Structural and optical properties of Cu-substitution of NiAl₂O₄ and their photocatalytic activity towards Congo red under solar light irradiation

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ABSTRACT

The present work focuses on the effect of Cu substitution on the crystal structure and photocatalytic activity of nano-spinel oxides NiₓCu₁₋ₓAl₂O₄ (x = 0.0–1.0). The synthesized compounds by co-precipitation route are characterized by X-ray diffraction, FT-IR, X-ray Photoelectron Spectroscopy, Scanning Electron Microscopy and UV–vis diffuse reflectance. The photocatalytic activity is followed by UV–vis spectroscopy and Electrochemical Impedance Spectroscopy in order to confirm the good performance of the catalyst and the charge separation of photogenerated (e⁻/h⁺) pairs. The photocatalytic efficiency of the synthesized catalysts is investigated through the decomposition of Congo Red dye under solar light irradiation. The efficient catalyst is Ni₀.₂Cu₀.₈Al₂O₄ with a removal conversion of 90.55% of the dye after 180 min. The parameters influencing the dye degradation like initial concentration are studied for the optimum degradation and the results have been discussed. This study shows that the adsorption kinetic of the Congo red has well followed the Langmuir isotherm model. The high photocatalytic activity of Ni₀.₂Cu₀.₈Al₂O₄ can be attributed to the valence band of the catalyst which enhances the mobility of the photoexcited charge carriers.

1. Introduction

Our earth needs urgent actions to save the environment from pollutant emissions such as heavy metals, organic compounds, pesticides, and dyes, generated by heavy manufacturing industries and complex technological activities. These environmental pollutants pose serious toxic risks to microorganisms and represent a threat to aquatic life and human beings [1–4].

In reality, large amounts of dyes generating specifically from activities such as printing in textile industries, leather tannery, chemical and food manufacture, as well as pharmaceutical industries are continuously introduced into the environment (water, soil, and air) without any control [5,6]. Despite the fact that they are considered the main pollutants, quantities of dangerous dyes produced worldwide through synthesis, treatment, and application are still released into the environment without any prior treatment [7]. Most of these dyes contain stable compounds and non-biodegradable which are difficult to be destroyed due to mesomeric effect [8]. In this context, Azo Congo red (CR) is cationic dye which contains one or more –N=N– groups with an aromatic structure and one of the most important and widely used dyes. Its degradation is essential and indispensable for ecological protection. In this respect, several techniques have been employed such as filtration, coagulation, adsorption, biological, and oxidation and advanced oxidation processes (AOPs).

However, these methods are costly and often become ineffective at low concentrations [9,10]. Recently, photocatalytic degradation of dyes through AOP under UV irradiation on semiconductors has received much attention mainly to its capacity to degrade numbers recalcitrant dyes [11–14]. Among the candidates, TiO₂, ZnS, ZnO, Fe₂O₃, WO₃ and CdS are semiconductors of choice which are widely used as photocatalysts but they require sometimes expensive UV irradiation for photocatalysis owing to their large band gap (Eg). Recently metal sulphide with doped semiconductors and spinel magnetic nanoparticles is also used as photo-catalyst for the degradation of various dyes [15–17]. The use of visible light can be another alternative. On the other hand, other researchers have investigated the degradation of CR in presence of narrow bandgap semiconductors like the spinels [18–24].

It is convenient to note that the photocatalytic process is focused on the creation of an electron/hole (e⁻/h⁺) pairs by illumination with visible or UV light, depending on the nature of the semiconductor...
(hv > E_g). Both electrons and holes may migrate to the catalyst surface of semiconductors and with the presence of the adsorbed azo dyes, redox reactions take place. The oxidizing radicals could attack the azo dyes and convert them partially into CO₂, H₂O and nontoxic inorganic molecules [25,26]. In this regard, Comparelli et al. [26] reported that the formation of free radicals is essential to reduce absorbed dyes and act as oxidizing species.

The metal oxide semiconductor materials have been generated great interest for photoysis, photocatalytic, solid oxide fuel cells, and photovoltaic applications due to their optical, electrical, and optoelectronic properties [27–30]. The spinel aluminate materials are widely used as ceramic pigments, magnetic devices, refractory materials, and catalytic material for chemical reactions and they have been studied for their dielectric properties, chemical and thermal stability, as well as for their mechanical resistance [31–33]. The optical and fluorescence properties of these compounds are dependent on their particles size and preparation methods. The nano-spinel oxides, have received a great attention due to their catalytic properties but to our knowledge and according to the literature, no study in which NiAl₂O₄ doped with copper was found for the dyes degradation of azo dyes.

The present study reports the application of the spinel solid solutions Ni₁₋ₓCuₓAl₂O₄ (x = 0.0–1.0) type spinel as an efficient photocatalysts for the degradation under solar irradiation of Congo red, a recalcitrant azo dye. The effect of different parameters such as, initial RC concentration and catalyst dose has been examined and the results obtained are discussed. The model of the photocatalytic kinetics degradation has also been studied.

2. Materials and methods

2.1. Synthesis and characterization of catalysts

The chemicals used in this work were CuCl₂.2H₂O 97% (Fluka AG), Ni(NO₃)₂.6H₂O 97% (Sigma-Aldrich), Al(NO₃)₃.9H₂O 98% (Biocom.Chemopharma). They were used without any further treatment. Nanopowder Copper doped Nickel Aluminates were prepared by coprecipitation method using nitrate salts (purity 98%) of Cu, Ni and Al and chelated by NaOH (4 N) as precursors. Congo red dye (molecular weight = 696.67 g/mol⁻¹, C₃₅H₃₇N₆O₆S₂.2Na) was used without any further treatment. The stock solution of CR was prepared by dissolving appropriate amount of CR in 1.0 L of distilled water. The working solutions were prepared by simple dilution with distilled water for the photocatalytic experiments.

 Adequate quantities of precursor were dissolved in distilled water and magnetically stirred for a few minutes. The obtained solutions were diluted in order to adjust the solution pH. After, a solution of NaOH (4 N) was slowly added until the neutralisation where a chelate was obtained. The obtained precipitate was centrifuged to remove the photocatalyst powders. The remaining RC aqueous solution before and after adsorption was evaluated as 750 W/m², while the temperature averaged 30 °C.

At regular time intervals, the aliquots (about 4 mL) were drawn and centrifuged to remove the photocatalyst powders. The remaining RC concentration was determined with UV–visible spectrophotometer at λₘₐₓ = 498 nm (UV-1800 Shimadzu, Japan) and the RC degradation rate was calculated using the difference in the CR concentration in the aqueous solution before and after adsorption as:

\[ \text{Degradation} \% = \left( 1 - \frac{A_t}{A_0} \right) \times 100 \]

(1)

Where A₀ and Aₜ are the absorbance of RC solution at initial time 0 and time (t), respectively. All the photocatalytic experiments were conducted during the months of May and June with direct exposure to sunlight.

3. Results and discussion

Fig. 1 shows the powder XRD patterns of Ni₁₋ₓCuₓAl₂O₄ (x = 0.0–1.0) obtained after calcination at 800 °C for 5 h in air. The samples were essentially pure and the patterns revealed single phases. All XRD peaks are indexed in a cubic spinel structure isotypic of NiAl₂O₄ (JCPDS, No 10-0339) cubic phase of space group Fd-3 m corresponding to the spinel structure. It should be noted that the XRD pattern of NiAl₂O₄ (x = 0.0) confirms the presence of impurity peaks attributed to NiO.

The Cu-substitution of NiAl₂O₄ in the Ni-site did not change the peak position, nevertheless the intensity of the peaks of the reflections (331) and (400) which corresponding to 38° and 45° of all the compositions does not evolve in the same way. The decrease of Cu content, corresponds to a continuously decrease of the peaks continuously. Indeed, these two peaks are very sensitive to the phenomenon of intensity inversion observed in the case of spinel structure [37]. Moreover, the intensity of the (422) peak increases with the increase of Ni²⁺ substitution by Cu²⁺.

The lattice parameters obtained after Rietveld refinements using the Fullprof software (Table 1) increases with the increase of Cu content, due to the difference in ionic radii between Ni²⁺ and Cu²⁺ (r_{Cu²⁺}+r_{Cu²⁺})
The obtained images (Fig. 2) confirm the polycrystalline nature of the powders and correspond to the 311 peak of NiAl2O4. Therefore, this situation suggests a harmonious substitution of Ni2+ by Cu2+.

The energy dispersive X-ray spectroscopy (EDS) results for the Cu-substituted NiAl2O4 compounds (Fig. 3) confirm the presence of Ni, Cu, and Al in the examined samples. The EDS spectra indicate the presence of Ni, Cu, and Al in the examined samples, with the atomic concentration of Cu increasing with increasing Cu-content. The Cu-content was determined through energy-dispersive X-ray spectroscopy (EDS), and the results are consistent with the XRD data.

The adsorption parameters for the two isotherm models are given in Table 2. The values of the correlation coefficient ($R^2$) and the standard error of estimate ($\epsilon$) were used to evaluate the model's fit. The Langmuir model provided a better fit than the Freundlich model, as indicated by the higher $R^2$ values and lower $\epsilon$ values. The maximum adsorption capacity ($Q_{\text{max}}$) for CuAl2O4 was 5.81 mg/g, while for NiAl2O4, it was 2.37 mg/g. The adsorption isotherms for the Cu-substituted NiAl2O4 compounds showed a decrease in the adsorption capacity with increasing Cu-content, which is attributed to the decrease in the number of active sites available for adsorption.

The change in the optical gap (Eg) of the as-prepared Ni1−xCuAl2O4 (x = 0.0–1.0) catalysts is shown in Fig. 7a. As can be seen, the amount of adsorbed CR per unit weight of adsorbent (Qe) is increased with increasing Cu-content. The E adsorption capacity for CuAl2O4 was 1.0 mg/g, while for NiAl2O4, it was 0.5 mg/g. The adsorption isotherms for the Cu-substituted NiAl2O4 compounds showed a decrease in the adsorption capacity with increasing Cu-content, which is attributed to the decrease in the number of active sites available for adsorption.

The effect of contact time on the adsorption capacity of the CR onto Ni1−xCuAl2O4 (x = 0.0–1.0) catalysts is shown in Fig. 7a. As can be seen, the amount of adsorbed CR per unit weight of adsorbent (Qe) increases quickly at the beginning, except for the composition x = 0 (NiAl2O4), and remains nearly unchanged after 180 min, attesting the
equilibrium achievement. This is due to the large availability of free active sites on the surface of catalysts. The maximum adsorption capacity of CR adsorbed on adsorbent at equilibrium is obtained for $x = 0.8$ ($\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4$). This catalyst is used to study the photocatalytic activity for the rest of this work.

The effect of the initial CR concentration on the adsorption capacity of $\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4$ is shown in Fig. 7b. It is clear that the increase in the initial CR concentration from 0 to 40 mg/L results in an increase of the amount of CR adsorbed per unit weight of adsorbent ($Q_e$), which reaches its maximum value for 15 mg/L. The excellent adsorption contributes to the increase of photocatalytic activity.

The Langmuir and Freundlich isotherm models were used to analyze the adsorption experimental data of CR on $\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4$ catalyst (Fig. 8). The mathematical Langmuir and Freundlich equations are the following [53,54]:

$$
\frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}} k_l} + \frac{C_e}{Q_{\text{max}}}
$$

(4)

$$
\ln Q_e = \ln k_f + \frac{1}{n} C_e
$$

(5)

where $Q_{\text{max}}$ is the maximum adsorption capacity (mg g$^{-1}$), $k_l$ is the Langmuir constant related to the energy of adsorption (L mg$^{-1}$), $C_e$ is the CR equilibrium concentration (mg/L), $K_f$ is the Freundlich constant related to the adsorption capacity of the adsorbent (mg$^{1-n}$ L$^n$ g$^{-1}$), and $n$ is the constant related to the facility of adsorption process.

The obtained adsorption parameters are summarized in Table 2. The experimental data were obeyed and fitted much better with the Langmuir isotherm than with the Freundlich, indicating that the Langmuir model describes well the CR adsorption. The maximum adsorption capacity determined from Langmuir isotherm model was 5.81 mg/g not far from the experimental value obtained at equilibrium (Fig. 7b). In addition, the result indicates that the adsorption process is mainly monomolecular layer on a catalyst surface.

The photocatalytic activity of $\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4$ catalyst has been investigated through the photodegradation of CR under solar light and the corresponding results are shown in Fig. 9a. The photocatalytic decolorization of CR solution in the absence of $\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4$ catalyst did not occur. In contrast, the decolorization is strongly improved in the presence of the catalyst. The photodegradation is quite slow at the
beginning and becomes faster after 50 min of exposure to solar light irradiation. The decolorization efficiency of 48% is obtained within 120 min which is better than commercial ZnO and TiO2 P25 under UV light irradiation [30], 31% and 41%, respectively. 90.55% of CR was degraded after 180 min under solar light. This behavior can be attributed to the large surface area of the catalyst and electrons transfer, which facilitates the diffusion of CR molecules and retards the recombination of photogenerated electrons and holes ($e^−/h^+$) pairs.

In order to study the kinetics of the photodegradation of CR, the linear plots of the pseudo-first order kinetic model is used to fit the experimental data. The plots $\ln(C_0/C)$ vs. irradiation time are given in Fig. 9b. The linear relationship between $\ln(C_0/C)$ and irradiation time is given by the equation:

$$\ln(C_0/C) = k t$$

where $k$ is the rate constant.

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**Fig. 4.** XPS spectra of Ni$_{1−x}$Cu$_x$Al$_2$O$_4$ oxides ($x = 0.0$–$1.0$): (a) O 1 s, (b) Al 2p, (c) Ni 2p and (d) Cu 2p.

**Fig. 5.** (a) UV–Vis diffused reflectance spectrum of the as-prepared Ni$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$ oxide, b) direct band gap estimation from the plot of $(\alpha h\nu)^2$ versus $h\nu$.

**Fig. 6.** Evolution of the band gap ($E_g$) as a function of $x$ for Ni$_{(1−x)}$Cu$_x$Al$_2$O$_4$. 

\[
\ln \left( \frac{C_0}{C_t} \right) = k_{app} \cdot t
\]

\( k_{app} \text{ (mm}^{-1}) \) is the apparent rate constant, \( C_0/C_t \) is the normalized CR concentration and \( t \) is the reaction time. The value of the rate constant obtained is 0.004 min\(^{-1}\).

The electrochemical impedance spectroscopy (EIS) is considered as the powerful technique to study the charge transfer at the solid / liquid interface. EIS is performed on the most efficient catalyst Cu\(_{0.8}\)Ni\(_{0.2}\)Al\(_2\)O\(_4\) to confirm the charge separation of photogenerated (e\(^-\)/h\(^+\)) pairs [55,56]. Fig. 10 shows the Nyquist plots of the EIS spectra measured in the dark and under visible light irradiation for Cu\(_{0.8}\)Ni\(_{0.2}\)Al\(_2\)O\(_4\) catalyst. The experimental data (symbol) suitably fit the calculated data (lines) using the equivalent circuit model (Fig. 10 insert). The error of the resistance (R) and Constant Phase Element (CPE) evaluated by the software Zview\textsuperscript{®} is less than 1%.

The resistance at high frequency (R\(_1\)) is attributed to the electrolyte solution. The interface Cu\(_{0.8}\)Ni\(_{0.2}\)Al\(_2\)O\(_4\)/electrolyte behavior was characterised by one arc at medium and low frequencies and can be fitted by the resistance R\(_2\) in parallel with the pseudo capacitance CPE attributed.
to the double layer capacitance. $R_2$ is attributed to the charge transfer resistance and reflects the reaction rate occurring at the Cu$_{0.8}$Ni$_{0.2}$Al$_2$O$_4$ surface electrode. As expected, the resistance $R_2$ under visible light irradiation is smaller than that in dark which suggests a more effective separation of photo-generated ($e^-/h^+$) pairs and faster interfacial charge transfer at the solid–liquid interface highly desired for photocatalytic reaction [56,57].

The flat band potential ($V_{fb}$) used to predict the photocatalytic reactions is determined from the Mott-Schottky relation:

$$\frac{1}{C_F^2} = \left(\frac{2}{\varepsilon \varepsilon_0 N_t}\right)(V - V_{fb})$$  \hspace{1cm} (7)

The extrapolated plot to $C^{-2} = 0$ gives the flat band potential $V_{fb}(\sim 0.39 \text{ V}_{SCCE})$ (Fig. 11a). The negative slope indicates a p-type semiconductor behavior.

The evolution of the electrical conductivity vs. $1000/T$ (Fig. 11b) shows that the electrical conductivity obeys the Arrhenius law with activation energy ($E_a$) of 0.17 eV obtained from the slope and attributed to the separation between the Fermi level and the valence band. The valence band position of Ni$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$ can be predicted using the known equation [58]:

$$E_{VB} = 4.75 + e \cdot V_{fb} + 0.059(pH - pH_{zeta}) + E_a$$  \hspace{1cm} (8)

$pH_{zeta}$ is the zeta potential determined by measuring the equilibrium pH of a solution containing an excess of Ni$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$ powder ($pH_{zeta} = 7.20$). The photocatalytic mechanism on Ni$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$ shows that both electrons and holes are involved in the CR degradation under solar light irradiation (> $E_g = 1.46$ eV). The photoelectrons produced in Ni$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$ – CB (1.68 V) were transferred to the surface and reduce the CR dye. The dissolved and/or adsorbed O$_2$ on the catalyst surface acting as the electron scavenger react with electrons and produce free radicals ·OH and ·OH radicals (Fig. 12). Concomitantly, the holes react with H$_2$O to yield ·OH radicals. The free radicals attack the adsorbed CR molecules on Ni$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$. OH· radical is a very strong oxidizing agent with a standard potential +2.8 V [59] that can degrade CR to CO$_2$ and mineral end products. The relevant reactions at the surface of the catalyst can be expressed as follows:

$$\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4 + \text{hv} \rightarrow \text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4 (e^-_{CB} + h^+_{VB})$$  \hspace{1cm} (9)

$$\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4 + (h^+_{VB}) + \text{H}_2\text{O} \rightarrow \text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4 + \text{H}^+ + \text{OH}^-$$  \hspace{1cm} (10)

$$\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4 + (h^+_{VB}) + \text{OH}^- \rightarrow \text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4 + \cdot\text{OH}^-$$  \hspace{1cm} (11)

$$\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4 + (e^-_{CB}) + \text{O}_2 \rightarrow \text{Ni}_{0.2}\text{Cu}_{0.8}\text{Al}_2\text{O}_4 + \text{O}_2^-$$  \hspace{1cm} (12)

$$\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^-$$  \hspace{1cm} (13)

CR Dye + OH· / O$_2^-$ → CO$_2$ + H$_2$O + other products nontoxic  \hspace{1cm} (14)

4. Conclusion

The results obtained in this study show that all spinel oxides Ni$_{1-x}$Cu$_x$Al$_2$O$_4$ ($x = 0.0$–$1.0$) prepared by co-precipitation route present a pure phase except the composition $x = 0$ which shows the presence of NiO confirmed by X-ray diffraction. The UV–vis reflectance confirm that the samples have a nanometric size and a direct optical gap between 1.45 and 2.37 eV. The Ni$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$ catalyst shows the best adsorption capacity of Congo red at natural pH with an equilibrium time of ~3 h. The adsorption kinetics of CR dye obeys the Langmuir model on Ni$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$. The electrochemical study with EIS confirms the charge separation of photogenerated electrons and holes with good photocatalytic performance of the catalyst under solar light irradiation. The photocatalytic degradation of CR shows a removal of 90.55% of the dye after 3 h under illumination and the photodegradation follows the pseudo-first order kinetic model with a rate constant of 0.004 min$^{-1}$.

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Fig. 12. A schematic illustration of the generation of electron-hole pairs and the corresponding redox reactions taking place on the Ni$_{0.2}$Cu$_{0.8}$Al$_2$O$_4$ surface.

References


