

Normal spinel CoCr_2O_4 and $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ nanocomposite as novel photocatalysts, for degradation of dyes

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For the first time, $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ nanocomposite as a novel photocatalyst with different TiO_2 contents have been prepared by the sol–gel method. The techniques of X-ray diffraction (XRD), scanning electron microscopy and transmission electron microscopy (TEM) have been employed to characterise the synthesised nanocatalysts. The XRD and TEM results indicated that CoCr_2O_4 has a cubic normal spinel structure and the particle size of CoCr_2O_4 is about 30 nm. As the first report, degradation of methylene blue and methyl orange is performed by CoCr_2O_4 and $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ nanocomposite under ultraviolet irradiation. The results showed that the rate of degradation of dyes with $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ is much higher compared with that of CoCr_2O_4 and TiO_2 . The photocatalytic activities were carried out under varying parameters such as irradiation time, the pH of the solution, the catalyst amount and substrate concentration.

1. Introduction: Spinel represents a large class of inorganic materials which possess many important properties not found in the more limited binary oxides. Spinel occurs in a wide variety of igneous and metamorphic rocks on the earth and other planets, making it a valuable indicator of petrological processes. Cobalt chromite has been widely used in dyes, as a catalyst, and as a substrate for preparation of film [1]. Synergetic effects in Co-based mixed oxide catalysts have been reported, which were rationalised on the basis of enhanced electron transfer and oxygen non-stoichiometry in these oxides [2]. Obviously, the preparation methods play a crucial role in the catalytic performance of mixed oxides. Photocatalyst systems using metal oxides have been extensively studied to aid the degradation of inorganic and organic pollutants in air and water and for several other applications [3–5].

Titanium dioxide has attracted much attention recently in the field of photocatalysis. Titania is a wide bandgap semiconductor with many interesting properties, such as transparency to visible light, a high refractive index and low absorption coefficient but its photocatalytic activity is limited by fast electron–hole recombination. Hence, research efforts in enhancing the photocatalytic efficiency of TiO_2 have come from extensive research performed by chemists, physicists and chemical engineers. The modification methods of photocatalyst involve noble metal deposition [6, 7], transition-metal ions doping [8, 9], coupled semiconductor systems [10, 11] etc. Wastewater contains two main types of pollutants, namely toxic metal ions such as Mn^{7+} , Cr^{6+} and Hg^{2+} [12] and organic compounds [13], among which dyes must be emphasised because of their toxicity and prevention of light penetration into contaminated water. In our previous works, we have attempted to decompose methylene blue (MB) and Eosin Y on wool and cellulosic fibres coated with $\text{TiO}_2/\text{ZrO}_2$ and Ag–Zr co-doped TiO_2 , respectively [14, 15]. To the best of our knowledge, cobalt chromite powder coupling with TiO_2 has not been reported so far. Thus, in this study, $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ nanocomposite was synthesised via sol–gel and its photocatalytic properties under ultraviolet–visible (UV–vis) light irradiation for degradation of MB and methyl orange (MO) were investigated to provide useful information for developing new types of highly active photocatalysts under irradiation.

2. Experimental

2.1. Photocatalysts preparation: CoCr_2O_4 was synthesised by the sol–gel method. First, 50 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 100 mmol $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved together in 50 ml of deionised water to obtain a mixed solution. Next, the mixed solution was

added into 100 ml 0.3 M of citric acid under stirring. The temperature was controlled at 50°C by using a water bath. Then the temperature was further kept at 95°C until a transparent and viscous gel was obtained. The as-obtained gel was subsequently transferred into an oven and kept at 110°C for 2 h. The as-prepared precursor was then calcined at 600°C for 3 h with a heating rate of 6°C/min. A $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ heterojunction was synthesised via the same route by adding a certain amount of fully anatase phase of TiO_2 in the raw materials preparation when the transparent mixed sol had been obtained.

2.2. Photocatalytic reactor set up and degradation procedure: The photocatalytic activity was tested by the degradation of MB and MO. The light was provided by a 400 W high pressure Hg lamp without a filter which was placed vertically in the reactor. The temperature of the photodegradation system was adjusted using a water bath in which heating or cooling water circulated through the jacket of the beaker. The pH was adjusted by using sulphuric acid (Merck) and ammonium hydroxide (Merck). Prior to illumination, the reaction suspension was stirred continuously in darkness for 50 minutes to ensure adsorption/desorption equilibrium. After irradiation, dye solutions were removed from the photocatalysts by centrifuge and were analysed MB quantitatively by measuring the absorbance at 664 nm and MO at 464 nm by means of a RAYLEIGH (UV-1800) UV–vis scanning spectrometer.

2.3. Characterisation of cobalt chromite catalyst: The crystal phase of the as-prepared products was identified by the powder X-ray diffraction method (XRD, D8 Bruker Advanced) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$). The patterns were collected in the range of ($2\theta = 10\text{--}80$), and continuous scan mode. Scanning electron microscopy (SEM) images were obtained on a Philips XL30 equipped with an energy dispersive X-ray spectroscope. The microstructural morphology of the final products was characterised with a Philips CM10 transmission electron microscope (TEM) by using a Cu grid operated at 100 kV.

3. Results and discussion

3.1. Characterisation

3.1.1 X-ray diffraction: Fig. 1 describes the XRD patterns of the synthesised photocatalysts. The diffraction peaks of these samples are strong and broad, indicating good crystallinity and small particle size. The diffractions of cobalt chromite can be indexed to the spinel-type CoCr_2O_4 ; JCPDS Card No. 22–1084 and the anatase

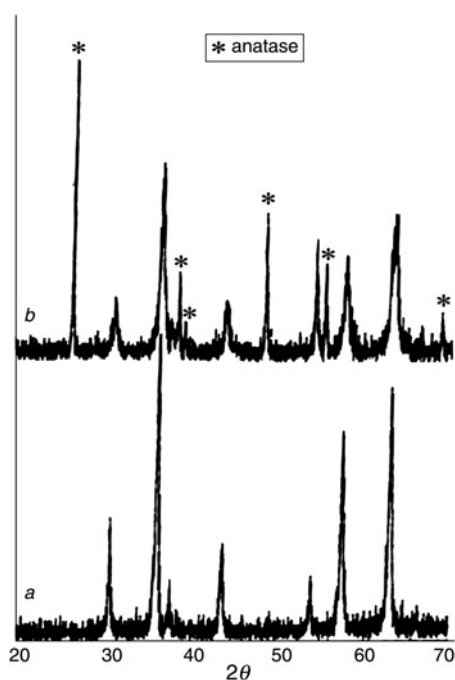


Figure 1 XRD patterns of the nanocomposites after calcination at 600°C temperature for 3 h
 a CoCr₂O₄
 b CoCr₂O₄/TiO₂ (7:10)

phase of powder is matched to JCPDS Card No. 73–1764. The presence of the diffraction peaks of TiO₂ and CoCr₂O₄ in the CoCr₂O₄/TiO₂ (7:10) composite indicates TiO₂ and CoCr₂O₄ crystallite phases separate from each other. The average particle size was estimated by applying the Scherrer formula on the major intense peak

and is found to be about 30 nm: $D = K\lambda/\beta \cos \theta$, where D is the crystal size of the catalyst, λ is the X-ray wavelength (1.54 Å), β is the full-width at half-maximum of the catalysts, $K = 0.89$ and θ is the diffraction angle. Indeed, the addition of anatase powder to the cobalt chromite sol resulted in both a broadened and crystallinity degree of all spinel phase peaks.

3.1.2 SEM-energy dispersive X-ray spectroscopy (EDX) and TEM micrographs: The morphology of the CoCr₂O₄ and CoCr₂O₄/TiO₂ were determined by SEM and TEM micrographs. SEM micrographs of CoCr₂O₄ and CoCr₂O₄/TiO₂ (7:10) nanocomposites are shown in Figs. 2a and b, respectively. It can be seen that CoCr₂O₄/TiO₂ (7:10) nanocomposites have larger size than pure CoCr₂O₄. It is also observed that nanocomposites are of pseudo-spherical shapes, with a particle size distribution of 30–50 nm. All samples present strong agglomeration when seen by SEM. TEM images of the pure CoCr₂O₄ and CoCr₂O₄/TiO₂ (7:10) nanocomposite calcined at 600°C is presented in Figs. 2c and d, respectively, which reveal that the particles exhibit cubic morphologies. The average particle size of the catalysts is about 30 nm, which is consistent with the XRD analysis. It can be seen that the CoCr₂O₄ and TiO₂ crystallite particles in the composite are homogeneously dispersed. The EDX data of the CoCr₂O₄ and CoCr₂O₄/TiO₂ (7:10) nanocomposites is shown in Fig. 3. As shown in Fig. 3b, there is an intense peak about 4.5 keV presenting a TiO₂ separate phase in the CoCr₂O₄ powder.

3.2. Photocatalytic procedure: Various conditions were tested for degradation of MB and MO. From Fig. 4, it can be seen that there was no considerable reaction rate when the irradiation was carried out in the absence of photocatalysts. However, it was found that about 15% concentration of MO was degraded under illumination without photocatalyst after 90 min. Direct photolysis of pollutants and dyes has already been reported in previous papers [16–18]. However, there is no report of any reason for this

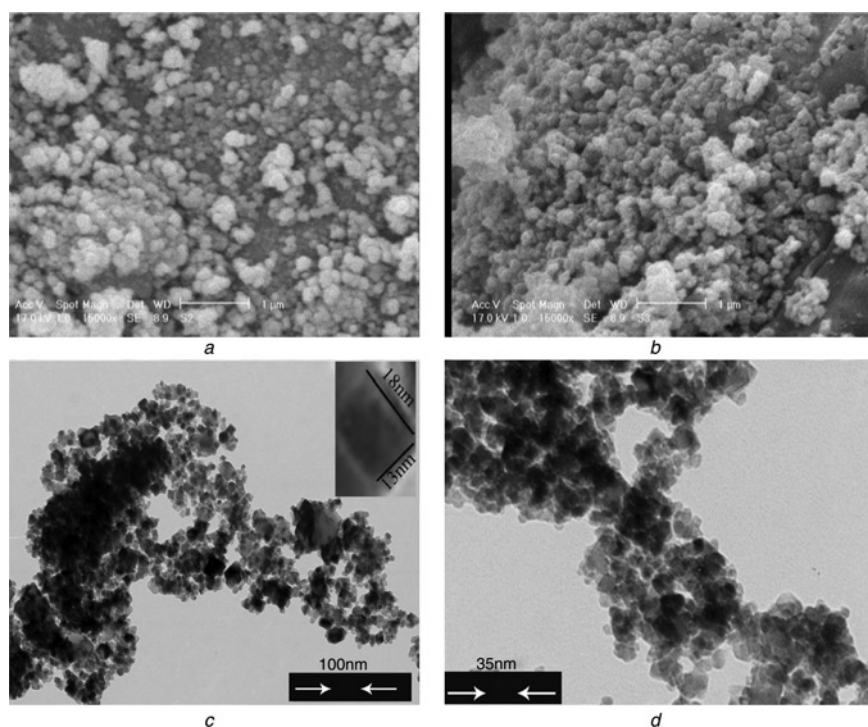


Figure 2 Micrographs of SEM
 a CoCr₂O₄
 b CoCr₂O₄/TiO₂ (7:10) and TEM
 c CoCr₂O₄
 d CoCr₂O₄/TiO₂ (7:10) samples calcinated at 600°C

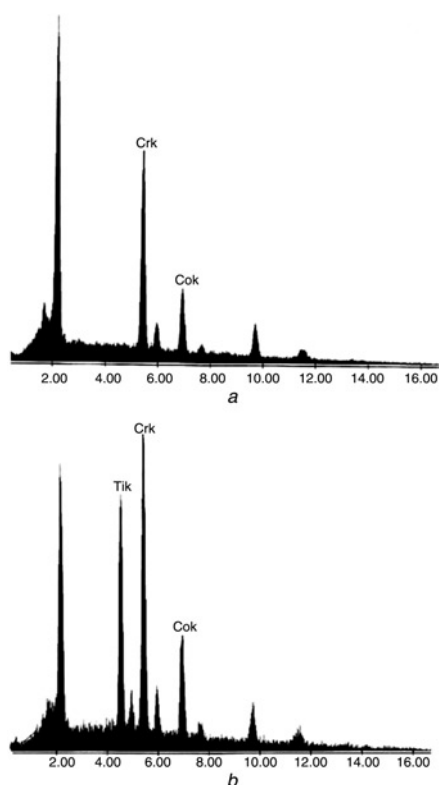


Figure 3 EDX patterns of powders
a CoCr_2O_4
b $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ (7:10)

manner. It may be because of the destruction of MO under UV-vis irradiation. In non-irradiated suspension, there was a slight loss, because of adsorption onto nanocomposite particles. However, in the presence of nanocomposite, a rapid degradation of MB and MO occurred by irradiation. In addition, the photocatalytic activity of pure TiO_2 was tested for decomposition of MB and MO, the results are shown in Fig. 5. As seen, pure TiO_2 can also decompose MB and MO. However, the performance of $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ nanocomposite is much higher than that of TiO_2 . This difference is seen to be better for degradation of MO than MB. A possible reaction model of the $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ heterojunction is proposed as shown in Fig. 6. For both the pure CoCr_2O_4 and

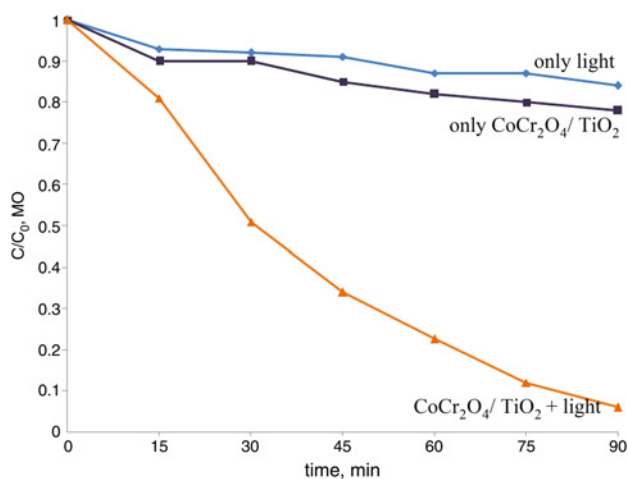


Figure 4 Photocatalytic degradation of $[\text{MO} = 1.52 \times 10^{-5} \text{ M}$ and catalysts dosage 20 mg]

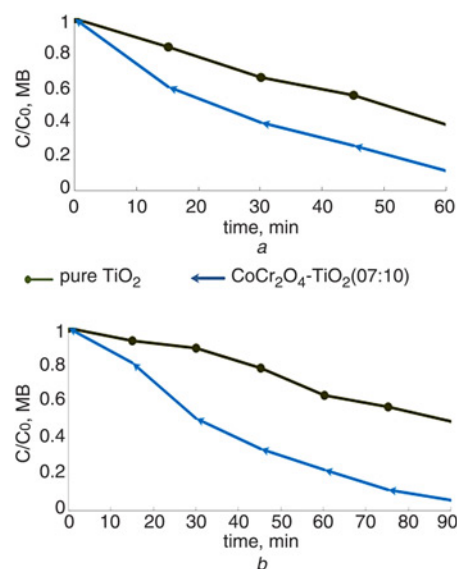
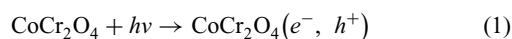


Figure 5 Activity of pure TiO_2 and $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ (7:10) nanocomposite
a MB = 3 ppm
b MO = 5 ppm, catalysts dosage 20 mg and neutral pH

$\text{CoCr}_2\text{O}_4/\text{TiO}_2$ heterojunction, mainly CoCr_2O_4 can be activated under light irradiation



During the photocatalytic process, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with adsorbed species. Specially, h^+ (vb) may react with

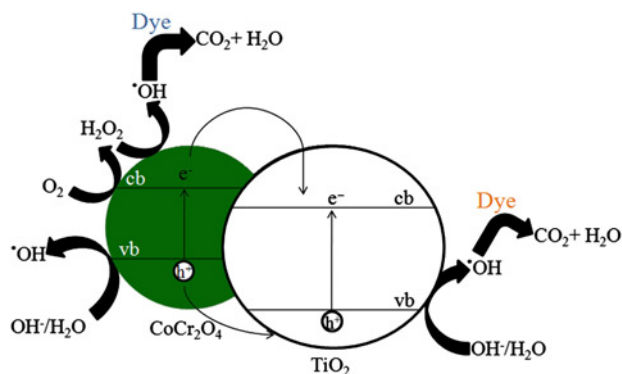


Figure 6 Energy level of nanocomposite and degradation mechanism

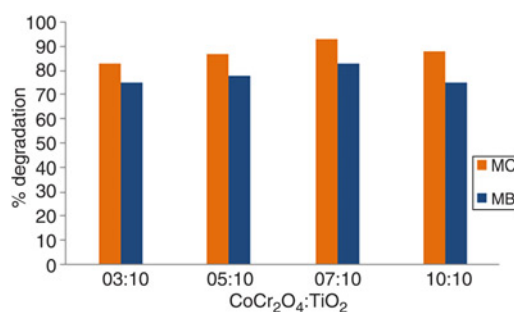


Figure 7 Degradation of MB and MO against $n\text{CoCr}_2\text{O}_4:n\text{TiO}_2$ [catalysts dosage 20 mg, neutral pH, initial concentration of MB = 9×10^{-6} and MO = 1.52×10^{-5}]

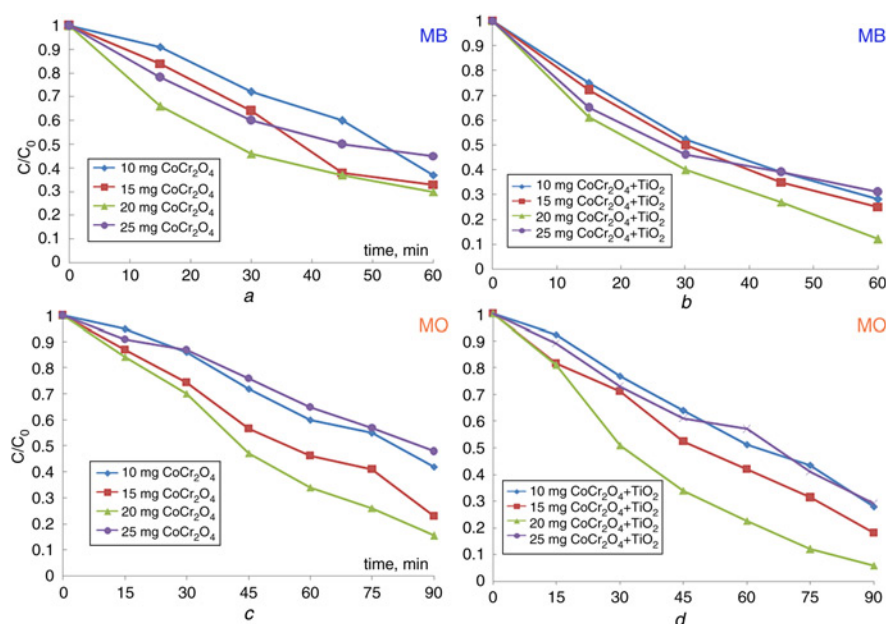
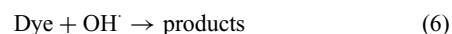
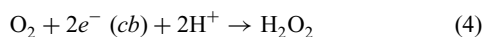
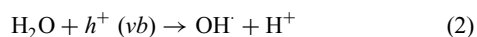


Figure 8 Effect of catalysts dosage on the degradation of MB
a CoCr₂O₄
b CoCr₂O₄/TiO₂ (7:10) and MO
c CoCr₂O₄
d CoCr₂O₄/TiO₂ (7:10) [initial concentration of MB = 9×10^{-6} M, MO = 1.52×10^{-5} M and neutral pH]

surface-bound H₂O or OH⁻ to produce the hydroxyl radical (OH[•]) and e⁻ (cb) is picked up by electron accepting species



It has been suggested that the hydroxyl radicals (OH[•]) is the primary oxidising species in the photocatalytic oxidation processes. These oxidative reactions would result in the removal of organic

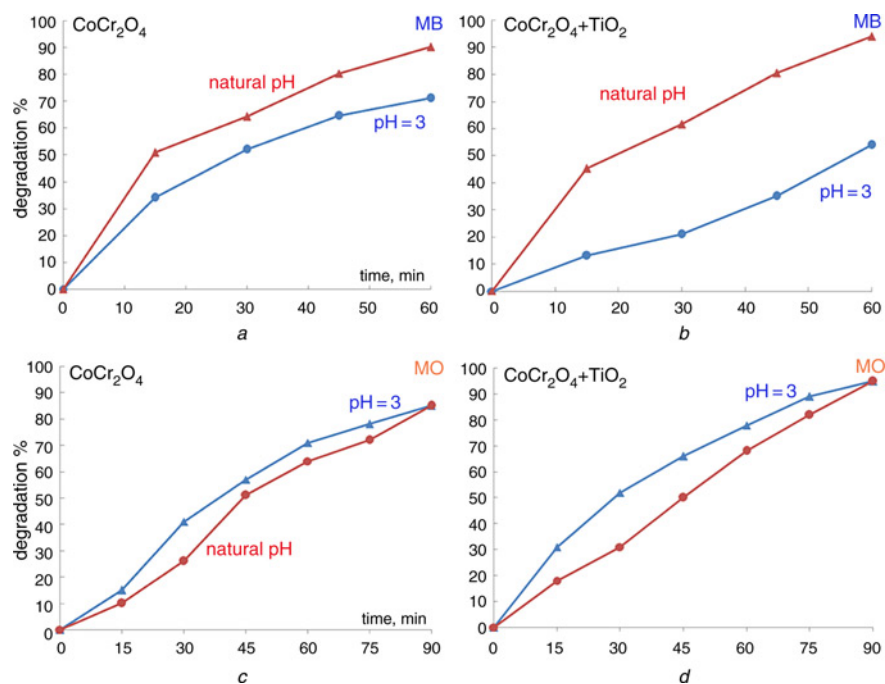


Figure 9 Effect of initial pH on the photocatalytic processes of MB
a CoCr₂O₄
b CoCr₂O₄ /TiO₂ (7:10) and MO
c CoCr₂O₄
d CoCr₂O₄/TiO₂ (7:10) [initial concentration of MB = 9×10^{-6} M, MO = 1.52×10^{-5} M and catalysts dosage 20 mg]

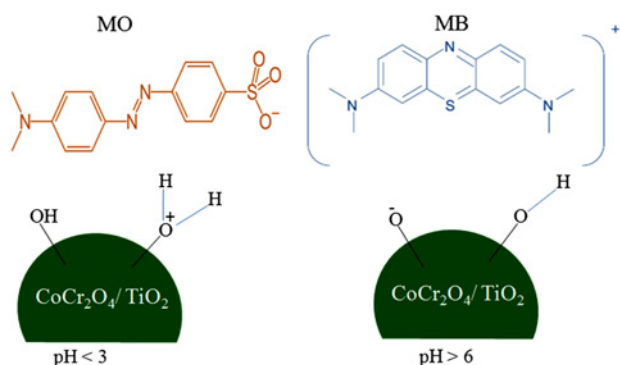
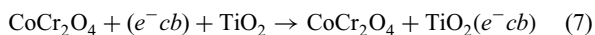


Figure 10 Adsorption of MB and MO on the $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ surface

compounds such as dye [19]. Since the Schottky barrier formed between the interface of CoCr_2O_4 and TiO_2 , the heterojunction can improve the separation of the photo-generated electrons and holes. When coupled with TiO_2 , the photo-generated electrons are injected from excited CoCr_2O_4 into the conduction band of TiO_2



As a result, the $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ heterojunction with an appropriate $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ ratio can enhance the separation of the photo-generated electrons and holes, and therefore improve the dye degradation.

3.2.1 Effect of $n\text{CoCr}_2\text{O}_4:n\text{TiO}_2$: Access to the best molar ratio of nanocomposite was achieved by using 20 mg of all catalysts for degradation of MB and MO at a neutral pH. Fig. 7 indicates that the highest amount of MB and MO degradation was found on the nanocomposites with a $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ molar ratio of 7:10.

Indeed, there is no significant difference between various molar ratios. Finally, to access maximum degradation we decide to use the 7:10 molar ratio for all degradation experiments.

3.2.2 Effect of catalyst dosage: Catalyst dosage in photocatalytic processes is an important factor that can strongly influence the dye degradation. Experiments were performed with different concentrations of CoCr_2O_4 and $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ (7:10). The results are shown in Fig. 8. It can be seen that the $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ (7:10) nanocomposite is stronger than the bare CoCr_2O_4 for degradation of MB at a neutral pH. Furthermore, MO is decomposed at a longer time compared with MB. Photodegradation efficiency increased with an increase in the nanopowder concentration up to 20 mg and then decreased as observed. This observation can be explained in terms of the availability of active sites on the catalyst surface and the penetration of light into the suspension. The total active surface area increases with increasing catalyst dosage. At the same time, there is a decrease in light penetration as a result of increased scattering effect because of an increase in the turbidity of the suspension [20]. As a result the photoactivated volume of suspension decreases.

3.2.3 Effect of pH: The pH of the solution is an important parameter in the photocatalytic reactions taking place on the surface of the particles as it dictates the charge on the particle surface and the size of the aggregate it forms. For investigation of the pH parameter on the degradation rate three values of pH were tested. Degradation results of MB and MO under acidic and neutral conditions are shown in Fig. 9. Spinels are soluble in basic conditions and it cannot be possible to have a heterogeneous catalyst. Finally, comparative experiments were performed at pH values 3 and 6. The increasing pH value results in a higher adsorption amount of MB on the photocatalyst surface. This statement is in good agreement because of cationic MB. On the other hand, MO adsorption as an anionic dye on nanocomposite is better in an acidic medium than a neutral condition. As shown in Fig. 10, in acidic media the surface of the catalyst is covered by more positive charge and

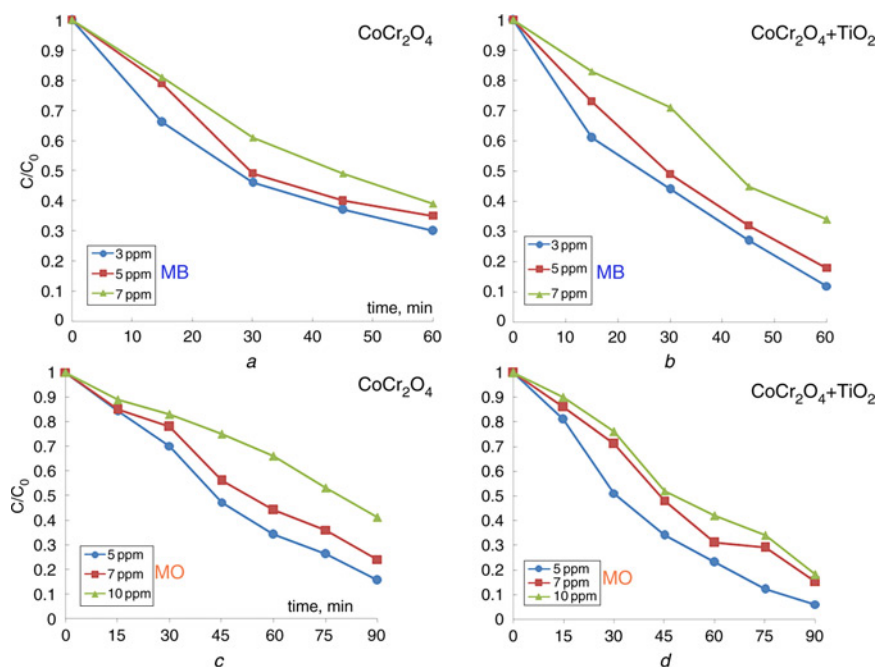


Figure 11 Effect of initial concentration MB

- a CoCr_2O_4
- b $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ (7:10) and MO
- c CoCr_2O_4
- d $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ (7:10) [catalysts dosage 20 mg and neutral pH]

subsequently anionic molecules can be absorbed better on the surface [21, 22]. Subsequently, it can be seen that maximum degradation for MB was achieved in the neutral condition, whereas MO can better decompose in acidic pH.

3.2.4 Effect of initial concentration of MB and MO on degradation: It is important from an application point of view to study the dependence of degradation on the initial concentration of dye. Fig. 11 shows the effect of initial concentrations of MB and MO on photocatalytic degradation efficiency. It can be seen that colour removal efficiency decreased as initial dye concentration increased. The possible explanation for this behaviour is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases. Thus the photocatalytic degradation efficiency decreases [23–25]. However, in low concentration the reverse effect is observed, thereby increasing the number of photon absorptions by the catalyst.

4. Conclusions: Normal spinel CoCr_2O_4 and $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ nanocomposites, as novel photocatalysts, were synthesised by the sol-gel method. It is observed that nanocomposites are in pseudospherical shapes, with a particle size distribution of 30–50 nm. Various conditions were tested for degradation of MB and MO. Several parameters such as irradiation time, pH, catalyst dosage and initial dye concentration were investigated. The results showed that MB and MO were not decomposed without light irradiation. Parent CoCr_2O_4 or TiO_2 displayed poor photocatalytic activity for MB and MO degradation from aqueous solution under UV-vis irradiation. However, after coupling, the $\text{CoCr}_2\text{O}_4/\text{TiO}_2$ heterojunction shows much improved photocatalytic activity. Photodegradation efficiency increased with an increase in nanopowder concentration up to 20 mg. In addition, it can be seen that colour removal efficiency decreased as initial dye concentration increased.

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