



## Wet Commixing Synthesis, Physical properties and Photocatalytic activity of Nickel oxide chromite spinel

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### ABSTRACT

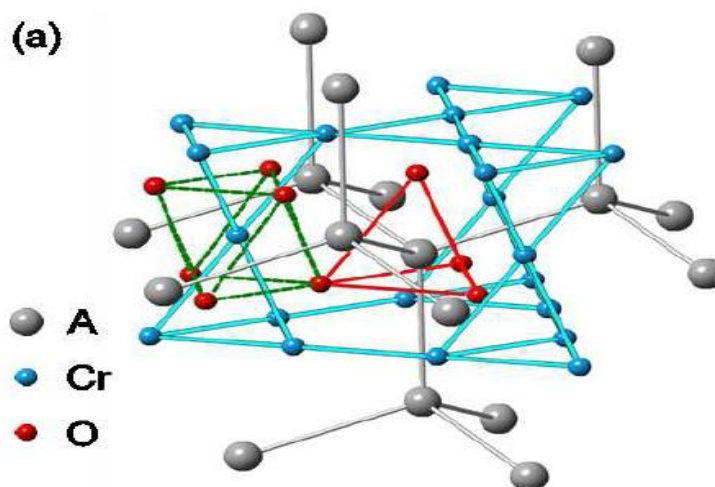
Homogeneous crystalline nickel oxide chromite spinels ( $\text{NiCr}_2\text{O}_4$ ) was prepared by wet commixing method by maxing chromium hexavelent oxide  $\text{CrO}_3$  and nickel oxide followed by calcination at  $700^\circ\text{C}$  for 6h. The crystalline structure of the synthesized chromate products were analyzed by X-ray diffraction (XRD) and FTIR. XRD powder diffraction data of specimens revealed the formation of a well-crystallized spinel structure of nickel oxide chromate after calcination at  $700^\circ\text{C}$ . The physical properties such as volume density of crystal was calculated. The photocatalytic activity of nickel oxide chromite ( $\text{NiCr}_2\text{O}_4$ ) was tested by using herpicide paraquat dichloride.

**Keywords:** Wet Commixing method, chromite spinel, X-ray diffraction, FTIR, herpicide photocatalytic activity.

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### INTRODUCTION

It is known since more than 40 years that chromium spinels ( $\text{ACr}_2\text{O}_4$ ) span an enormous range of magnetic exchange strengths and different magnetic ground states [1]. Chromite ( $\text{FeO}.\text{Cr}_2\text{O}_3$ ) is one of the principal ores of chromium and is found in peridotite, intrusive igneous rocks [2,3]. It is commonly associated with olivine, magnetite, serpentine and corundum [4]. Most of the chromite is of metallurgical grade with 40%  $\text{Cr}_2\text{O}_3$  and a chrome-to-iron ratio of 2.6:1[5-7]. Spinel (oxides of the composition  $\text{AB}_2\text{O}_4$  with A(II) and B(III) cations) are an important family of crystalline systems and are an important class of mixed-metal oxides and has the general chemical formula of  $\text{AB}_2\text{O}_4$  where A and B are cations occupying tetrahedral and octahedral sites, respectively [8]. Normally, A is a divalent and B is a trivalent atom. The nature of the A and B elements and their distribution over the sites determine the physical and chemical properties of the material, e.g., conductivity and detailed knowledge [9]. The cations occupy only one-eighth of the tetrahedral sites and one-half of the octahedral sites [10] as show in Fig1 [11]. Transition metal chromites  $\text{MCr}_2\text{O}_4$ (where M = Co, Cu, Mn, Ni, and Zn), with spinel-like structures, have attracted much attention because of their tremendous technological importance as ceramic pigment. Most of the ceramic dyeing materials used in pigment industries are of transition metal oxides with the spinel structure having high surface area, thermal stability and chemical resistance, as an absorbent material to remove sulfur-containing materials from hot-coal gas[12], refractories with optical properties[13] and protective coating materials for interconnects in solid oxide fuel cell stack systems[14].



**Fig. 1:** (a) In the structure of  $ACr_2O_4$  spinels the  $Cr^{3+}$  ions (light blue spheres) and the  $A^{2+}$  ions (grey spheres) are located on a pyrochlore and a diamond lattice, respectively. The oxygens (red spheres) form octahedral environment around  $Cr^{3+}$  ions, while  $A^{2+}$  ions are surrounded by tetrahedral oxygen cages.

As catalysts for the decomposition of chlorinated organic pollutants [15].  $CoCr_2O_4$ ,  $MnCr_2O_4$ , and  $NiCr_2O_4$  are ferromagnetic spinels; in single-crystal samples the collinear ferromagnetic ordering occurs at  $T_c = 51$  K, 93 K and 74 K for Mn, Co and Ni respectively. Yamasaki et al [16] reported the presence of ferroelectricity in zinc chromites ( $ZnCr_2O_4$ ) are effective catalyst materials for the synthesis of biodiesel and the removal of methane from compressed natural gas engines. Copper chromite ( $CuCr_2O_4$ ) spinel is one of the most effective catalysts for CO oxidation in automobile-emission control and is also used as a burning catalyst to increase the rates of combustion of solid rocket propellants [17]. It increases the burning rate of propellants at all pressures, producing a good catalytic effect on the decomposition and deflagration rate of ammonium perchlorate and polystyrene solid composite [18], battery materials [19] and electronic storage media [20].

The spinel materials can be prepared by many methods such as solid-state reaction of metal oxides at high temperatures [21]. In the wet chemical process, the powders are synthesized in liquid systems by means of coprecipitation[22], microemulsion, citrate-nitrate gel combustion[23], sol-gel, sol-spray processes, polymeric gel [24] and hydrothermal processes [25]. In the present work, we tried the synthesis of nickel oxide chromite spinel by wet commixing method. To evaluate the prepared material, characterization and use in photooxidation of the herbicide paraquat dichloride is done.

## MATERIALS AND METHODS

Nickel oxide ( $NiO$ ) and chromium oxide ( $CrO_3$ ) (all from BDH, 99.9%), and (1,1'-dimethyl-4,4'-Bipyridinium dichloride) (from Aldrich, 99.8%) and all other chemicals used were of analytical reagent grade.

$NiCr_2O_4$  was synthesized by wet commixing method [26] as per the conditions given in table 1. In the procedure, aqueous solutions containing the respective nickel oxide and chromium oxide ( $CrO_3$ ) in different molar proportions were combined and dissolved in a 250 mL beaker and maintained at a temperature of 70-80 °C for 4 h until a homogeneous suspension was obtained on hot plate. Then the suspension was transferred to crucible, which was kept in an oven at 180-200 °C for 3-4 h to dry and finally cooled to room temperature. A dark green soft powder was obtained. The dried powder specimens were calcined at different temperatures (500-700 °C) for 6 h.

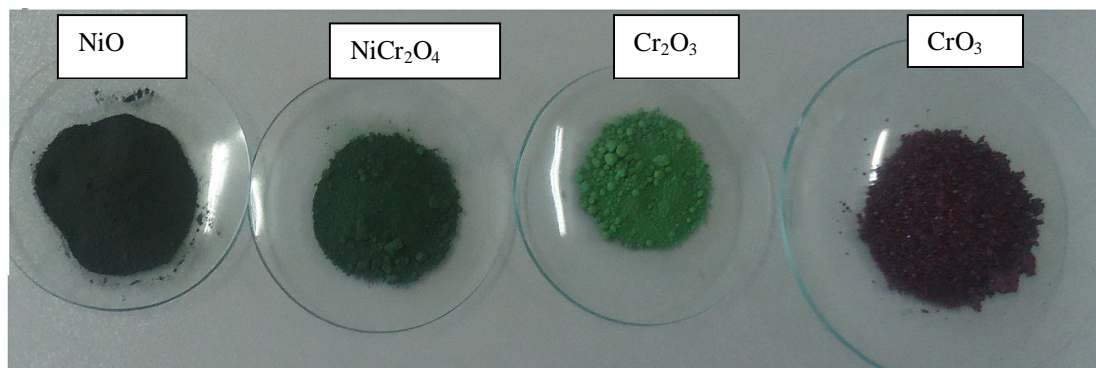
**Table. 1.** Wet commixing reaction conditions for formation of nickel chromites.

Compound	1	2	3	4
NiO	60%	80%	85%	90%
CrO <sub>3</sub>	40%	20%	15%	10%
NiO:CrO <sub>3</sub>	1:0.6	1:0.25	1:0.17	1:0.11

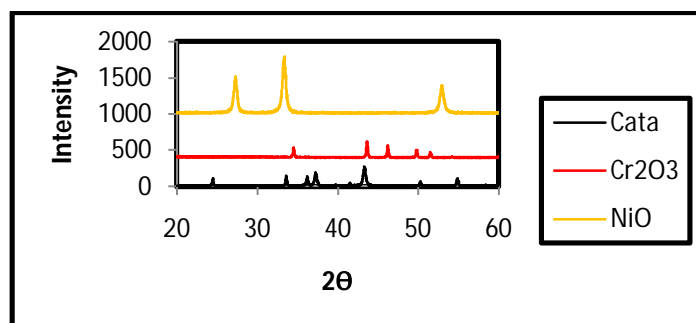
**Characterization:** The crystallinity and phase analyses were conducted by XRD using a Geiger flux instrument (Rigaku) with CuK $\alpha$  radiation ( $\lambda = 0.154056$  nm). The XRD data were collected in the  $2\theta$  range from  $15^\circ < 2\theta < 80^\circ$  with step-scanning increments of  $0.05^\circ$  and a scanning rate of  $5^\circ \text{ min}^{-1}$ . The morphologies of the metal chromites were observed by Fourier-Transform FTIR-8400S Shimadzu, Japan. The physical properties such as porosity, pore size and densities of the powder chromite nickel oxide was measured with an IMPACT-Test Equipment Ltd CT340-CT440.

**Experimental procedure for photocatalytic decolorization of paraquat dichloride:** Paraquat dichloride was used in the present investigation. The solution of paraquat dichloride was prepared in double distilled water. The photocatalytic bleaching of paraquat dichloride was studied in the presence of semiconducting nickel oxide chromium catalyst and light. 0.015 g of paraquat dichloride was dissolved in 100 mL of double distilled water so that the concentration of dye solution was  $3.7 \times 10^{-3}$  M. This solution was used as a stock solution. The photocatalytic bleaching of the dye was observed using  $1 \text{ g L}^{-1}$  nickel oxide chromite. Comparison was made with nickel oxide and chromium oxide separately. A 200 watt tungsten lamp (Philips) was used for irradiation purpose. The intensity of light at various distances was measured by Suryamapi (CEL model SM 201). A UV-VIS spectrophotometer (Systronics Model 108) was used for measuring absorbance at different time intervals.

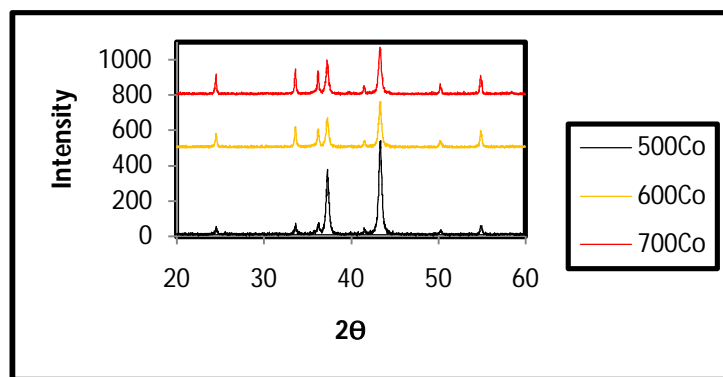
**X-ray diffraction results:** Figure.3 shows characteristic parts of the X-ray powder diffraction patterns of samples NiO, CrO<sub>3</sub> and NiO-Cr<sub>2</sub>O<sub>3</sub>. It can be seen that the CrO<sub>3</sub> (red crystalline) is completely decomposed to the chromium oxide (green powder color) after heating CrO<sub>3</sub> up to  $390^\circ \text{ C}$  [27]. Thermally decomposed product was amorphous, as proved by XRD (fig2 and figure 3). Fig4 show the XRD patterns of calcined (400 and  $700^\circ \text{ C}$ ) nickel chromite powders. The sharp and broad peaks appearing in the diffractograms confirm the formation of a fine structure, single-phase chromite spinel structure. A few characteristic peaks of Cr<sub>2</sub>O<sub>3</sub> and nickel oxide were also observed. 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 with the increase of calcination temperature, indicating that the size of the particles increases.

**Fig.2:** simple NiCr<sub>2</sub>O<sub>3</sub> prepared and it precursors oxides

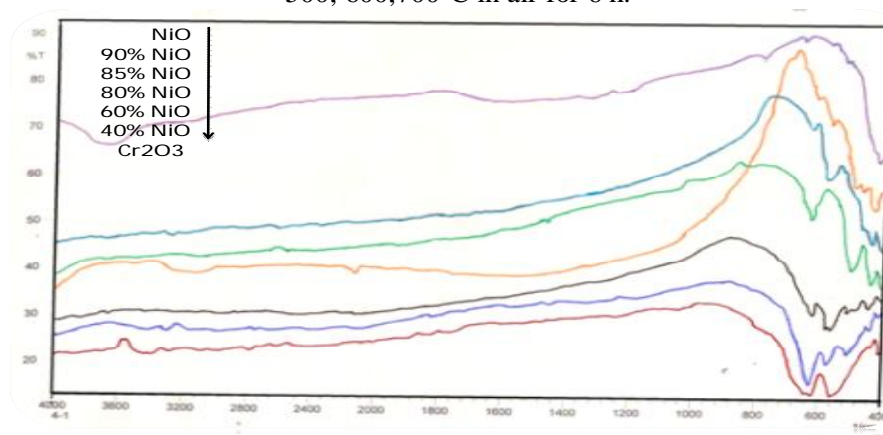
**FTIR Spectra:** The Fourier transform infrared (FTIR) spectra of  $\text{NiCr}_2\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{NiO}$  are shown in figure 5. The IR bands of  $\text{NiCr}_2\text{O}_4$  are given in table 2. Nickel chromite spinel are expected to exhibit the characteristic absorption bands in the shortwave region around  $580\text{-}540\text{ cm}^{-1}$ , and  $450\text{-}420\text{ cm}^{-1}$  due to Cr-O and Ni-O stretching frequencies, respectively [28]. The IR bands ( $600\text{-}540\text{ cm}^{-1}$ ) for nickel chromite sample could be attributed to the stretching vibration of the Cr-O bands of chromium atoms in the tetragonal environment of the O atom. Some properties of the nickel chromite, nickel oxide and chromium oxide, such as density, apparent porosity, pore volume and IR bands, are summarized in table 2.



**Fig.3:** XRD patterns of nickel oxide chromite spinel( $\text{NiCr}_2\text{O}_4$ ) [15%  $\text{NiO}$ +85% $\text{CrO}_3$ ], nickel oxide and chromium oxide powders calcined at  $700^\circ\text{C}$  in air for 6 h



**Fig.4:** XRD patterns of nickel oxide chromite spinels ( $\text{NiCr}_2\text{O}_4$ )[15%  $\text{NiO}$ +85% $\text{CrO}_3$ ], powders calcined at 500, 600,700 $^\circ\text{C}$  in air for 6 h.

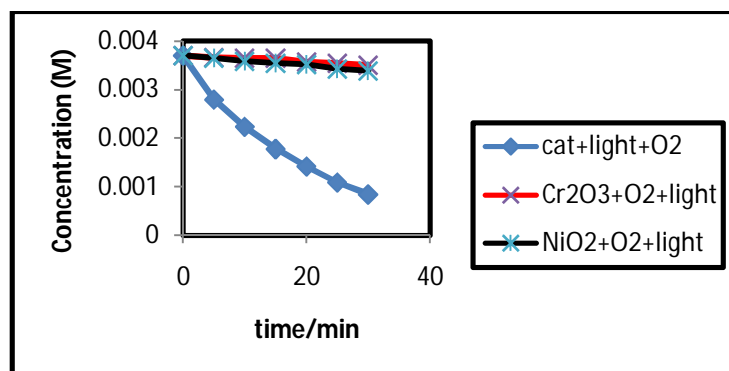


**Figure.5:** FTIR spectra of Nickel oxide chromite spinels with different percentages of chromium and nickel oxides.

**Table 2:** Physical properties and IR bands of nickel oxide chromite spinel, chromium oxide and nickel oxide.

No	Materials	Volume Density (g Cm <sup>3</sup> )	Apparent Porosity (%)	Pore volume (Cm <sup>3</sup> g <sup>-1</sup> )	Bands of FTIR spectrum (Cm <sup>-1</sup> )
1	Nickel oxide	2.96	21.7%	0.073	443.64 ,420.50
2	Chromium oxide	1.47	46.3%	0.67	619.19 ,561.3 ,441.71
3	Nickel oxide chromite spinals	2.71	40.1%	0.14	617.24,580.59, 479.65, 441.71

**Photocatalytic activity:** The photocatalytic decolonization of paraquat herbicide in presence of nickel oxide chromium semiconductor at different time intervals was observed at  $\lambda_{\text{max}}$  633 nm. The results for a typical run are graphically represented in the fig6. It was observed that absorbance of paraquat dichloride solution decreases with the increase in the time of irradiation, thus indicating that paraquat dichloride is photocatalytically degraded. Control experiments were also performed which indicate that herbicide degrades only in the presence of photocatalyst on irradiation.

**Fig.6:** Photocatalytic degradability of paraquat dichloride by using 1.5g L<sup>-1</sup> of catalyst, NiCr<sub>2</sub>O<sub>4</sub>,NiO,Cr<sub>2</sub>O<sub>3</sub>.

**Effect of Catalytic Weight:** The effect of catalyst weight on the photodegradation of the herbicide was investigated in the range of 0.4 to 1.4 g L<sup>-1</sup>. It can be seen in figure 7 that the initial degradation rate of the dye was increased with increase in catalyst amount up to 1 g L<sup>-1</sup>. Further increase in catalyst weight decreased the reaction rate. Initially with increasing amount of NiCr<sub>2</sub>O<sub>3</sub> the availability of semiconductor particle for absorption of photon increases, thereby producing more number of oxidizing sites, which consequently increase the rate of the reaction. The decrease of degradation rate at higher dosage of NiCr<sub>2</sub>O<sub>3</sub> may be attributed to the decrease of light penetration through the catalyst suspension and scattering of light by the catalyst particles [29]. Therefore, optimum catalyst weight for the reactor system was 1 g L<sup>-1</sup>.

**Effect of pH:** The pH of the solution can be one of the most important parameters for the photocatalytic process, since the particle size, surface charge and band edge positions of the semiconductor oxide are strongly influenced by pH[30]. The photocatalytic experiment was carried out at various pH values in the range 4–10 to find out the optimum pH. As can be seen from figure 8, when the initial pH of the herbicide solution varied, the initial degradation rate of the herbicide increased with increase in pH from 4 to 9 and thereafter it decreased. With increasing pH, the hydroxyl ion concentration increases and so the hydroxyl radical formation increases. The decrease in the rate of degradation at pH>9 may be attributed to the

instability of  $\text{NiCr}_2\text{O}_3$ , which tends to undergo photo-corrosion. A similar influence of pH on the photocatalytic degradation rate of the reactive red 22 dye was reported by Onda et al[31].

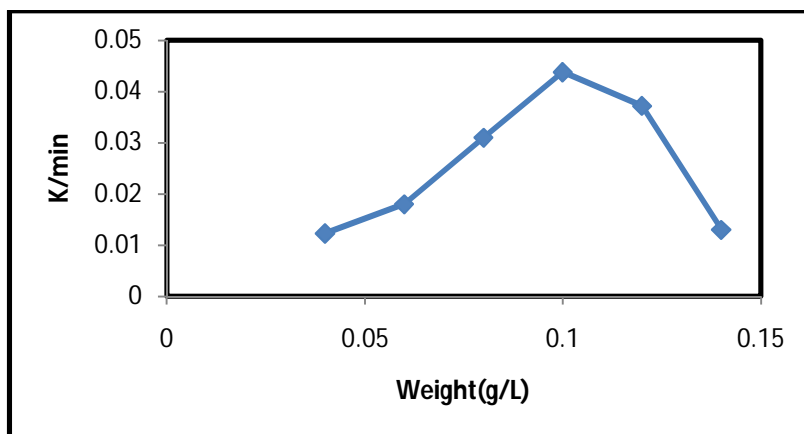


Fig.7: Effect of catalyst weight on the photocatalytic degradation of paraquat dichloride (catalyst  $\text{NiCr}_2\text{O}_4$  [PQ], 100 mL)

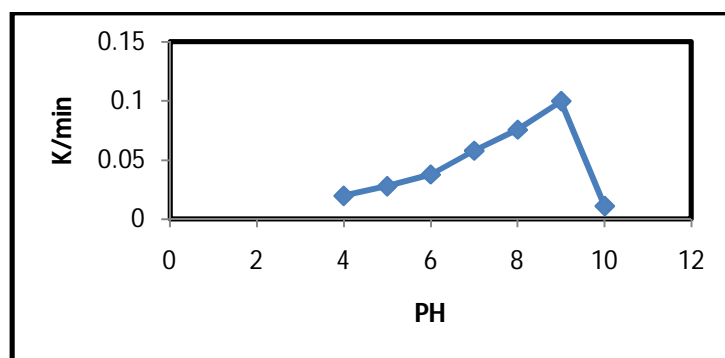
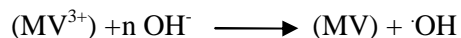
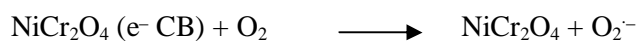
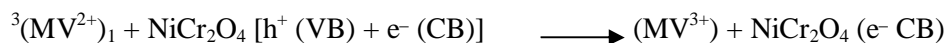
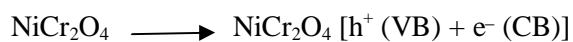
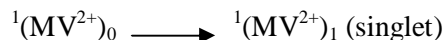


Fig.8: Effect of pH on the photocatalytic degradation of paraquat dichloride (catalyst  $1 \text{ g L}^{-1} \text{ NiCr}_2\text{O}_4$ ; [PQ], 100 mL).

**Mechanism:** On the basis of the observed data, the following mechanism may be proposed for the photocatalytic bleaching of dichloride herbicide.



When the solution of the herbicide was exposed to light in the presence of a semiconductor, initially the paraquat dichloride molecules are excited first to their singlet state. These excited singlet molecules are converted to their triplet state through inter system crossing (ISC). The triplet state may donate its electrons to the semiconductor and the paraquat dichloride becomes positively charged. The dissolved oxygen of the solution may pull an electron from the conduction band of semiconductor, thus regenerating the semiconductor and forming superoxide anion radical. The positively charged molecule of paraquat dichloride will immediately reacts with hydroxyl ions to form OH radicals. These OH radicals will oxidize the paraquat dichloride molecule into colorless products. The participation of OH radicals as an active oxidizing species was confirmed by carrying out the reaction in the presence of hydroxyl radical scavenger e.g., 2-propanol, where the reaction rate was drastically retarded.

### APPLICATIONS

Nickel oxide chromite preparation by wet commixing is successful and is useful in the photocatalytic oxidation of paraquat dichloride dye.

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