Synthesis of an optical catalyst for cracking contaminating dyes in the wastewater of factories using indium oxide in nanomaterial and usage in agriculture

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Herein, the photocatalytic degradation of the Congo Red (CR) and Crystal Violet (CV) dyes in an aqueous solution were discussed in the presence of an indium(III) oxide (In$_2$O$_3$) as optical catalyst efficiency. The caproate bidentate indium(III) precursor complex has been synthesized and well interpreted by elemental analysis, molar conductivity, Fourier transform infrared (FT-IR), UV-Vis, and thermogravimetric (TGA) with its differential thermogravimetric (DTG) studies. The microanalytical and spectroscopic assignments suggested that the associated of mononuclear complex with 1:3 molar ratio (M$^{3+}$/ligand). Octahedral structure is speculated for this parent complex of the caproate anion, CH$_3$(CH$_2$)$_4$COO$^-$ ligand. The In$_2$O$_3$ NPs with nanoscale range within 10–20 nm was synthesized by a simple, low cost and eco-friendly method using indium(III) caproate complex. Indium oxide nanoparticles were formed after calcination of precursor in static air at 600°C for 3 hrs. The structural, grain size, morphological and decolorization efficiency of the synthesized NPs were characterized using the FT-IR, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and transmission electron microscopy (TEM) analyses. It was worthy mentioned that the prepared In$_2$O$_3$ NPs showed a good photodegradation properties against CR and CV organic dyes during 90 min.

Keywords: Photocatalyst; In$_2$O$_3$; precursors; Crystal Violet; Congo Red; NPs.

EXPERIMENTAL

Chemicals

The caproic acid (CH$_3$(CH$_2$)$_4$COOH) and anhydrous InCl$_3$ were received from Fluka (UK) and Alfa Aesar chemical manufacturing company (USA), respectively. These chemicals used as received.

Analyses

I. Elemental analyses

II. Indium metal ion percentage

III. Molar conductivity

IV. FTIR spectra

V. Electronic absorption

VI. Thermogravimetric

VII. X-ray powder diffraction

By Perkin Elmer CHN 2400

By Bruker FT-IR

By Shimadzu TGA-50H

By XPer Philips X-ray diffractometer
Synthesis of indium(III) caproate complex

Indium(III) chloride (3 mmol, 0.664 g) was dissolved in 20 mL of bi-distilled water then mixed to 30 mL of an aqueous solution of caproic acid (9 mmol, 1.1 mL) with contentiously stirring. The mixture was neutralized at pH = 7.5 using ammonia solution (10%). The mixture was refluxed at 60°C for 2 hrs, then left to evaporate at room temperature overnight. The yellowish white precipitate was filtered, wash with hot water and little amount methanol solvent and dried at 60 oC. [In(CH3(CH2)4COO)3] complex, Anal.: (Calc.) Found, %: C, (46.97) 46.55; H, (7.23) 7.19; In, (24.95) 24.71; yield 82%; ΛM = 2.1 Ω−1.cm2.mol−1.

Synthesis of the In2O3 NPs

Calcination of the [In(CH3(CH2)4COO)3] complex as a precursor material at temperature up to 600°C gives rise to nanocrystalline particles of In2O3 with nanoscale size.

Photocatalytic degradation experiment

A 250 mL conical flask including a 100 mL solution of the Congo Red or Crystal violet (Fig. 1) in water (50 mg · L−1) and (50 mg) of synthesized In2O3 NPs. While the solution was stirred for approximately 1½ hrs and then exposed to a UV lamp. The absorbances were measured each 15 min. in a spectrophotometer at the maximum wavelength for the Congo Red (498 nm) or Crystal violet (590 nm). The decolorization rate of the dye was determined as expressed in Eq. (1):

Dye decolorization, % = (A0 − At)/ A0 · 100 (1)

Where At is the absorbance at requested time and A0 is the initial absorbance of each solution.

RESULTS AND DISCUSSION

Characterization of [In(CH3(CH2)4COO)3] complex precursor

The main objective from the synthesized of indium(III) caproate complex is to be acquired of good precursors to prepared In2O3 oxide in nanostructure form. The new [In(CH3(CH2)4COO)3] complex precursor was synthesized and well characterized using microanalytical, (FT-IR, UV-Vis) spectroscopy, thermal analyses. Elemental analyses results as seen from these data (experimental section), 1:3 (In : Ligand) binary complex was associated with good agreement matching between experimental and theoretical values. The results indicate that CH3(CH2)4COOH ligand behave as uninegative bidentate molecule. This lose the carboxylate hydrogen atom on complexity with the indium(III) ion. The preparation of this binary complex (Fig. 2) can be proceed as follows:

InCl3 + 3CH3(CH2)4COOH → [In(CH3(CH2)4COO)3] + 3HCl

The structure of the indium(III) caproate complex suggested form the elemental analyses agree well with their proposed formula. The solubility of this complex display that its insoluble in most organic solvents (e.g. CHCl3, C6H6, CH3OH, but soluble in DMF and DMSO solvents. The [In(CH3(CH2)4COO)3] complex is dissolved in DMF and the molar conductivity of 10−3M solution at 30 oC is measured. It is deduced from the experimental result (2.1 Ω−1.cm2.mol−1) that the indium(III) precursor complex is 1:3 nonelectrolyte.

Figure 1. Chemical structures of A: Congo Red (CR) and B: Crystal violet (CV) dyes

Figure 2. Chemical structure of indium(III) caproate complex

The FT-IR spectrum of the synthesized indium(III) caproate complex is shown in Figure 3. The FT-IR spectrum of free capric acid, CH3(CH2)4COOH, display strong frequency band at 1700 cm−1 that is assigned to vibration motion of carbonyl νC = O of (COOH) group. This band is disappeared in case of FT-IR spectrum of the [In(CH3(CH2)4COO)3] complex and it has been replaced by two new vibration bands at 1549 and 1402 cm−1 which are attributed to the asymmetric and symmetric vibration motions of the COO group, respectively.

Literature survey revealed that the carboxylate group can be chelated with any metal ions by three coordination modes as monodentate (Δν > ionic form), bidentate (Δν ≈ ionic form) or bridged bidentate (Δν < ionic form) that

Δν = νs(COO−) − νas(COO−).

In case of infrared spectrum of indium(III) caproate complex, the Δν difference frequencies is 147 cm−1. This value concluded
that the carboxylate group coordinated to indium(III) ion through two oxygen atoms as bidentate binding mode1, 2 (Fig. 2). There are two new absorption bands at 580 and 454 cm⁻¹ attributed to the ν(In-O) frequencies30.

½In₂O₃ oxide but the In(III) caproate complex has an intermediate step due to the association of indium(III) carbonate, In₂(CO₃)₃, at about 350°C. This hypothesis is supported by the FT-IR spectrum (Fig. 6) resulted from calculations of the indium(III) caproate complex at 350°C, as refereed in Figure 6. So that, the proposed thermal degradation equation 2 is:

\[
\text{[In(CH}_3\text{(CH}_2\text{)}_4\text{COO)}_3] \rightarrow \text{In}_2\text{(CO}_3\text{)}_3 \rightarrow \text{In}_2\text{O}_3
\]  

Eq. (2)

The absorption spectrum of the free CH₃(CH₂)₄COOH acid ligand displayed two bands at 225 and 265 nm that were assigned to π → π* and n → π* transitions of alkyl group (-CH₃ and -CH₂) and carboxylic groups, respectively31. Normal absorption spectrum of indium(III) caproate complex (Fig. 4) show maximum absorption bands at λₘₐₓ = 237, 252, 274, 314, and 383 nm. The UV bands at 314 and 383 nm are attributed to metal charge-transfer and d–d transition32–34. The relative increases in absorbance due to complex association at 274 and 314 nm. This resulted data was supported the coordination of indium(III) ions via COOH group.

Thermal decomposition of indium(III) caproate complex was investigated based on controlled heating rate at 10°C min⁻¹ under nitrogen atmosphere and weight loss was measured from room temperature until 800°C. The TG-DTG curves (Fig. 5), displayed that the thermal degradation of [In(CH₃(CH₂)₄COO)]₃ complex passed in a broad peak at DTGₘₐₓ = 499°C. The total mass loss (Calc. 71.59 %, found 71.40 %) was attributed to the elimination of the three caproate organic parts of the indium(III) caproate complex. It is worthy mentioned that, indium(III) caproate complex decompose to

![Figure 3. FT-IR spectrum of [In(CH₃(CH₂)₄COO)]₃ complex](image)

![Figure 4. UV-Vis spectrum of [In(CH₃(CH₂)₄COO)]₃ complex](image)

![Figure 5. TGA diagram of [In(CH₃(CH₂)₄COO)]₃ complex](image)

![Figure 6. FT-IR spectrum of [In(CH₃(CH₂)₄COO)]₃ complex after calcinations at 350°C](image)

The kinetic thermodynamic parameters (DG/kJmol⁻¹, DH/kJmol⁻¹, DS/Jmol⁻¹K⁻¹, Z/s⁻¹, E/kJmol⁻¹) have been elucidated for the differential thermogravimetric step DTGₘₐₓ 499°C using Coats-Redfern35 and Horowitz-Metzger36 methods (Fig. 7). Both values of activation energy E* and entropy DS* of the reaction have been calculated using both methods and found to be in close agreement. The order of reaction in each case is one. The enthalpy of reaction has been calculated, using the TG37 and DTG curves, respectively38,39. The kinetic parameters for the thermal decomposition of the indium(III) caproate complex are given in Table 1. The reaction for which ΔG is positive and ΔS is negative considered as unfavorable or as a non spontaneous reaction. The entropy of activation was found to have negative values in most the complexes which
indicate that the decomposition reactions proceed with a lower rate than the normal ones. It is clear that the thermal decomposition process of studied complex is non-spontaneous, i.e., this complex is thermally stable. XRD spectrum of the [In(CH₃(CH₂)₄COO)₃] complex (Fig. 8) was measured within the 2θ = 4–80° range. This spectrum displayed that the synthesized indium(III) caproate precursor complex has a crystalline behavior. The new diffraction patterns presence in the spectrum of In(III) caproate complex are due to the formation of chelation between caproic acid and indium ions. The maximum diffraction patterns of In(III) complex is exhibited at 2θ = 16.8°. The particle size was calculated from XRD diagram by applying FWHM of the characteristic peaks using Deby-Scherrer equation:

\[ D = \frac{K\lambda}{β\cos θ} \]

where “D” term is the particle size of the crystal gain, “K” term is a constant (0.94 for copper grid), “λ” term is the X-ray wavelength (1.5406 Å), “θ” term is the Bragg diffraction angle and “β” term is the integral peak width. The particle size of the synthesized complex was calculated based on the highest 2θ in comparable with the other peaks. This value referred that the particle size exhibited at (70 nm) within nano scale range.

The examination of surface morphology of the [In(CH₃(CH₂)₄COO)₃] complex was performed using SEM technique (Fig. 9). It can be seen that it gave a shape of the plates which are not compacted. This micrograph of indium(III) caproate complex indicated that the presence of well defined crystals free from any shadow of the impurities on the external surface. It is clearly from the SEM image that the synthesized In(III) complex, crystals were found to grow up from just a single molecule to several molecules in an aggregate distribution with particle sizes starting from a few nanometers to several hundred.

**Table 1.** Kinetic thermodynamic parameters based on Horowitz-Metzger (HM) and Coats-Redfern (CR) methods

|          | HM method* | CR method* |
|----------|------------|------------|
| E        | 70         | 52.8       |
| Z        | 1.91E+02   | 9.44E+00   |
| ΔS       | -209       | -234       |
| ΔH       | 63.6       | 46.4       |
| ΔG       | 225        | 227        |

*ΔG/kJmol⁻¹, ΔH/kJmol⁻¹, ΔS/Jmol⁻¹K⁻¹, Z/s⁻¹, E/kJmol⁻¹

![Figure 7.](image) **Figure 7.** Kinetic thermodynamic CR and HM diagrams of [In(CH₃(CH₂)₄COO)₃] complex

Characterization of In₂O₃ oxide NPs

This study describes the synthesis of In₂O₃ by the thermal decomposition route for the [In(CH₃(CH₂)₄COO)₃] complex in static air. The discussions of the intermediate and the final thermal decomposition products were carried out by thermogravimetry, FT-IR spectroscopy, XRD, SEM, EDX, and TEM analyses. The analyses of these data show that the indium(III) caproate complex decomposed to In₂O₃ with the formation of an intermediate carbonate, In₂(CO₃)₃ compound. The In₂O₃ NPs with crystallite size in the nanosize range was formed after calcination at temperature 800°C. The suggested reaction occurring during the thermal decomposition of the indium(III) caproate complex is summarized below, according to TG/DTG and FT-IR results:

\[ [\text{In(CH₃(CH₂)₄COO)₃}] \xrightarrow{800 \degree C} \text{Static O}_2 \text{ gas} \rightarrow \text{In}_2\text{O}_3 \]

FT-IR spectrum of the synthesized In₂O₃ NPs by the thermal decomposition technique is shown in Figure 10. There are three distinguish vibration bands at 589 and 665 cm⁻¹ were existed, these are attributed to the ν(In–O)
stretching and $\delta$(In–O–In) bending vibrations, respectively in cubic $\text{In}_2\text{O}_3$ structure\(^{41-43}\). This result support that the phase formation is complete for the as-prepared $\text{In}_2\text{O}_3$ NPs and there is no evidence for the presence of any organic impurities in the synthesized indium(III) oxide sample. On the other hand, the presence of broad band at 3434 cm\(^{-1}\) and medium band at 1642 cm\(^{-1}\) can be assigned to the stretching and bending vibrations of the v(O-H) bands regarding water moisture.

The X-ray powder diffraction patterns of the indium(III) caproate complex after calcination at 800 oC for 3 hrs is shown in Figure 12. The distinguish patterns attributed to cubic structure indexed on ICDD card 6–416\(^{48}\). Figure 12 shows the strong and sharp diffraction patterns reveal that the $\text{In}_2\text{O}_3$ NPs has a well crystalline structure. The diffraction patterns agree with those given in JCPD card 6–416 of cubic $\text{In}_2\text{O}_3$ reflections as 211, 221, 222, 400, 413, 440, and 622 planes. Calculation of particle size of indium oxide using Scherrer’s equation gives 20 nm value, confirmed that the particle size of the $\text{In}_2\text{O}_3$ which was prepared by thermal decomposition method of indium(III) caproate complex is in the nanosize range < 100 nm.

The morphology of $\text{In}_2\text{O}_3$ NPs was investigated with SEM as shown in Figure 13. SEM micrograph (Fig. 13) reveals the overall appearance of indium(III) caproate complex calcined at 800 oC for 3 hrs. The particles are nearly thick threads in shape has uniform size and distribution with symmetrical sizes, might be due to distribution of temperature during calcinations. It can be observed that product aggregation is constituted by many regular particles with a variety of porosity due to the evolution large amount of gases during synthesis. The porosity of $\text{In}_2\text{O}_3$ NPs facilitates and enhances the adsorption properties. The EDX analysis (Fig. 13) exhibited clear distinguish peaks of both indium and oxygen elements from the desired detected site. The atomic percentages of these elements are 82.71% and 17.29% for indium and oxygen, respectively.

The electronic UV-Vis spectrum of synthesized $\text{In}_2\text{O}_3$ NPs was used to calculate the energy gap “$E_g$”. The spectrum display absorption band at 347 nm (Fig. 11). The $E_g$ value was estimated using the wood and Tauc plot\(^{44}\) as referred in the following equation 3:

$$\alpha h \nu = A(h \nu - E_g)^{1/2} \quad \text{Eq. (3)}$$

where “$A$” term is a constant, “$h \nu$” term is the photon energy, and “$E_g$” term is the energy gap. Plotting $(\alpha h \nu)^2$ as a function of photon energy, and extrapolating the linear portion of the curve to the absorption equal to zero as shown in the insets of Figure 11 give the value of the direct band gap ($E_g$) to be 2.99 eV for the $\text{In}_2\text{O}_3$ sample calcined at 800°C. This value is less than that of $\sim$3.6 eV for the $\text{In}_2\text{O}_3$ mentioned in the literature\(^{45-47}\). This value indicate the semiconductor behavior of $\text{In}_2\text{O}_3$ that can be used in photocatalyst applications\(^{46, 47}\).
Figure 14 shows a presented TEM image of the indium(III) caproate complex after calcination at 800°C for 3 hrs. The morphology of particles observed in the bright-field image is characterized by agglomerated NPs, most of them having a spheroidal shape. The particle size of the In$_2$O$_3$ NPs estimated by XRD was in agreement with the particle size obtained by TEM analysis (10–20 nm).

Photocatalytic degradation properties

In our study, the prepared In$_2$O$_3$ nanoscale size can be used as a photocatalyst smart material for the photodegradation of Congo Red (CR) and Crystal Violet (CV) organic dyes which are found in the wastewater of factories and rehabilitated for use in agriculture. The photocatalytic data of the In$_2$O$_3$ NPs confirm that the degradation of these dyes after 90 min for the UV-irradiation reached the maximum results ≈ 93%, and 95% for the CR and CV, respectively. The photocatalytic degradation experiments were operated at i-different contact time, ii-dose of In$_2$O$_3$ NPs adsorbent, and iii-effect of pH.

Effect of time

The effect of time on the degradation of CR and CV dyes onto In$_2$O$_3$ NPs adsorbent was investigated spectrophotometrically. These results are clearly displayed in Figure 15, which the degradable of industrial dyes (CR & CV) increased with the increasing of contact time of 90 min. The rate of adsorption is very fast at first with most of the compound being condensed during the first 45 minutes. It was found that more than >40% adsorption of dyes (CR & CV) occurred at the 90 minutes. After that the rate of adsorption was found slow. This shows that it can be assumed that the balance is achieved after 45 minutes. This is mainly due to the saturation of the active site which does not allow more adsorption to occur. In general, the adsorption capacity and the color removal efficiency of the adsorbents are directly related to the contact time, thus increasing the adsorption of the surface while increasing the contact time due to increased contact with the dye molecules (CR & CV) with the adsorbed surface. However, it reaches a fixed value at a specific time. At this moment, the amount of dyes absorbed in a dynamic balance with a quantity not absorbed by the dyes, and after this time, the amount of adsorption of the dyes by the adsorbents is almost constant. After adjust time the adsorbent was filtered from the solution for 15 min. The residual concentration of dye in solution was spectrophotometrically scanned at λ$_{max}$ = 498 nm for CR and λ$_{max}$ = 590 nm for CV (λ$_{max}$) using a UV–Vis spectrophotometer. The % Adsorption was calculated according to Eq. (1).

Figure 15. Dyes decomposition degree versus time of Congo Red (CR) and Crystal Violet (CV) dyes treated with In$_2$O$_3$ NPs at different contact time

Effect of In$_2$O$_3$ adsorbent doses

Degradation of the dyes (CR & CV) is strongly affected by the amount of In$_2$O$_3$ NPs adsorbents. The Congo Red (CR) and Crystal Violet (CV) adsorptions were studied on In$_2$O$_3$ NPs with a change in the adsorbents from 10 mg to 50 mg · L$^{-1}$ at a 90 minutes continuous stirring rate with an optimal dye concentration of 50 mg · L$^{-1}$. It was observed from Figure 16 that by increasing the dose, the adsorption of dyes (CR & CV) increased the excellent amount of adsorbents. The maximum >60% and >70% for CR and CV dyes, respectively, are adsorbed at a dose of 50 mg of adsorbents. An additional increase in the absorbed dose reduces the absorption rate. This

Figure 16. Dyes decomposition degree versus catalyst dosage of Congo Red (CR) and Crystal Violet (CV) dyes treated with different mass doses of In$_2$O$_3$ NPs
may be due to overfilling or aggregation of adsorption sites, resulting in a reduction in the available surface area of respected sites.\textsuperscript{50}

**Effect of pH value**

The pH of the photocatalytic degradation process has a significant effect on the adsorption efficiency of most organic dyes. The effect of pH on adsorption of CR & CV dyes on In\textsubscript{2}O\textsubscript{3} NPs was performed at 50 mg L\textsuperscript{-1} of primary dye concentration with a 50 mg mass of In\textsubscript{2}O\textsubscript{3} NPs adsorbent at 90 min of stirring rate at room temperature. As shown in Figure 17, In\textsubscript{2}O\textsubscript{3} nanoparticles show maximum absorption of >79\% of represented dyes at pH 12 which decreased at low acidic pH. This assures that low pH < 7 is unsuitable for dye absorption by In\textsubscript{2}O\textsubscript{3} NPs.

Based on the semi-conductor photovoltaic behavior of the catalyst, the radiation of this catalyst has a wide-band gap energy that leads to the electron pairing of the electron holes. These pairs then spread to the surface, where the electrons adsorbed hydroxide, the hole, and oxygen molecules, to form a hydroxyl radical. Before holes and electrons form on the surface, there is a great chance of recombination\textsuperscript{51}.

**CONCLUSION**

A nanoparticles of In\textsubscript{2}O\textsubscript{3} resulting from the thermal decomposition of a [In(CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{4}COO)\textsubscript{3}] complex as a precursor. The assignments of thermal analysis and FT-IR support that during the decomposition of the precursor complex a carbonate molecule is formed. The assignments of thermal analysis and FT-IR support that during the decomposition of the precursor material at temperature 800\textdegree C gives rise to nanocrystalline particles of cubic In\textsubscript{2}O\textsubscript{3} with sizes 10–20 nm. Energy band gap was calculated using UV-Vis spectroscopy. Photodegradation studies of CR and CV dyes on the surface of the In\textsubscript{2}O\textsubscript{3} NPs were performed with various parameters such as contact time, effect of adsorbent dosage, and effect of pH. The results suggest that the In\textsubscript{2}O\textsubscript{3} NPs are good photocatalyst for the removal of CR and CV dyes.

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