Effective photocatalytic degradation of dye pollution in synthetic wastewater using nanocomposites of chromium and potassium oxides

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**Electronic supplementary information**

**Abstract**

In the present work, chromium(III) oxide (Cr$_2$O$_3$) and potassium oxide (K$_2$O) nanoparticles (NPs) were synthesized using the combustion method. Mixed oxides of varying concentrations in the form of (1−$x$)Cr$_2$O$_3$/xK$_2$O ($x$ = 0.1, 0.3, 0.5, and 0.7) were prepared. X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and optical measurements were used to investigate the properties of NPs. XRD indicates that the grain size of the mixed oxides decreased as the K$_2$O content increased. Additionally, HRTEM revealed several types of shapes, such as hexagonally shaped NPs. The optical measurements showed a blue shift, indicating that the band structure was slightly modified during the Cr$_2$O$_3$/xK$_2$O mixing. The optical band gap obeys the direct allowed transition and varies from 2.29 to 2.59 eV as the K$_2$O ratio in the composites increases from $x$ = 0.1 to 0.7. The (1−$x$)Cr$_2$O$_3$/xK$_2$O NPs were used as catalysts in wastewater during a photocatalytic process. Orange G was chosen as an impurity in the water. The absorbance curves of Orange G in the water were measured at different times in the presence of the same quantity of Cr$_2$O$_3$/xK$_2$O NPs. It was found that after 120 min, the efficiency reached 11% and 33% for (1−$x$)Cr$_2$O$_3$/xK$_2$O NPs with $x$ = 0.1 and 0.7, respectively. Furthermore, the experimental results were analyzed by pseudo-first-order model. A first-order kinetic model had the best fit for the (1−$x$)Cr$_2$O$_3$/xK$_2$O NPs. The strongest relationship occurred with a composition of 0.1Cr$_2$O$_3$/0.7K$_2$O. The formed composites could be used to degrade organic dyes for water purification.

**Keywords:** Cr$_2$O$_3$; K$_2$O; High-resolution transmission electron microscopy; Photocatalysis; Optical properties; Dye pollution

1. Introduction

Environmental pollution has recently emerged as one of the most serious issues in the modern world, with a large number of people dying each year and many more suffering from chronic illnesses. Drinkable water is becoming increasingly scarce as a result of contamination of source water. Water pollution is exacerbated by the extensive presence of organic contaminants, particularly dyes, in industrial effluent from the textile, garment, leather, leather goods, footwear, and paper sectors. Moreover, artificial dyes are used in nearly every area of the consumer products industry. Furthermore, industrial effluents collected after various operations are typically highly colorful, non-biodegradable, poisonous, and carcinogenic and contain harmful colored pigments. Both artificial and organic colors are resistant to sunshine and other degradative environmental factors. Before industrial effluents are discharged into the aquatic environment, they must be remedied. In particular, dyes are discharged by many dye industries and homes through wastewater into the environment. Research is currently being conducted to develop semiconductor
photocatalysts that can be used to remedy this damage through water disinfection, hazardous waste remediation, and water purification [1–4].

Metal oxides are important in environmental science, electrochemistry, biology, chemical sensors, magnets, and other fields. Chromium oxide (Cr$_2$O$_3$) is one of the most crucial transition metal oxides and is widely used in many industries as a semiconductor photocatalyst. Chromium oxide is a p-type semiconductor with wide band gap energy (~3 eV) [5], also possesses excellent optical and electrical properties, is of low cost, chemically stable, and nontoxic, and has surface properties that affect its usage as an industrial catalyst in many reactions [6–8]. Chromium has different stable oxidation states; hence, the formation and properties of chromium oxide (Cr$_2$O$_3$) are essential for applied applications, such as in high-temperature-resistant materials [9], corrosive resistant materials [10], liquid crystal displays [11–13], green pigment, and catalytic performance was examined.

2.1. Dyes and materials

Cr(NO$_3$)$_2$·6H$_2$O (C.I. 16230, m.w. 452.37 g/mol), other fields. Chromium oxide (Cr$_2$O$_3$) is one of the most effective way to improve and control their electrical and optical properties [14]. However, the preparation of Cr$_2$O$_3$/K$_2$O catalysts has not been studied.

This study aims to prepare (1–x)Cr$_2$O$_3$/xK$_2$O nanomaterials with different K$_2$O contents. Pure K$_2$O mixed Cr$_2$O$_3$ NPs (nanoparticles) were synthesized through combustion. The structural and optical characterizations of these NPs were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), and UV-Vis spectroscopy techniques. Finally, applications of the synthesized nanomaterials, such as photocatalysts, were studied for the degradation of organicGs (Orange G). Orange G is extensively used in the textile and dyeing industries. There is no available report on the electrochemical degradation of Orange G. The effect of K$_2$O mixed Cr$_2$O$_3$ in different concentrations, quantities, and irradiation time on the photocatalytic performance was examined.

2. Materials and methods

2.1. Dyes and materials

The structure of Orange G dye (C$_{16}$H$_{16}$N$_4$Na$_2$O$_5$S), a crystal orange color anionic dye (C.I.16230, m.w. 452.37 g/mol), is illustrated in Fig. 1. Cr(NO$_3$)$_2$·6H$_2$O, K(NO$_3$)$_2$·6H$_2$O, and CO(NH$_2$)$_2$·6H$_2$O were used in the research work. All chemicals used were of an analytical grade without any additional purifications. The deionized water was used as the solvent for all experiments.

2.2. K$_2$O/Cr$_2$O$_3$ nanocomposite preparation

Combustion was used to prepare Cr$_2$O$_3$ NPs [15–17]. Then, 25 mL of a water solution containing 0.1 M Cr(NO$_3$)$_2$·6H$_2$O was mixed with 25 mL of a water solution containing 0.1 M Co(NH$_2$)$_2$·6H$_2$O. Then the mixture was heated for 20 min in a 650 W microwave oven. Cr$_2$O$_3$ NPs of green powder was extracted. The procedure was used for preparing K$_2$O NPs using 0.1 M KNO$_3$·6H$_2$O as a starting material. A mixture of Cr$_2$O$_3$/K$_2$O powder was prepared with different concentrations of (1–x)Cr$_2$O$_3$/xK$_2$O, where x = 0.1, 0.3, 0.5, and 0.7.

2.3. Characterizations

CuKα radiation (λ = 1.546 Å) was used in the X-ray (Philips PW 1710 X-ray Diffractometer) to study the crystal structure at temperatures between 5°C and 90°C. JCPDS-ICDD was used to analyze the XRD phases. High-resolution transmission electron microscopy (HRTEM, JEM-2100) was used to analyze the images of the prepared NPs. Additionally, scanning image observation was used for bright and dark-field TEM at 200 kV. Absorption was used for optical measurements at wavelengths from 200 to 900 nm.

The photocatalytic effect was illustrated by the Orange G degradation rate using (1–x)Cr$_2$O$_3$/xK$_2$O NPs, where x = 0.1, 0.3, 0.5, and 0.7. NPs as a catalyst. Then, 2 mg of these NPs was added to 3 mL of Orange G solution. The solution was added in the ultrasonic instrument for 10 min and then transferred to glass tubes under an ultraviolet lamp with a power of 6 W separated by 15 cm. The absorbance of the solution Orange G in the presence of the catalyst (1–x)Cr$_2$O$_3$/xK$_2$O NPs, where x = 0.1, 0.3, 0.5, and 0.7, was measured in a range of time of 0–120 min.

3. Results and discussion

3.1. Structural characterization

Fig. 2 depicts the XRD patterns of (1–x)Cr$_2$O$_3$/xK$_2$O NPs, where x = 0.1, 0.3, 0.5, and 0.7. The XRD analysis pattern of the (1–x)Cr$_2$O$_3$/xK$_2$O nanocomposite agrees well with standard JCPDS No. 00-026-1327 (K$_2$O) and 04-021-0178 (Cr$_2$O$_3$), confirming the existence of two phases in the single matrix. The observed diffraction peaks were monoclinic structures of Cr$_2$O$_3$ and hexagonal structures of K$_2$O. Several observations with increasing K$_2$O content can be illustrated with XRD charts. There is a shift in peaks (–112), (–204), (020), (–113), and (–316) to small diffraction angles, indicating the incorporation of K$_2$O with the Cr$_2$O$_3$ matrix. Moreover, by adding K$_2$O with varying concentrations, diffraction peaks related to the K$_2$O phase were observed at 2θ = 25.08°, 27.07°, 29.08°, 29.72°, 31.23°, and 38.76°. Lastly, the figure confirms that most of the mixture is composed of Cr$_2$O$_3$.

The size and strain of the Cr$_2$O$_3$ crystals were estimated using the Scherrer formula [18]:

Fig. 1. Orange G chemical structure.
\[ D = \frac{0.99 \beta}{\cos \theta} \]  \hspace{1cm} (1)

\[ \varepsilon = \frac{\beta}{4 \tan \theta}, \]  \hspace{1cm} (2)

where \( D \) is the crystalline size, \( \lambda \) is the radiation wavelength, and \( \beta \) is the full width at half maximum at diffraction angle \( 2\theta \). Celref unit cell software was employed to calculate lattice parameters from the XRD data. The calculated lattice parameters and \( d \)-spacing of \( \text{Cr}_2\text{O}_3 \) were compared to the standard data recorded in Card No. 04-021-0178, which are listed in Table 1. This table shows that the average crystalline size decreased with increasing \( \text{K}_2\text{O} \) concentration from 33.54 to 28.37 nm.

The HRTEM images of \((1-x)\text{Cr}_2\text{O}_3/x\text{K}_2\text{O}\), where \( x = 0.1 \) and 0.7, are shown in Fig. 3. The TEM observations provide information about shape and size. It was found that the average diameter of \((1-x)\text{Cr}_2\text{O}_3/x\text{K}_2\text{O} \) NPs, where \( x = 0.1 \) and 0.7, is ~100 and 70 nm, respectively. Different shapes, such as irregularly shaped and hexagonally shaped nanoparticles, are also visible. The inset electron diffraction pattern (SAED) taken from the selected \( \text{Cr}_2\text{O}_3 \) NPs confirms the XRD pattern.

### 3.2. Optical spectra of the nanoparticles

The changes in optical absorption spectra of \((1-x)\text{Cr}_2\text{O}_3/x\text{K}_2\text{O} \), where \( x = 0.1, 0.3, 0.5, \) and 0.7, are shown in Fig. 4. The absorption edge of the \((1-x)\text{Cr}_2\text{O}_3/x\text{K}_2\text{O} \) samples varies with the varying content of \( \text{K}_2\text{O} \) in the \( \text{Cr}_2\text{O}_3 \) nanoparticles. As \( \text{K}_2\text{O} \) content increases, a blue shift of the optical band gap can be clearly observed, which indicates a minor modification in the band structure when mixing \( \text{Cr}_2\text{O}_3/x\text{K}_2\text{O} \). The absorption coefficient \( \alpha \) was calculated for each wavelength using the following equation [19]:

\[ \alpha = \frac{2.3 A}{t} \]  \hspace{1cm} (3)

where \( A \) is the absorbance equal to \( \log I_0/I \) (according to Beer–Lambert’s law), \( t = 1 \) cm is the path length, and \( I_0 \) and \( I \) are the intensity of incident and transmitted light, respectively.

The dependence of absorption spectra on the optical band gap energy \( (E_g) \) was described by Tauc’s expression [19,20]:

\[ a h \nu = \beta \left( h \nu - E_g \right)^r \]  \hspace{1cm} (4)

where \( \beta \) is the constant and \( r = \frac{1}{2} \) for direct transition due to photon absorption. The plot of \( (a h \nu)^2 \) vs. \( h \nu \), as shown in Fig. 5, is linear at the absorption edge, indicating a direct transition. The energy gap is determined by extrapolating the straight-line portion of the energy axis at \( (a h \nu)^2 = 0 \). It is observed that the resultant values of \( E_g \) range from 2.29 to 2.59 eV as the \( \text{K}_2\text{O} \) content increases from \( x = 0.1 \) to \( x = 0.7 \) as shown in Fig. 5.

### 3.3. Photocatalysis applications of \( \text{Cr}_2\text{O}_3/\text{K}_2\text{O} \) NPs

Photocatalytic debasement is a procedure for disposing of both organic and inorganic contaminants in wastewater,
where distinctive nanoparticles are utilized to eliminate these contaminants. Metal oxides are particularly effective catalysts on the other hand; mixed NPs could have an even greater efficiency. Therefore, \((1-x)\text{Cr}_2\text{O}_3/x\text{K}_2\text{O}\) NPs, where \(x = 0.1, 0.3, 0.5,\) and 0.7, were tested as catalysts with varying contents of \(\text{K}_2\text{O}\) NPs. Fig. 6 shows Orange G absorption spectra for \((1-x)\text{Cr}_2\text{O}_3/x\text{K}_2\text{O}\) NPs, where \(x = 0.1, 0.3, 0.5,\) and 0.7 at various exposure times. It can be seen that the absorbance of Orange G is distinguished by one peak at 480 nm. Moreover, these spectra show that Orange G was diminishing as the UV light time increments for each \((1-x)\text{Cr}_2\text{O}_3/x\text{K}_2\text{O}\) NP, where \(x = 0.1, 0.3, 0.5,\) and 0.7. To quantify the impact of \(\text{K}_2\text{O}\) content \((x)\), the photocatalytic efficiency \((\eta\%)\) of Orange G was determined with the following equation \([21,22]\):

\[
\eta\% = \frac{C_i - C_t}{C_i} \times 100 = \frac{A_i - A_t}{A_i} \times 100
\]

where \(C_i\) is the initial Orange G concentration, \(C_t\) is the residual Orange G concentration after the specified time,
\( A_i \) is the initial Orange G absorbance, and \( A_t \) is the residual Orange G absorbance after the specified irradiated time. Fig. 7 shows the photocatalytic efficiency of Orange G with \((1-x)Cr_2O_3/xK_2O\) NPs, where \( x = 0.1, 0.3, 0.5, \) and \( 0.7.\) Photocatalytic degradation occurred with a maximum of 35.6\% after irradiation time of 120 min at \( x = 0.7.\) The photocatalytic process [23] is explained as a photoinduced molecular transformation occurring at the surface of the metal oxide NPs. As shown in Fig. 8, the electron–hole pair is generated when light is utilized in the photocatalytic process. When the catalyst is exposed to UV light with higher energy than its band gap, the electron is transported to the conduction band, creating a hole in the valence band. These holes are important for photocatalysis because they are a source of oxidized hydroxyl radicals that react to the electrons in the dyes [17,24].

The following equations describe the previous procedures [25]:

\[
\text{catalyst} \left( \frac{Cr_2O_3}{K_2O} \right) + h\nu \rightarrow e^- + h^+
\]

(6)

![Fig. 4. UV-Vis Spectrum of \((1-x)Cr_2O_3/xK_2O\) (\( x = 0.1, 0.3, 0.5, 0.7\) NPs.)](image)

![Fig. 5. Plot of \((\alpha h\nu)^2\) vs. photon energy \((h\nu)\) for different concentration of \((1-x)Cr_2O_3/xK_2O\) NPs where \( x = 0.1, 0.3, 0.5, 0.7\).](image)
The \( \ln(C/\text{Co}) \) as a function of the irradiation time, \( t \), is calculated by [25]:

\[
\ln\left(\frac{C}{\text{Co}}\right) = -kt + K \text{C}_i \tag{11}
\]

where \( \text{C}_i, \text{C}_0 \) are the primary dye concentration and the rest concentration after irradiation light, \( t \), \( k \) is the first-order reaction rate constant, and \( K \) is the degradation equilibrium at light constant. Fig. 9 illustrates the straight line produced by Eq. (11), which describes the semi-logarithmic relationship between absorbance and irradiation time.

\[
e^- + \text{O}_2 \rightarrow \text{O}_2^2^- \tag{7}
\]

\[
h^+ + \text{Orange G} \rightarrow \text{degradation product} \tag{8}
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+ \tag{9}
\]

\[
\text{OH}^- + \text{Orange G} \rightarrow \text{degradation product} \tag{10}
\]
between the Orange G concentrations as a function of the irradiation time. This formula can be used to compute the degradation equilibrium constant ($K$) and the degradation rate constant ($k$) [25] which is listed in Table 2. The determined values of the $k$ and $K$ constants are shown in Table 3.

For Orange G, it was discovered that these $k$ and $K$ constants were reliant on UV light exposure as well as $K_2O$ content.

The mass of Orange G degraded per unit of $(1-x)Cr_2O_3/xK_2O$ NPs ($q$, mg/g) at a fixed time and equilibrium state were calculated using the following equations [26]:

$$q = (C_i - C_r) \frac{V}{W},$$

where $q$ is the quantity of degraded Orange G at time ($t$) in mg/g, $C_i$ and $C_r$ are the initial and residual concentration of degraded Orange G at time ($t$), respectively. $V$ is the volume of the solution in L, and $W$ is the mass in g.

Fig. 9. Semi-logarithmic graph of Orange G concentration vs. irradiation time in the presence of $(1-x)Cr_2O_3/xK_2O$ ($x = 0.1, 0.3, 0.5, 0.7$) NPs.

Table 2

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<th>$k$</th>
<th>$K$</th>
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<tr>
<td>0.7</td>
<td>0.68</td>
<td>0.00120</td>
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Table 2. The absolute values of first-order reaction rate constants ($k$) and degradation equilibrium constant ($K$), for Orange G dye of $(1-x)Cr_2O_3/xK_2O$ nanoparticles.

4. Conclusions

Different compositions of $(1-x)Cr_2O_3/xK_2O$ composites, where $x = 0.1, 0.3, 0.5$, and 0.7 wt.%, were synthesized using the microwave irradiation method. The structural parameters, optical band gap, $E_g$, and their photocatalytic degradation of Orange G were investigated. From the XRD data, the samples are crystalline and have monoclinic structures.
The prepared (1–\(x\))Cr\(_2\)O\(_3\)/K\(_2\)O wastewaters were investigated using (1–\(x\))Cr\(_2\)O\(_3\)/K\(_2\)O NPs, where \(x = 0.1, 0.3, 0.5, \) and 0.7. The efficiency obtained with (1–\(x\))Cr\(_2\)O\(_3\)/xK\(_2\)O, where \(x = 0.1\) and 0.7, was 11% and 33%, respectively. The prepared (1–\(x\))Cr\(_2\)O\(_3\)/xK\(_2\)O composites could qualify for the degradation of some organic dyes for water purification assisted by UV irradiation.

References


