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Photocatlytic oxidation of congo red dye by using Co_2O_3–Cr_2O_3 as a Photocatalyst

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Abstract

Homogeneous crystalline chromium and cobalt oxides (Cr_2O_3- Co_2O_3) was prepared by co-precipitation method by mixing metals nitrate in the basic medium and the precipitate was calcinated at 700 ^oC for 6 hrs. The crystalline structure of the synthesized products were analyzed by X-ray diffraction (XRD). The obtained XRD patterns of specimens revealed formation of a well-crystallized structure of double oxides after calcination at 700 ^oC. The photocatalytic activity of double prepared oxides was investigated via following removal of congo red dye from the aqueous solution upon irradiation of reaction suspension under irradiation with UV light. .

Keywords; co-precipitation method, XRD-diffraction, Congo red, chromium and cobalt oxides photocatalytic oxidation.

Introduction

There are many industrial applications for Dyes and pigments such as, their usage as colorant material for artificial fibers, paper, and textiles, as well as their applications as plasticizers in the plastics manufactures[1]. There are many classes of synthetic organic pigments which have wide uses in the different fields of industry. Theses classes of dyes are Azo dyes, which are one of the important classes of

synthetic organic pigments utilize in manufactured coloured productions Worldwide. now the Organic dyes appear in many industrial effluents[2] because use of these dyes along with lots of water in textile industries has resulted in the production of polluted and coloured waters being discharged into the environment (nearby land or rivers) without any treatment because the conventional treatment methods are not Effective[2,3]. These coloured compounds are aesthetically objectionable and inhibiting sunlight penetration into these waters (e.g. streams, rivers etc)[4].

Ground-water are also affected by these pollutants because of leaching from the soil. Congo red one of important dye that can be found in wastewater have higher solubility in the water about 1 g/30 mL[5]. There are many Various physical and chemical techniques have been employed to eliminate dyes from wastewaters, like adsorption[4,5], reverse osmosis[6], coagulation[7], flocculation[8], membrane technology[7,8,9], biological treatments, and photo catalytic oxidation but in developing countries, these methods are still too expensive to be used widely. but photo catalytic oxidation Among these methods Various is the utilize most in the wastewater treatment (purification, decolorization and the removal of toxic organics)[10], because efficient, economical, safety and achieve the reaction with ambient temperature and atmospheric pressure[11].

The photocatalyst that is used in these fields, have two bands, valance band filled by electrons in lower orbitals and conduction band which is impute from electrons in higher orbitals, separation between these two bands gape called gape energy. When the particle of photo catalyst irradiation with light have energy equal or more the band gape. The electron in the valance band is transferred from valance band to the conduction band leaves its location positive hole. Generally, the pairs (electron-hole) enter in many reactions as shown in the following mechanism[12]:

$$\text{semiconductor} + \text{light} > \text{or} = (BG) \longrightarrow e^- + h^+ \quad .....(1)$$

$$O_2 + e^- \longrightarrow 2\cdot O^- \quad .....(2)$$

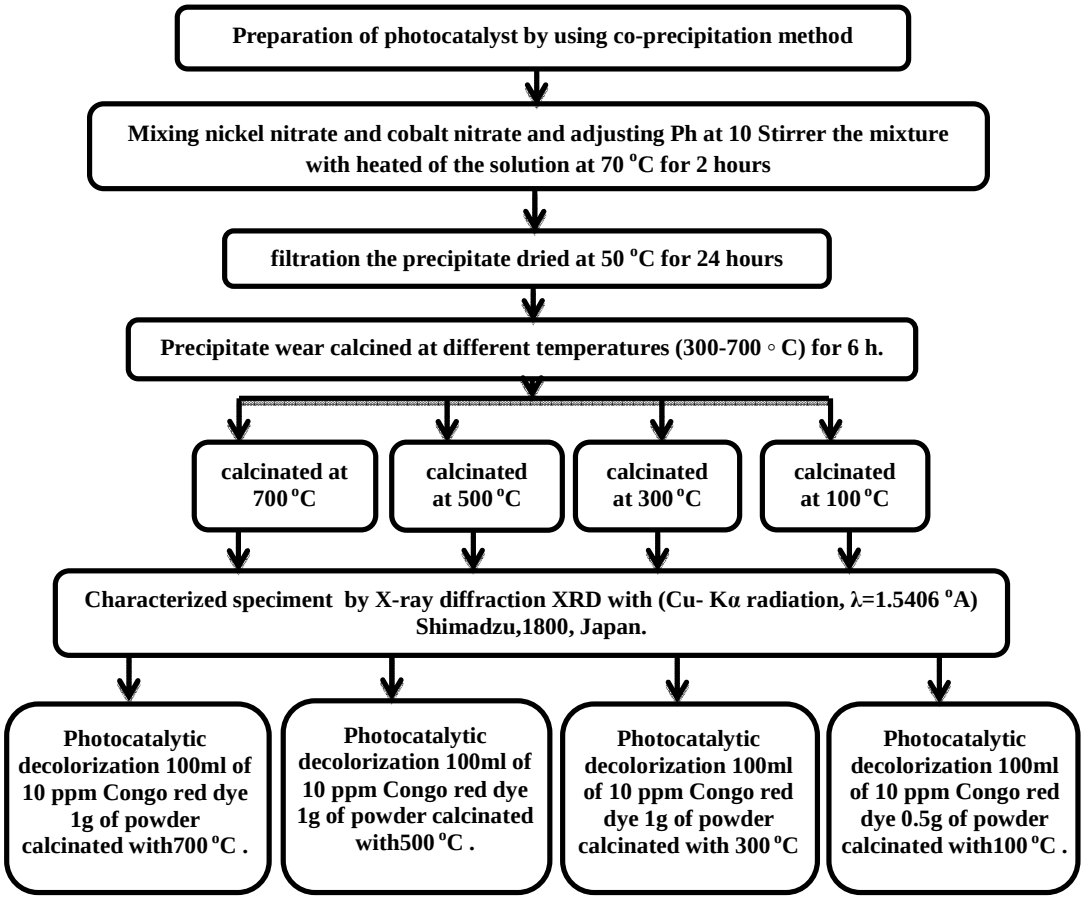
$$H_2O + h^+ \longrightarrow \cdot OH + H^+ \quad .....(3)$$

$$OH^- + h^+ \longrightarrow \cdot OH + \quad .....(4)$$

$$\cdot OH + H^+ \longrightarrow \cdot OH_2 \quad .....(5)$$

The super oxide anion and hydroxide radicals which are generated in equation reaction 2 and 4 are important in the oxidation process because haves more activity compare with generated others radicals. In the present work, we tried the synthesis of (nickel Oxide - cobalt oxide) as couple photo catalyst by co-precipitation method, and evaluate the prepared material, characterization, and examination of its activity in photooxidation of the Congo red dye.

Experimental Design :



Preparation Congo red dye Solution

Congo red dye (Chemical formula=$C_{23}H_{22}N_6O_6S_2Na_2$, Formula weight=696.65g.mol^{-1}) supplied by BHD Chemicals. The solution of Congo red were prepared by dissolving appropriate amounts (accurate weighed) of dry powdered dye in double distilled water to prepare Stock solution (100 mg L^{-1}). The experimental solution was obtained by dilutions were made to obtain the working solution at desired concentrations[13].

Photocatalytic studies

Photocatalytic decolorization of Congo red dye was carried out in glass reactor with an outer jacket for water circulating. A sample of 0.2 g of prepared catalyst was suspended by stirring magnetically in 100ml of 10ppm aqueous CR solution. The solution was stirred in drake for 30 minutes to attain adsorption desorption equilibrium, and it was irradiated using 125 watt middle pressure mercury lamp. The irradiation was carried out in the unit show in the picture.1, for 90 minutes. Then these samples were centrifuged at 15,000 rpm to remove suspended catalyst particles, and then analyzed using a UV-VIS spectrophotometer

(UV/VIS-JENWAY,1600, Jerman), was used for measuring absorbance at different time intervals. The efficiency of dye removal was calculated from following equation:

$$removal\% = \frac{(A^\circ - A)}{A^\circ} \times 100...$$

A^o and A is the absorption of concentration of dye before and after irradiation respectively[14]. A graph of photocatalytic decolorization Congo read percentage versus time (hour) was plotted for Congo red.

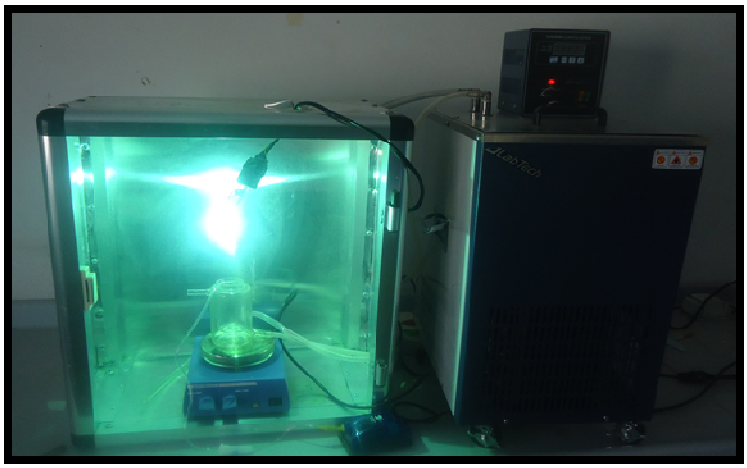


Plate1: the unit that used in the photo decolonization of Congo red dye by use the new prepared couple semiconductor.

Results and discussion

The XRD patterns of the prepared coupled oxides powders that were calcinated at different temperatures are shown in Fig. 1.

There are many peaks broad and sharp with different intensities were observed in the diffractograms, which indicating formation of fine single phase of coupled oxides structure, A few characteristic peaks of cobalt and cromium oxides[15] were also observed in the diffractograms. The XRD results revealed that an increase in calcination temperature leads to a considerable increase in peak intensity. Meanwhile, the widths of the diffraction peaks become narrower (The diffraction peaks are continuously getting sharper) with the increase of calcination temperature, indicating that the grain size become larger when calcination temperature was increased from 100 ^oC to 700 ^oC . Scherrer formula [15], and the phases and the mean size are listed in Table 1

$$D = K\frac{\lambda}{\beta}\cos\theta$$

Where the K is Sharpe factor, λ is λ is the wavelength of X-ray radiation (λ = 0.154 nm), β is the line broadening at the half maximum intensity (FMWH) in the radian, and θ is Bragg angle. generally the practical size at maximum intensity was found 40.8nm.

Table. 1. shows that the mean size of prepared coupled oxides.

Temperature ^{o}C	Peak position	Intensity	grain size (nm)
100	**……..**	**……**	**……..**
300	**59.04**	**0.282**	**53.5**
500	**59.44**	**0.306**	**79.5**
700	**59.1**	**0.353**	**83.7**

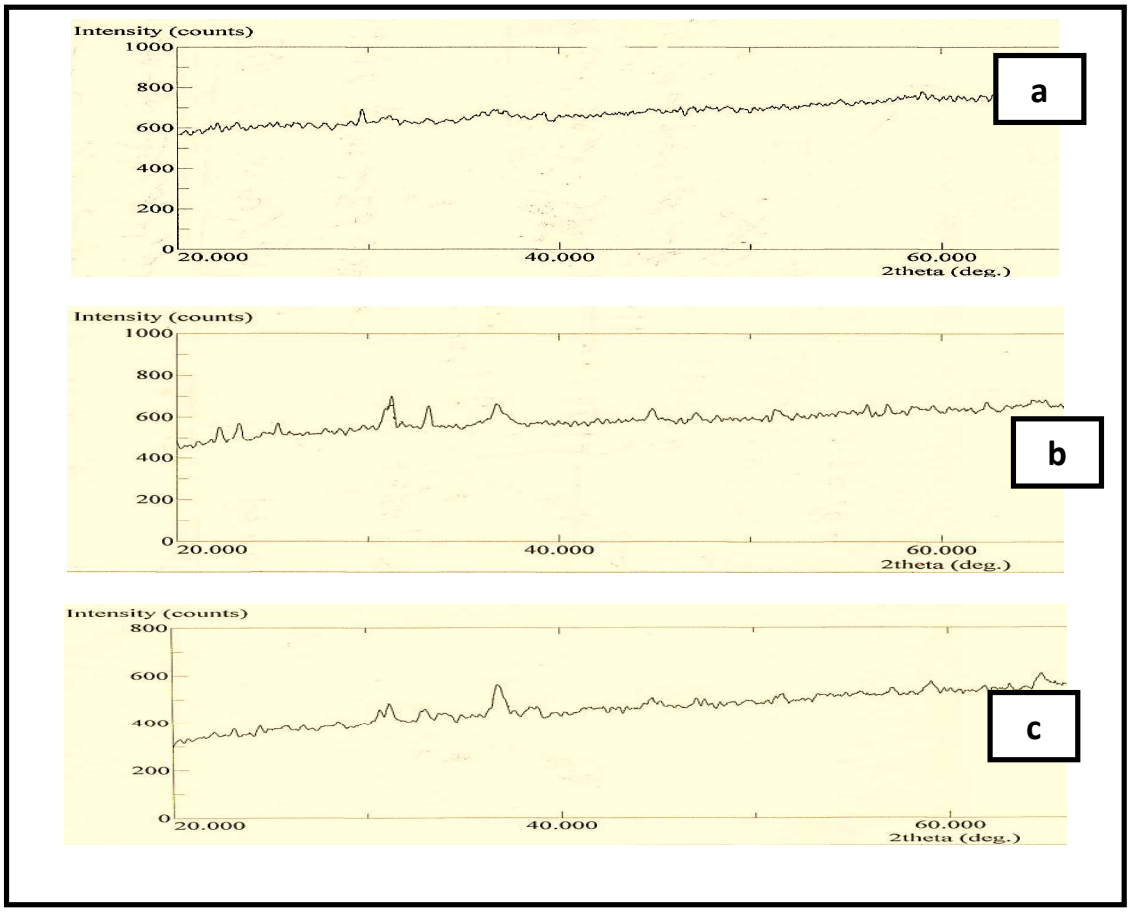


Fig.1. XRD patterns of the prepared coupled oxides powders calcinated at different temperatures 300 ^{o}C Fig.a, 500 ^{o}C Fig.b, and 700 ^{o}C Fig.c .

Photocatalytic activity

The photocatalytic removal of Congo read dye in presence of prepared coupled oxides (nickel Oxide - cobalt oxide) at different time intervals was observed at λmax 497 nm. The results revealed that absorbance of Congo red dye solution was decreased with the increase in the irradiation time for all the prepared coupled oxides , and thus Congo red dye can be photocatalytically degraded. The activity of coupled photocatalyst can be explained through inter- particle electron transfer pathway of the couple semiconductor[16]. The higher activity of (Cr_2O_3-Co_2O_3) show the roles of the electrons and holes of the catalyst which can be possess through different redox energy levels for their corresponding conduction and valence bands[17].

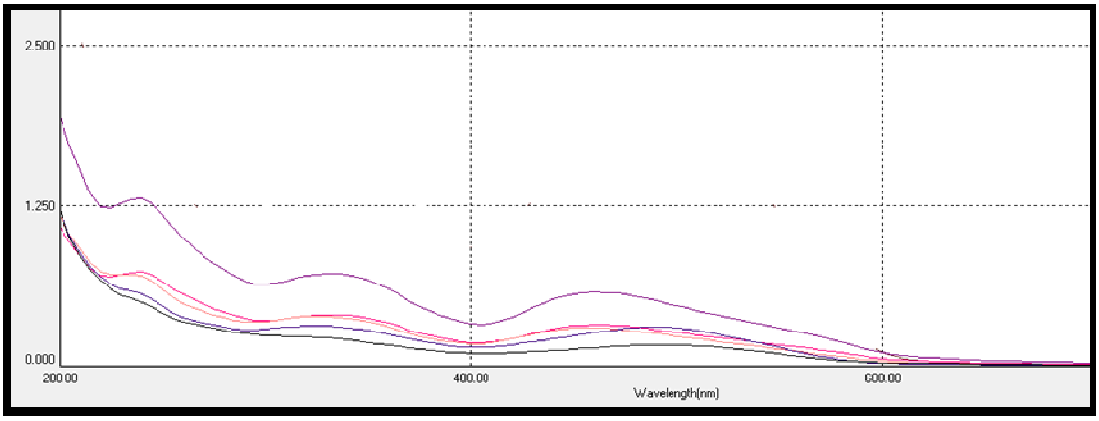


Fig.2. Photocatalytic declorization of congo red dye using 0.15g of (Cr_2O_3-Co_2O_3) calcienated at 700^{o}C.

Fig. 3 shows the ln(A_o/A) versus time curves of the Congo red dye photocatalytic decolorization using prepared coupled oxides photocatalyst, where A_o and A were the Absorbance's of the Congo red dye before and after irradiation, respectively. Curve shown in Fig. 4 was linear, revealing that the kinetic data of the azo dye photocatalytic decolorization fit well to the first-order reaction kinetic model. Assuming first-order reaction kinetics for thephotocatalytic oxidation process, the decolorization rate constant was determined from the equation

$$\ln(A_o/A_t)=-kt$$

where A_o and A_t are the dye Absorptions at times 0 and t , respectively, and k is the first-order rate constant.

Table.2. show the rate constant, R^2 values and, decolorization percentage for prepared coupled oxides at different calcination temperatures .

Sample	Temperature/^{O}C	R^2	Rate constant	Decolorization%
1	300	0.984	0.0044	53.8%
2	500	0.861	0.0073	79.2%
3	700	0.9907	0.0127	88.5%

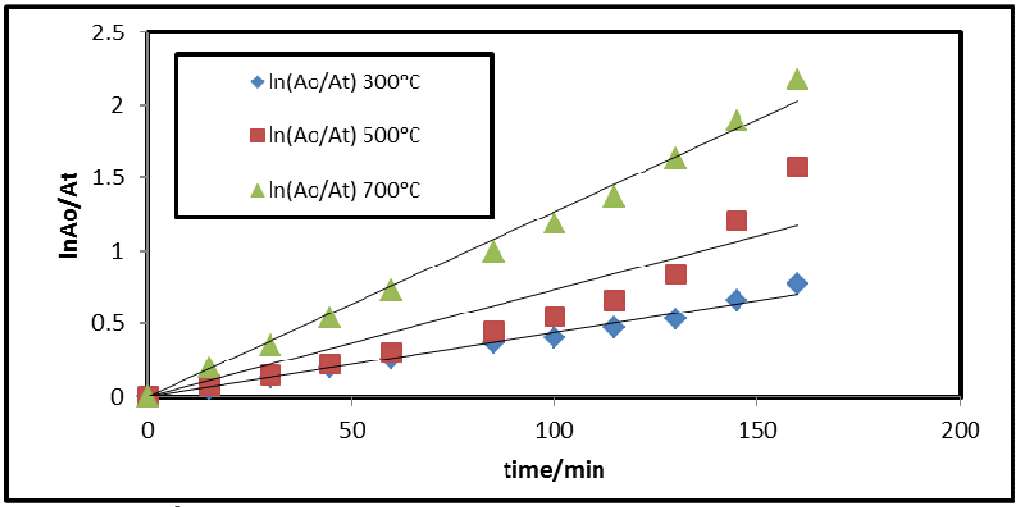


Fig.3. A plot of Ln(A^o/A_t) versus time was linear and follows pseudo first order kinetics.

Conclusions

In this study, photocatalytic oxidation of Congo Red dyes in aqueous solutions had been carried out using prepared coupled chromium and cobalt oxides powder as photocatalyst. This prepared coupled oxides may be viewed as useful photocatalyst for wastewater treatment. The obtained results can be summarized as follows

- The gran size was increased with increase of calcination temperature.
- The optimum calcination temperature was 700^{o}C.
- The photocatalytic activity was increasinged with increase of calcination temperature.

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