of achievement, diverse approaches for eliminating dyes have been explored and implemented, encompassing physical, chemical, and biological methodologies [25,26]. These approaches encompass diverse criteria and procedures like precipitation–coagulation, aerobic and anaerobic processes, adsorption, ion exchange, membrane filtration, adsorption membrane filtration, coagulation, adsorption, and reverse osmosis [27–33]. Photocatalysis stands as one of the most auspicious methodologies extensively utilized in wastewater treatment, representing an oxidation mechanism that surpasses others in terms of advancement [34]. Photocatalysis is distinguished by its considerable oxidizing capability, which enables the decomposition of detrimental dyes [35,36].

Reactive Orange 13, an azo dye, incorporates cyanuric chloride as its reactive moiety. Studies indicate that dyes featuring reactive cyanuric chloride components exhibit greater resilience against anaerobic degradation when compared to those containing the vinyl sulfone group [37].

Presently, the primary goal is to amalgamate environmentally conscious, renewable materials derived from living organisms [38]. Different natural biopolymers can be used for the synthesis of important nanocomposites for wastewater treatment. Among the various biopolymers in nature, starch stands out as the second most abundant. It enjoys widespread usage due to its plentiful availability, lack of toxicity, customizable surface area, pore size, cost-effectiveness, biocompatibility, and structural versatility [39–43].

Currently, the prevailing filler employed to surmount the obstacles of biopolymers when creating composites is double-layered hydroxide (LDH) [39,44]. Double-layered hydroxides represent a category of anionic clays, often referred to as hydrotalcite clays. These clays possess positively charged outer layers with anions present in the interlayers [45–48]. LDHs can be represented by the overall chemical equation: \[ \text{M}_{1-x}^{2+} \cdot \text{M}_x^{3+} \]
(OH)\(_2\)]\(^{x+} \cdot [A_{x/n}^\text{n−} \cdot \text{mH}_2\text{O}\). In this formula, M\(^{2+}\) and M\(^{3+}\) stand for bivalent and trivalent metal cations, correspondingly. The variable x indicates the molar ratio of trivalent cations (0.2 < x < 0.33), m shows the number of water molecules between the layers, whereas A\(^{-}\) denotes the interlayer anion with a specific charge \([39,49–53]\). These materials including layered double hydroxide (LDHs) and their calcined forms (oxides) can be fabricated efficiently and economically to reveal tailored characteristics suitable for specific applications \([54,55]\). LDHs can be prepared in a variety of shapes and sizes and have been widely studied across various fields such as wastewater treatment, energy, and catalysis. A high surface area and the ability to exchange anions make them more effective for adsorbing various organic and inorganic pollutants \([56]\). Furthermore, double-layered hydroxides hold favorable properties as a catalyst in AOPs because of their low cost fabrication, tunable properties, high surface area, layered structure, and diverse chemical state \([57]\).

Numerous researchers have devoted their efforts to decolorizing various azo dyes using biological methods. However, there has been comparatively less focus on decolorizing cyanuric chloride-based reactive azo dyes. It was noted that reactive dyes incorporating cyanuric chloride as a reactive group exhibited greater resistance to anaerobic reduction when compared to reactive dyes utilizing vinyl sulfone as the reactive group \([58]\). To the best of our knowledge, starch-based ternary double-layered hydroxide for the decolorization of RO13 is not reported in the open literature.

In this research, an important, starch-based photocatalyst is synthesized by modification of the starch with a novel ternary double-layered hydroxide of nickel, chromium, and manganese, using the coprecipitation method. This novel starch-modified catalyst is used for the photocatalytic degradation of reactive orange 13. Different parameters like pH effect, effect of dye concentration, effect of sacrificial reagents, effect of photocatalyst dose, effect of hydrogen peroxide amount, and effect of inorganic species were used to study the removal of reactive orange 13 in the presence of sunlight.

2. Results and Discussion

2.1. XRD Test

The X-ray diffraction spectrum of starch, NiCrMn-LDH, and its composite starch/NiCrMn-LDH is demonstrated in Figure 1. Different significant peaks are examined in the XRD spectra of NiCrMn-LDH. Peaks present in spectra can be assigned as (003), (006), (012), and (110) according to their diffraction degree 12.95°, 19.89°, 29.18°, 37.27°, and 59.90°. Similarly, all the peaks of NiCrMn-LDH were observed in the XRD spectra of the starch/NiCrMn-LDH composite except one small peak, which was present at 59.90° in the NiCrMn-LDH pattern \([39]\). The existence of all peaks of simple double-layered hydroxide in the XRD pattern of the composite proves that starch did not destroy the structure of NiCrMn-LDH. Furthermore, the intensity of the peaks already present in NiCrMn-LDH was decreased in the XRD pattern of the composite (starch/NiCrMn-LDH) \([50,59]\). The decrease in the intensity of the peaks were due to shedding of the NiCrMn-LDH sheet over the surface of the starch \([60]\). Overall, this confirmed that the double-layered structure of NiCrMn-LDH easily settled in a final composite. In the same way, some extra peaks were also observed in the XRD spectra of the composite, which confirmed the crystallinity of the starch structure \([61]\). Finally, with the XRD studied, it was concluded that insignificant modification of the crystallinity structure of the composite improved the hydrophilicity of the final composite.
Figure 1. X-ray diffraction spectra of starch, NiCrMn-LDH and its composite.

2.2. SEM Analysis

Morphological images of NiCrMn-layered double hydroxide and its starch-based composite is shown in Figure 2. SEM images revealed the porosity and surface roughness before and after attachment of the extra precursor. Figure 2a–c show the irregular surface of NiCrMn-LDH. Figure 2d–f display the porous and coarse microstructure of the nanocomposite, and additional images of high magnification exhibited the cracks and raptures on the surface of the starch/NiCrMn-LDH composite, which shows the even distribution of NiCrMn-LDH particles over the polymeric chain of the starch molecule. It also confirmed the proper association between different functional groups of NiCrMn-LDH and starch during the reaction and caused roughness of the composite surface [39,50]. By comparing SEM images of NiCrMn-LDH and its starch composite, it can be noted that the attachment of starch with LDH causes the increase in surface porosity and also surface area. Furthermore, the fabrication of NiCrMn-LDH with starch is also confirmed with the EDX analysis (Figure 2g,h). The EDX of pure starch is given in Figure S1.
Figure 2. Cont.
Figure 2. Cont.
2.3. FTIR Test

The chemical composition and functional groups of the starch/NiCrMn-LDH composite can be confirmed using FTIR spectrometer. The attained results are indicated in Figure 3. The prominent peak at 3401 cm\(^{-1}\) indicates the presence of hydroxyl groups (–OH) and is associated with hydrogen bonding. This hydrogen bonding caused by the presence of water molecules between layers leads to bonding in the interlayer spaces [50]. FTIR peaks below 1000 cm\(^{-1}\) confirm the presence of stretching vibrations in the metal lattice, specifically involving the bonds between metal and oxygen (M–O, M–O–M and O–M–O) [39,62]. Furthermore, the appearance of a distinct and intense peak at 1401 cm\(^{-1}\) indicates the existence of a nitro group (–NO\(_3\)) [49,63]. The identification of a peak at 1632 cm\(^{-1}\) provides confirmation of the occurrence of bending vibrations of water molecules within the starch/NiCrMn-LDH composite. The presence of a distinct peak at 1157 cm\(^{-1}\) in the FTIR spectrum confirms the stretching vibrations of the C–O of the starch molecule [62,64,65]. The FTIR spectrum confirms the association of starch with NiCrMn-LDH. The FTIR spectrum of pure NiCrMn-LDH and starch is given in Figure 3b,c.
2.4. DLS and ZETA Potential Analysis

The DLS and zeta potential analysis are considered electrokinetic studies. The DLS study of the starch/NiCrMn-LDH composite is related to the hydrodynamic size of particles. According to DLS analysis, the hydrodynamic size for bare NiCrMn-LDH particles is 404 nm, and it increases up to 667 nm when starch (689 nm) is combined with NiCrMn-LDH, as revealed in Figure 4a. The deposition of starch over the bare NiCrMn-LDH surface is the main reason for the shift in the final particle size of the composite. Similarly, the zeta potential is related to the surface charge properties of LDH and its starch composite. According to Figure 4b, the zeta potential value of LDH increases from $-14.56$ to $0.95$ mV with the incorporation of starch ($24.41$ mV) to form a final composite. The reason for the increase in zeta potential value after the attachment of starch is due to some interaction like hydrogen bonding between hydroxyl groups of starch and water molecules, making surface charge more positive [39].
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Figure 4. DLS analysis (a) and ZETA potential study (b) of starch/NiCrMn-LDH composite, NiCrMn-LDH, and starch.

2.5. PZC

The determination of the point of zero charge (PZC) for the nanoparticles involved a procedure in which 0.01 g of starch/NiCrMn-LDH, NiCrMn-LDH, or starch were dispersed into eight separate 50 mL Erlenmeyer flasks, each containing a 0.1 M NaNO₃ solution. The pH of each solution was systematically adjusted within the range of 2 to 9 using either 0.01 mol/L HNO₃ or NaOH solutions. After allowing the solutions to equilibrate for 24 h at a constant temperature of 25 °C on an isothermal shaker, the final pH values were measured [66]. The PZC was determined as the point at which the initial pH matched the final pH, and the PZC value for starch/NiCrMn-LDH, NiCrMn-LDH, and starch were 7.2, 6.8, and 5.6, respectively (Figure 5).

Figure 5. Determination of PZC value for starch/NiCrMn-LDH composite, NiCrMn-LDH, and starch (black line represent the pH initial).

2.6. BET Analysis

The structural characteristics of the synthesized particles were assessed through parameters like surface area and pore size, as depicted in the Brunauer–Emmett–Teller (BET) plots presented in Figure 6. The adsorption–desorption plot (Figure 6a) exhibited a type IV curve with an H2b hysteresis loop behavior for the nanoparticles. The BET-specific surface
area of the nanoparticles was observed to be $2.5 \times 10^2$ m$^2$/g. However, the pore radius of the nanoparticles was found to be 45.56 nm in the BJH analyses, as shown in Figure 6b. The BET surface area of pure starch and NiCrMn-LDH are found to be 656.1 m$^2$/g and 35.5 m$^2$/g, respectively (Figure S2). Results showed that the composite is mesoporous. The notably enhanced surface area/microporous structure of the composite endow it with the capacity to serve as a host for various organic functional groups, biomolecules, and dyes, facilitating applications across diverse fields [67,68].

Figure 6. N2 adsorption-desorption isotherm (a) BJH analysis for pore radius (b) for starch/NiCrMn-LDH composite.

2.7. TGA and DSC Analysis

Thermogravimetric analysis (TGA) of starch/NiCrMn-LDH, NiCrMn-LDH, and starch is shown in Figure 7a. The TGA curves of starch and starch/NiCrMn-LDH exhibited basically a three-step degradation process in the range of 25 to 700 °C. According to analysis, almost a 12% mass loss was noted in the first step of the starch degradation, mainly due to the evaporation of embedded water molecules. Following this dehydration process, in the second step of degradation, a 95% mass loss was observed at temperatures up to 525 °C, and at the end of the second step, 5% of the total residual mass was obtained. In the third step of the degradation of the starch, curves showed a broader peak, which was due to ash forming. Starch with NiCrMn-LDH showed an almost similar TGA curve with more than 20% residual, which confirms that starch with NiCrMn-LDH has more thermal stability than simple starch. The main reason for this stability is that, after modification of starch, some hydroxyl groups of starch are replaced by carboxymethyl groups [69–71]. On the other hand, DSC analysis (Figure 7b) of starch/NiCrMn-LDH, NiCrMn-LDH, and starch collectively confirms the formation of the starch/NiCrMn-LDH composite and also informs about its thermal stability. According to the DSC thermogram, the broad endothermic transition peak noted for simple starch is indicated at 113 °C, which corresponds to the heat required for the melting of the final formed composite. But in the case of starch with NiCrMn-LDH, the thermal transition peak for starch moves up to 163 °C with more than 50 °C extra after attachment of LDH with starch. This behavior is due to the presence of LDH, which causes an obstruction of heat to biopolymer and increases thermal stability [72,73].
2.8. Photocatalytic Degradation of Reactive Orange 13

A synthesized, novel photocatalyst starch/NiCrMn-LDH was used in the presence of light for the degradation of reactive orange 13 dye. The photodegradation results were obtained using a UV-visible spectrophotometer. The lambda max for reactive orange 13 was noted to be at 489 nm. Different parameters were studied in this research, like pH effect, photocatalyst dose, initial dye concentration, hydrogen peroxide concentration, and the effect of inorganic salts on the photocatalytic degradation of RO 13. Photocatalytic degradation of RO13 with respect to time is shown in Figure 8. The broadening of absorption peaks observed is attributed to the formation of intermediates during the reaction. These intermediates overlap with the dye spectrum, causing the observed effect on the absorption band.

![Figure 7. TGA analysis (a) and DSC analysis (b) of starch/NiCrMn-LDH, NiCrMn-LDH, and starch.](image)

Figure 8. The gradual decrease in absorbance peak of RO13 during photocatalytic degradation.

Additionally, a slight shift towards lower wavelengths, known as a blue shift, is evident in the absorption peak. This shift can be attributed to a C–N bond cleavage. The departure of the amino group, a typical auxochrome from the benzene ring, may cause a decrease in the peak’s intensity along with a noticeable blue shift [37].

2.8.1. Effect of Photocatalyst Dose

The influence of the photocatalyst dosage on the degradation of RO13 was observed by employing varying quantities of the starch/NiCrMn-LDH photocatalyst, ranging from 5 to 40 mg, in a 50 mL of dye solution (at 10 mg/L) at an optimized pH. Each photoreaction spanned a duration of 60 min. The increase in the catalyst dosage resulted in a heightened...
generation rate of \( \cdot O_2^- \) and \( \cdot OH \) radicals, attributable to the increased presence of catalytically active sites [74]. However, beyond the 30 mg threshold, there was a decline in the degradation rate, primarily attributed to the surplus catalyst hindering light penetration, with the results shown in Figure 9. As per the results, 30 mg per 50 mL is considered an optimum photocatalyst dose.

![Figure 9. Effect of photocatalyst dose in photocatalytic degradation of RO13.](image)

### 2.8.2. Effect of Initial Dye Concentration

Various initial reactive orange 13 dye concentrations ranging from 5 to 40 mg/50 mL were assessed. The findings are depicted in Figure 10. The outcomes indicate that, as the dye concentration increases, more dye fragments are adsorbed onto the catalyst's surfaces. This increase in fragments obstructs the penetration of light, thereby reducing the generation of active sites during the photoreaction. Consequently, the photocatalyst efficiency substantially diminishes due to the limited availability of active sites [75]. It is evident that a reduced absorption of solar light results in a lower count of active sites on the catalyst, while a higher absorption of light photons on the catalyst surfaces anticipates a greater number of photogenerated charges for dye degradation. Furthermore, the production of photocatalytic \( \cdot OH \) and \( \cdot O_2^- \) on the photocatalyst surface remains consistent since the quantity of the catalyst remains unchanged. Typically, for higher dye concentrations, a greater concentration of \( \cdot OH \) and \( \cdot O_2^- \) reactive species is required to maintain equilibrium when the catalyst quantity is held constant.

![Figure 10. Effect of initial dye concentration in photocatalytic degradation of RO13.](image)
2.8.3. Effect of pH

The pH of the reaction mixture can influence the surface charge of the adsorbent, the ionization levels of pollutants, the dissociation of functional groups on the active sites of the adsorbent, and the structure of dye molecules [76]. For the sake of this study, analytical graded reagent hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to stabilize pH. The pH range was selected for experiments 3–11 for 10 mg/L of reactive orange 13 in 10 mg of photocatalyst in 50 mL for 60 min of every photocatalytic reaction. The dye degradation process undergoes a fast response in acidic conditions because the effectiveness of pollutant removal of photocatalysts is enhanced due to the strong electrostatic interaction resulting from the positive charge layer of the adsorbent and the anionic properties of the pollutant [77]. Experimental results of photoreaction at different pH are illustrated in Figure 11. Results show that, as the pH of the reaction moves toward acidic conditions, the photodegradation of reactive orange 13 increases. At a pH of 3, the maximum degradation efficiency is noted, so the optimum pH for the photoreaction as mentioned earlier is 3.

![Figure 11. Effect of pH in photocatalytic degradation of RO13.](image)

2.8.4. Effect of Inorganic Salts

The effect of inorganic salts on photocatalysis can vary. However, certain salts may inhibit photocatalysis by competing with reactants, scavenging reactive species, or screening light. The impact depends on the specific salt used for specific photoreaction [74]. For the sake of testing the effect of different inorganic moieties like PO$_4^{2-}$, Cl$^-$, SO$_4^{2-}$, and NO$_3^-$, photoreaction was performed for 60 min with 10 mg/L of reactive orange 13, and the photocatalyst dose was 10 mg/50 mL at an optimum pH. Experimental analysis, as shown in Figure 12, confirms that inorganic ions have some effect on overall photodegradation of reactive orange 13 with this sequence PO$_4^{2-}$ > SO$_4^{2-}$ > NO$_3^-$ > Cl$^-$. The maximum decrease in the percentage degradation of dye was noted from 86.68% to 59.42%.
2.8.5. Effect of Hydrogen Peroxide

One of the primary photo-oxidants utilized in water purification is hydrogen peroxide. It is employed in the presence of visible light to monitor the generation of hydroxyl radicals, which play a vital role in breaking down harmful organic contaminants [68]. Photoreaction was performed with various amounts of hydrogen peroxide in the range of 5–20 mL, using 10 mg/L of dye concentration with 10 mg/50 mL of the starch/NiCrMn-LDH photocatalyst for 60 min at an optimized pH. The effect of hydrogen peroxide concentration, as shown in Figure 13 and photodegradation of reactive orange 13 directly relates to the amount of hydrogen peroxide, because H$_2$O$_2$ increases the amount of hydroxyl radicals (OH) and the degradation of dye. However, this increasing effect is up to the limit, because excessive amounts of hydrogen peroxide cause a scavenging impact and use extra electrons, inhibiting reactive oxygen species. According to experimental data, 15 mL of hydrogen peroxide is considered to be the optimum quantity for photoreaction.

![Figure 13. Effect of hydrogen peroxide ($H_2O_2$) concentration in photocatalytic degradation of RO13.](image-url)

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**Figure 13.** Effect of hydrogen peroxide ($H_2O_2$) concentration in photocatalytic degradation of RO13.
2.8.6. Effect of Sacrificial Reagents

To understand the phenomenon of active species, i.e., holes (h+), electrons (e−), and hydroxyl groups (−OH), the photodegradation of reactive orange 13 dye before and after the sacrificial reagent was observed. The sacrificial reagents used to trap hole (h+), superoxide radical (O2−), and hydroxyl radical (−OH) are ethylene diamine tetra acetate (EDTA), benzoquinone (BQ), and isopropyl alcohol (IPA) respectively [78–81]. According to experimental data, as shown in Figure 14, degradation decreased up to 70.98% by the addition of IPA (−OH scavenger), which shows that the hydroxyl radical has a minor role in degradation. Similarly, for EDTA (h+ scavenger) and BQ (O2− scavenger), degradation decreased up to 45.61% and 58.11%, respectively. The results show that EDTA suppressed degradation maximum, so hole (h+) plays the main role in the photodegradation of RO13.

2.9. Kinetics Study

The linear form of pseudo-first-order kinetics used to study the photocatalysis process of RO13 is expressed in Equation (1):

\[ \ln \frac{C_0}{C_t} = kt. \]  

(1)

Here, Co and Ct are the concentration at 0 and time t, respectively. k is the rate constant, and t is time. The value of the regression coefficient (R²) and rate constant for the pseudo-first-order reaction are 0.9979 and 0.034 min−1, respectively. Overall, the photocatalytic degradation process for RO13 follows pseudo-first-order kinetics, as shown in Figure 15.
2.10. Mechanism of Photodegradation

The mechanistic study of photodegradation is presented in Figure 16. Water and hydroxyl groups adhere to the nanoparticle surface, establishing hydrogen bonds with exposed polar groups within the starch. When exposed to visible light, electrons in the valence band (VB) of NiCrMn-LDH become excited and transfer to the conduction band (CB), leaving holes in the VB. These migrated electrons in the CB function as potent reducing agents, capable of oxidizing adsorbed oxygen on the catalyst surface, yielding superoxide anionic radicals (\(\cdot O_2^-\)). Meanwhile, holes in the valence band interact with surface-bound water or hydroxyl (OH), generating hydroxyl radicals (\(\cdot OH\)). Both (\(\cdot O_2^-\)) and OH, known for their strong oxidizing properties, can eventually transform reactive orange 13 into benign inorganic compounds like CO\(_2\) and H\(_2\)O.
Starch sheets play a pivotal role by facilitating a charge transfer for NiCrMn-LDH photocatalysts, amplifying photocatalytic activity due to their high conductivity and electron transport capabilities. Similarly, adsorbed oxygen and water on the starch sheet can interact with photogenerated electrons (e\(^{-}\)) and holes (h\(^{+}\)) to generate superoxide (\(\cdot O_{2}^{-}\)) and hydroxyl (\(\cdot OH\)) radicals, which participate in the breakdown of reactive orange 13 molecules.

To deeply understand the degradation mechanism, it is essential to determine the conduction band (CB) and valence band (VB) potentials of the starch/NiCrMn-LDH composite. The \(E_{CB}\) and \(E_{VB}\) were found using the following equations.

\[
E_{VB} = \chi - E_{e} + 0.5E_{g}
\]

\[
E_{CB} = E_{VB} - E_{g}
\]

where \(\chi\), \(E_{e}\), and \(E_{g}\) represent the electronegativity of the composite, the energy of free electrons (4.5 eV vs. NHE), and optical band gap energy (\(E_{g}\)), respectively [58].

The \(E_{g}\) of the starch/NiCrMn-LDH composite was calculated to be 2.4 eV, which is lesser than the pure starch (3.5 eV) and NiCrMn-LDH (2.9 eV) (Figure S3). The \(E_{CB}\) and \(E_{VB}\) of starch/NiCrMn-LDH were estimated as \(-0.34\) eV and +2.05 eV, respectively, versus the normal hydrogen electrode (NHE). The \(E_{CB}\) of the starch/NiCrMn-LDH composite is more negative than that of \(O_{2}/O_{2}^{-}\) (\(-0.282\) eV versus NHE), indicating that the electrons can reduce \(E_{VB}\) \(O_{2}\) to generate superoxide anions \(\cdot O_{2}^{-}\). However, the \(E_{VB}\) of the starch/NiCrMn-LDH composite (+2.05 eV versus NHE) is not positive enough to fully oxidize \(OH^{-}/H_{2}O\) (2.27 V versus NHE) to form active species \(\cdot OH\) [78]. This suggests that the degradation of MB dye primarily occurs through the active species \(\cdot O_{2}^{-}\) and the accumulation of holes. The improved photocatalytic degradation efficiency may be attributed to the high concentration of hydroxyl ions in the alkaline medium.

3. Experimental

3.1. Materials and Method

Materials used included beet starch, nickel (II) nitrate hexahydrate, chromium (III) nitrate nonahydrate, manganese (II) chloride tetrahydrate, sodium hydroxide, distilled water, and reactive orange 13 from Sigma Aldrich, Taufkirchen, Germany.

3.2. Preparation of Starch Modified NiCrMn-LDH (S/NiCrMn-LDH) Composite

Starch-modified NiCrMn-LDH was fabricated by applying the coprecipitation method (Figure 17). In this method, a known amount of divalent (Ni and Mn) and trivalent (Cr) salt in 2:1:2 ratio was added to 70 mL of distilled water. To dissolve all the salts, the solution underwent stirring for almost 40 min. In a separate beaker containing 100 mL of distilled water, nearly 2.5 g of starch was added, and the solution was sonicated for 20 min. After sonication, the starch solution was added to the salt solution via dropwise. After the complete addition of the starch solution, the mixture was stirred vigorously, and the temperature was raised to 85 °C for 25 min. Subsequently, the pH was maintained about 9–10 by adding 0.1 M solution of sodium hydroxide dropwise to the reaction mixture. After stabilizing the pH, the reaction mixture underwent a continuous stirring for 24 h, and the mixture color changed to brownish black. After that, the mixture was centrifuged at 4000 rpm for 10 min, and the precipitates separated out from the mixture. The precipitates were washed with distilled water and ethanol to remove extra impurities, dried at 70 °C overnight, and then, by using a mortar and pestle, were ground to form a fine powder.
After the complete addition of the starch solution, the mixture was stirred vigorously, and the temperature was raised to 85 °C for 25 min. Subsequently, the pH was maintained about 9–10 by adding 0.1 M solution of sodium hydroxide dropwise to the reaction mixture. After stabilizing the pH, the reaction mixture underwent a continuous stirring for 24 h, and the mixture color changed to brownish black. After that, the mixture was centrifuged at 4000 rpm for 10 min, and the precipitates separated out from the mixture. The precipitates were washed with distilled water and ethanol to remove extra impurities, dried at 70 °C overnight, and then, by using a mortar and pestle, were ground to form a fine powder.

Figure 17. Schematic diagram for preparation of starch/NiCrMn-ldh composite.

4. Conclusions

In summary, by using an environmentally friendly and cost-effective coprecipitation method, a novel photocatalyst is synthesized by modifying NiCrMn-layered double hydroxide with starch. This photocatalyst was then employed for the efficient degradation of reactive orange 13 dye. Comprehensive characterization of the synthesized photocatalyst was carried out using various techniques, including X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), Brunauer–Emmett–Teller (BET), point of zero charge (PZC), zeta potential, dynamic light scattering (DLS), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Hydrodynamic size increased from 404 nm to 667 nm after the attachment of starch with bare NiCrMn-LDH in the DLS analysis. The zeta potential value increased from $-14.56$ mV to $0.95$ mV after deposition of starch over simple NiCrMn-LDH, which confirmed the successful incorporation of starch into the trimetallic double-layered hydroxide, which confirmed the successful incorporation of starch into the trimetallic double-layered hydroxide. This starch association significantly enhanced the photocatalyst properties, particularly its surface area, which caused an increase in the number of active sites over the photocatalyst surface. Overall, the photocatalysis process for RO13 follows pseudo-first-order kinetics. Various parameters were systematically investigated, including pH value, initial dye concentration, photocatalyst dosage, scavenger effect, hydrogen peroxide concentration, and the influence of inorganic anions on RO13 degradation. Remarkably, the highest degradation percentage was achieved at pH value of 3, photocatalyst amount 20 mg/50 mL, and $H_2O_2$ concentration 20 mL/L. As a synthesized photocatalyst, it is very effective in wastewater treatment regarding the photocatalysis of dyes.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal14070449/s1, Figure S1: EDX spectrum of pure starch; Figure S2: BET analysis of starch (a) and NiCrMn LDH (b); Figure S3: DRS spectrum of Starch/NiCrMn-LDH (a), starch, and NiCrMn LDH (b).


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Catalysts 2024, 14, 449


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