Catalytic behavior of chromium supported silica for decolorization of neutral red dye using oxidation reaction

Atheel Alwash.
Chemistry Department,
Collage of Science
AL-Nahrain University
Baghdad, Iraq

Abstract

The heterogeneous catalyst, chromium doped silica was prepared by impregnation method and investigated for the decolorization of neutral red dye which was used as a pollutant molecule in this study. The XRD result detected new diffraction peaks for chromium oxide at 24.6°, 32.92°, 40.8°, 41.4° and 44°. The FTIR results improved the existence of Cr+3 within the structure of silica due to the shifting of the absorption peaks to the higher wave numbers. The TGA/DSC results detected the significant influence of temperature on the appearance of chromium phases supported silica. This was evidence during the experimental work through the change in color of the synthesized catalyst from light green for the catalysts calcined at 200°C and 300°C to yellow for that calcined at 500 °C. Different reaction variables such as, effect of chromium ions, pH values, amount of hydrogen peroxide and effect of reaction temperature were studied to estimate their effect on the decolorization efficiency of neutral red dye. The maximum catalytic activity achieved was 92% at a solution pH of 5.5, catalyst dosage of 1.5 g/L, 0.1 mL of H_2O_2 /100 mL of reaction volume and initial dye concentration of 10 mg/L after 60 min of reaction time.

Keywords Chromium ions, Oxidation process, Heterogeneous catalyst, Wastewater treatment

1-Introduction

Pollution of the environment can be caused by bleaching and coloring compounds used in dying process. Different chemical compounds are generated from these industries including large quantities of sodium, chloride, sulphate, hardness, dye ingredients and total dissolved solids with very high BOD and COD values [1]. Physical methods such as adsorption, biological biodegradation) and chemical methods such as chlorination and ozonation are the most frequently used methods for removal of the textile dyes from waste water. However, the efficiency of the traditional wastewater treatment processes for dyes removal is still limited. For this reason, advanced oxidation techniques are considered as quite promising solution. Advanced oxidation process have been widely developed to enhance the generation of hydroxyl radicals ($^{\bullet}$OH) that have a high efficiency to oxidize organic matters[15]. Many AOPs used hydrogen peroxide instead of other compounds such as gaseous oxygen to concern the contaminants mineralization and eliminate the treatment time [14]. However, during the last decades great efforts had been focused on the synergic between the heterogeneous catalysts and hydrogen peroxide in oxidation process. The presence of the heterogeneous catalysts in any waste water treatment processes is particularly beneficial because of increasing the production of hydroxyl radicals, enhances the efficiency of the degradation process and the easy separation of the catalysts from the treated wastewater. In addition, the presence of catalyst facilitates the adsorption of the pollutant due to their high specific surface areas thus, enhance the degradation process [12].

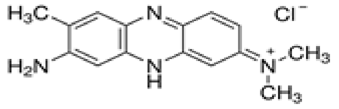
Various studies had been reported the catalytic activity of different heterogeneous catalysts i.e. transition metals ions doped different supports. These ions affect the surface properties, optical properties and the catalytic activity of the prepared catalysts. Among these transitions metals, chromium ions have attracted a considerable attention because of the unusual characteristics of these oxide species on the surface of the support, including oxidation state and coordination environment [3].

Chen *et al.* [4]; Chen and Liu, [6] and Elías *et al.* [8] reported the superior activity of Cr ions doped titanium in photocatalytic reaction for different application owing to its ability in reducing the wide band gap of TiO_2 (3.2 eV) and altering the fast charge electron–hole recombination. However, few reports were focusing on the decolorization of organic dyes using chromium doped supports in catalytic wet oxidation process. As such in this study, a series of Cr/SiO_2 catalysts were prepared using impregnation method and investigated for the decolorization of neutral red dye which was used as pollutant model in this study using catalytic wet oxidation process. The silica was used as a support due to its unique properties such as high surface area, thermal and mechanical stability and controllable pore size [24]. Different characterization techniques have been made to characterize the catalyst and to elucidate the process behavior under various conditions such as, the effects of initial dye concentration, addition of H_2O_2, solution pH and the temperature of reaction. As the objectives of the study demands a lot of experimental works covering thorough characterization and process study under various conditions.

2.Materials and Methods

Commercial Silica was used as a support for Cr ions loading. Hydrogen peroxide (30% analytical grade) was used as oxidizing reagent; chromium chloride was purchased from Merck. While neutral red dye was obtained from Fluka. The properties of the neutral red dye are listed in Table 1.

Table 1: The structure and properties of Neutral red dye

Molecular structure	
Other names	3-Amino-7-dimethylamino-2-methylphenazine hydrochloride
Molecular weight	288.78 g/mol
Color Index	50040
λmax	529 nm

2.1Preparation method

The heterogeneous catalyst of Cr loaded silica was prepared using impregnation method [21]. One gram of silica support was suspended in 50 mL of distillate water with different wt. % of Cr (III) ranging from 0.4 – 0.8 wt. % and mixed for 6 h at 70 °C. The resulting samples were then dried and placed in an oven at 100 °C for 4 h. Then, the produced solids were calcined at 500 °C for 4 h. The produced catalysts were denoted as *x*Cr % - SiO_2 where *x* is the wt. % of Cr ions.

2.2 Characterization of the catalysts

The characterization of the catalysts with different analytical techniques was performed on the catalysts. Among various catalysts loadings, the best catalyst was demonstrated by activity of 0.4% Cr-SiO_2. Thus it was chosen to completely characterize. X-ray diffraction patterns were obtained by means of XRD (Philips Goniometer PW 1820) diffractometer. The FTIR spectroscopic analysis was carried out using Bruker Alpha spectrophotometer. The spectra were recorded in the wave number range of 400–4000 cm^{-1}. Thermogravimetric analysis (TGA) was carried out using LINSEIS STA PT- 1000.

2.3 Reaction procedure and analytical method

The experimental runs were carried out in a 250 mL conical flask as a reactor equipped with a magnetic stirrer and heater. Water containing neutral red dye was transferred to the glass reactor. Thereafter, the catalyst was added to the solution. The temperature of the reaction mixture was controlled using heater to the desired value. Hydrogen peroxide was added, the runs were conducted at 60 °C and the samples were taken at periodic intervals i.e. (10 min). Prior to the photometric analysis, spectrophotometric analysis was carried out to determine the maximum absorption of the dye which was fixed at 529 nm. The absorbance of the dye solution was determined at the maximum absorbance wavelength then the concentration of solution was calculated based on the Beer-Lambert law. The decolorization efficiency of the catalyst was calculated according to the following equations:

$$\mathrm{D\,E\,\%} = \left[1 - \frac{C_t}{C_o}\right] \times 100$$

where, D E% is the decolorization efficiency, C_o (mg/L) is the initial concentration of dye, C_t (mg/L) is the concentration of dye at certain reaction time and t (min).

3. Result and discussion

3.1 X-ray diffraction

Fig. 1 (a and b) shows the X-ray diffraction patterns for both pure silica and 0.4% Cr doped silica calcined at 500 °C. The results showed that pure silica has a crystalline structure with diffraction peaks at 25.47°, 31.37°, 38.63°, 48.68° and 55.7°. The crystallinity of SiO_2 calcined at 500 °C was also reported by Li Cheng *et al*. [18]. On the other hand, after the loading of 0.4 wt.% chromium ions into silica structure, an increase in the crystallinity of the catalyst (the diffraction peaks became sharper) was detected that could be ascribed to effect of Cr^{3+} loading and the growth of the mixed crystal during the calcinations step. Furthermore, a new diffraction peaks for chromium oxide phase were detected in 0.4%Cr-SiO_2 catalyst sample i.e. 24.6°, 32.92°, 40.8°,41.4° and 44°.

Chen *et al*. [5] in their attempt for Cr_2O_3 treated carbon nano tube/TiO_2 composites also detected a new diffraction peaks in the range between 24.5° to 50.5°. Meanwhile the peaks at 31.35° and 48.35° for 0.4% Cr-SiO_2 catalyst slightly shifted to lower angle compared to the diffraction peaks of pure silica. This shifting might indicates that Cr^{3+} ions have entered the crystal structure and consequently induce distortion to crystal lattice [23]. In addition, a reduction in peaks intensity of 31.35° and 38.65° was indicated due to the effect of Cr^{3+} loading into silica structure.

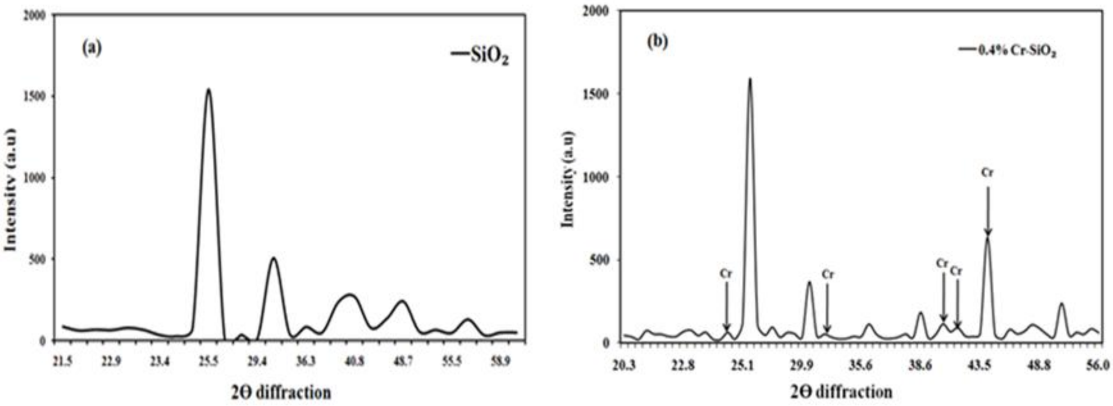


Fig. 1. X-ray diffraction patterns of (a) SiO_2 (b) 0.4%Cr-SiO_2

3.2 Fourier transformed infrared spectroscopy (FTIR) analysis

Fig. 2 shows the FTIR spectra of pure silica and chromium doped silica calcined at 500 °C. The FTIR spectrum of SiO_2 consists of bands 1094 cm^{-1}, 960 cm^{-1}, 821 cm^{-1} and 470 cm^{-1}. The band at 1094 cm^{-1} and 470 cm^{-1} are assigned to the asymmetric stretching vibrations as well bending vibration of Si-O-Si framework. Meanwhile, the shoulder at 960 cm^{-1} and the band at 821 cm^{-1} was ascribed to the Si-OH and Si-O bending, respectively [22]. As the chromium ions were incorporated into silica structure, all the absorption peaks were shifted to higher wave numbers. The shifting of the absorption peaks was ascribed to the existence of Cr^{+3} within the structure of silica. Similar results were detected by Bai *et al*. [2]. Furthermore, the small absorption band at 960 cm^{-1} in silica sample was disappeared after the loading of Cr^{+3}. This might be due to the replacement of OH group with Cr^{+3} ions within silica framework. On the other hand, all the absorption peaks of 0.4% $Cr\text{-}SiO_2$ catalyst showed a reduction in peaks intensity compared to pure silica and this might be ascribed to the difference in bond energy influenced by the amount of chromium ions presented in the silica support.

3.3 Thermal gravimetric analysis (TGA)

The thermal gravimetric analysis was carried out for the 0.4% $Cr\text{-}SiO_2$ catalyst in order to investigate the suitability of the selected calcination temperature i.e. 500 ºC used in this study. The TGA/DSC profiles versus temperature ranging from 30 – 800 ºC under air condition are shown in Fig. 3. In the first temperature region up to 100 °C, an endothermic peak situated at 75 °C results from the evaporation of excess absorbed water molecules.

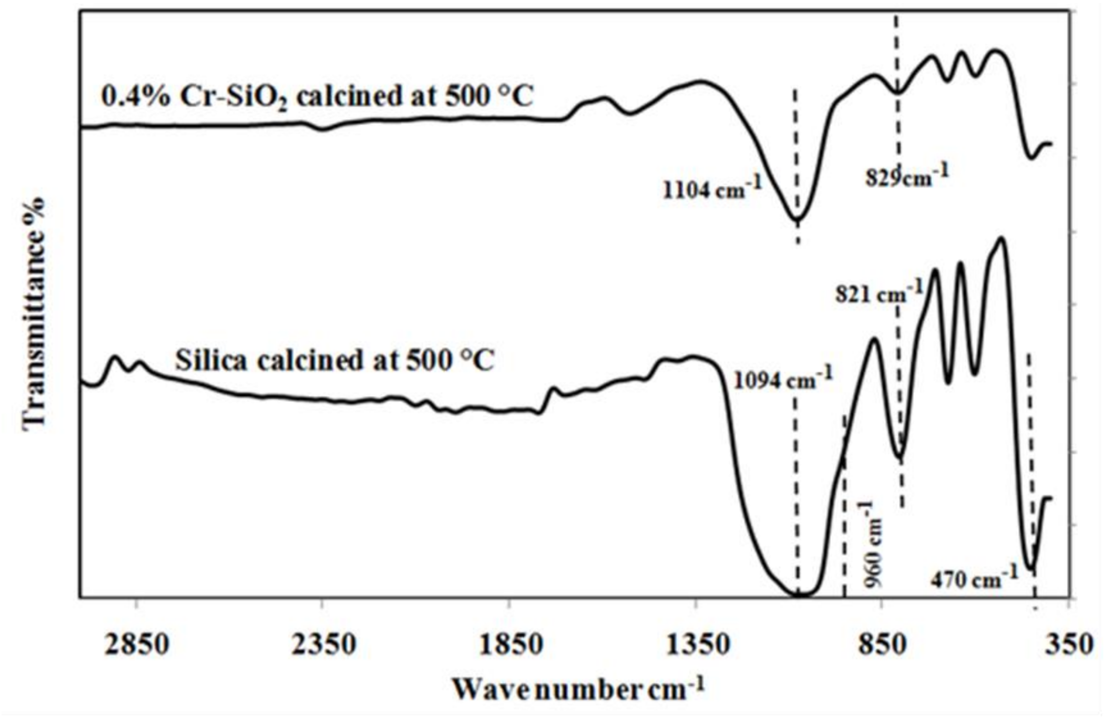
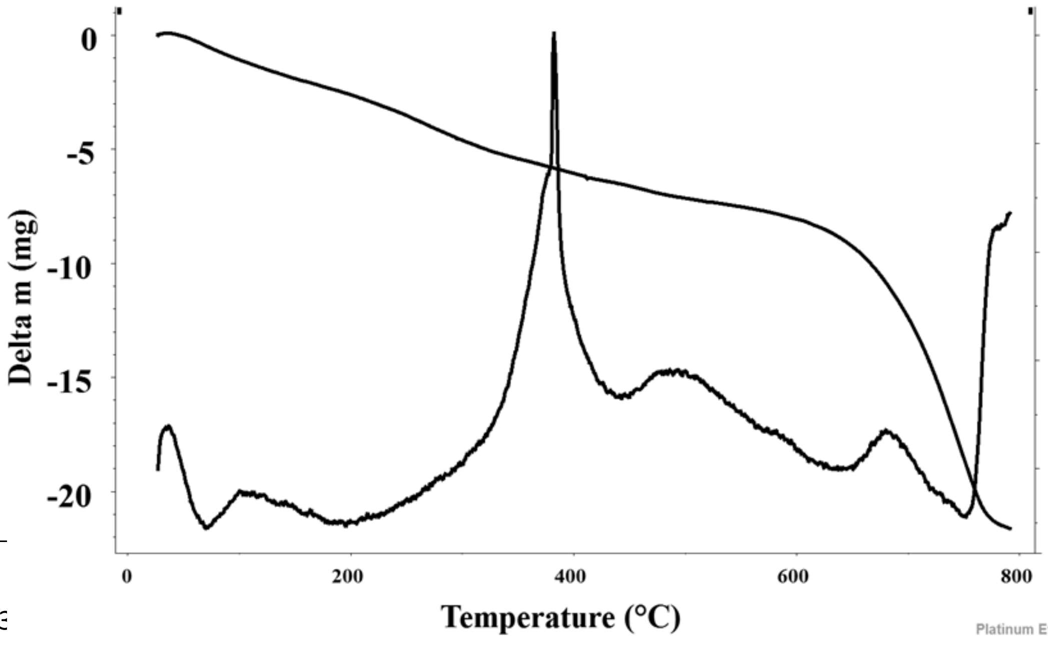


Fig. 2. FTIR spectrum of pure silica and 0.4%$Cr\text{-}SiO_2$ catalyst

One endothermic peak situated at ~380 °C represents the decomposition of organic compounds and the formation of chromium oxide. The activation of silanol groups to form surface bond chromate or dichromate species occurs at a relatively low temperature of about 150-350 °C. The third weight loss at 500 °C, associated with an exothermic peak, due to the formation of dichromate. This was evidence during the experimental work by the change in color from light green for the catalysts calcined at 200°C and 300°C to yellow for that calcined at 500 °C.

Increasing the calcination temperature probably introducing more strain into the Si-O-Cr-O-Si bonds making the chromate site more active [11]. One the other hand, by increasing the temperature to 600 °C and above, the TGA/DSC curve showed large weight loss with an exothermic peak situated at 700 °C and followed by an endothermic peak at 745 °C. The annealing of the silica surface changes the bonding geometry and/or the degree of bonding of reduced chromium with the surface. This was evidence by the color change of 0.4% Cr-SiO2 catalyst before and after the analysis due to the effect of annealing temperature on the formation of chromium-silica phase as in Fig. 4



Bulk density (kg/m^3)	637
Particle porosity	0.6876

Fig. 3. TGA/DSC analysis of 0.4% Cr-SiO_2 catalyst

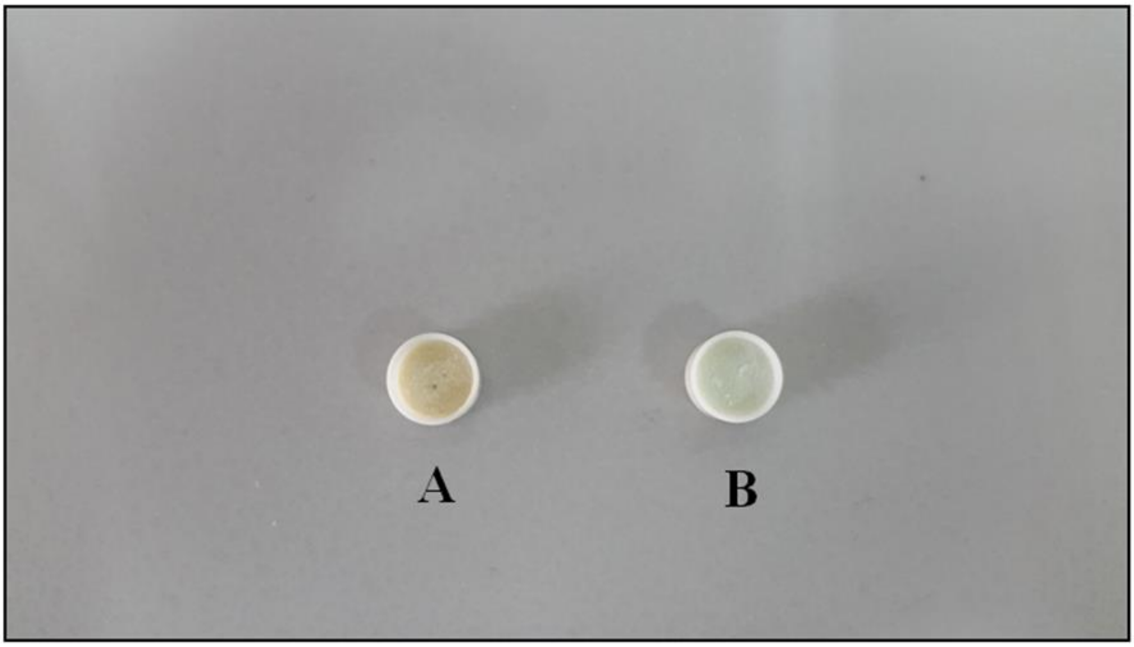


Fig. 4. The color change of 0.4% Cr-SiO_2 catalyst, A) before and B) after analysis

From the above results, it was clear that the calcination temperature controlled the phase stability of chromium ions doped silica. However, the selected calcination temperature i.e. 500 °C showed the best catalytic activity for the decolorization of neutral red dye.

4. Control experiment

A preliminary study was carried out to characterize the influence of the supported chromium ions for the decolorization of neutral red dye as in Fig. 5. The reaction conditions was fixed at initial dye concentration of 10 mg/L, 1.5 g/L of catalyst loading with controlled temperature at 60 °C for 60 min of reaction time and the pH of the dye solution around 5.5 was kept at its normal level without any prior adjustment. The results showed that the bare silica sample, without any chromium ion doping have very high adsorption rate about 92 % after 30 min of mechanical stirring without any addition of H_2O_2. Indeed this high adsorption ability refers to its high mesoporous structure as it is well known. However, after the addition of H_2O_2 and the starting of oxidation reaction, there was no change in the decolorization efficiency after 60 min of reaction. Therefore, the support has no catalytic role in dye removal other than adsorption. Meanwhile, for 0.4% Cr-SiO_2 catalyst, the adsorption rate after 30 min of mechanical stirring was only 16% compared to that of bare silica due to the effect of Cr^{+3} ions loading occupied silica surface. Next, the reaction of 0.4% Cr-SiO_2 catalyst with dye solution was started, the catalytic activity was found to be 92 % after 60 min of reaction in the presence of H_2O_2. This high catalytic efficiency was ascribed to the synergetic effect between H_2O_2 and chromium ions within silica structure. The reaction between the prepared catalyst and H_2O_2 led to the formation of the efficient hydroxyl radicals that consider as the main active species for the decolorization of neutral red dye. This result was supported by the reaction of 0.4% Cr-SiO_2 catalyst without the addition of H_2O_2 where no catalytic activity was detected for the decolorization of dye after 60 min of reaction. As such, the efficient redox properties of chromium ions supported silica mainly depends on the presence of H_2O_2 in wet oxidation process.

4.1 Factors influencing the catalytic activity

4.1.1 Effect of Cr loading

An investigation on the effect of different Cr^{+3} ions supported silica ranging from (0.4-0.8) wt. % was carried out to study the effect of this metal on the catalytic activity for the decolorization of neutral red dye under wet oxidation process. The result indicates that the decolorization efficiency is remarkably depends on the chromium ion concentration at fixed dye and H_2O_2 concentration as illustrated in Fig. 6.

The synergetic between chromium ions and silica as a support was expected to enhance the efficiency of the synthesized catalyst due to the oxidation/ reduction properties of Cr ions. The reaction was conducted by fixing the catalyst loading at 1.5 g/L, dye concentration of 10 mg/L, H_2O_2 concentration of 0.1 mL and reaction temperature at 60 °C. Meanwhile, the pH of the reaction was kept at the original pH of 5.5 without any adjustment. The adsorption-desorption equilibrium between the catalyst and dye solution under mechanical

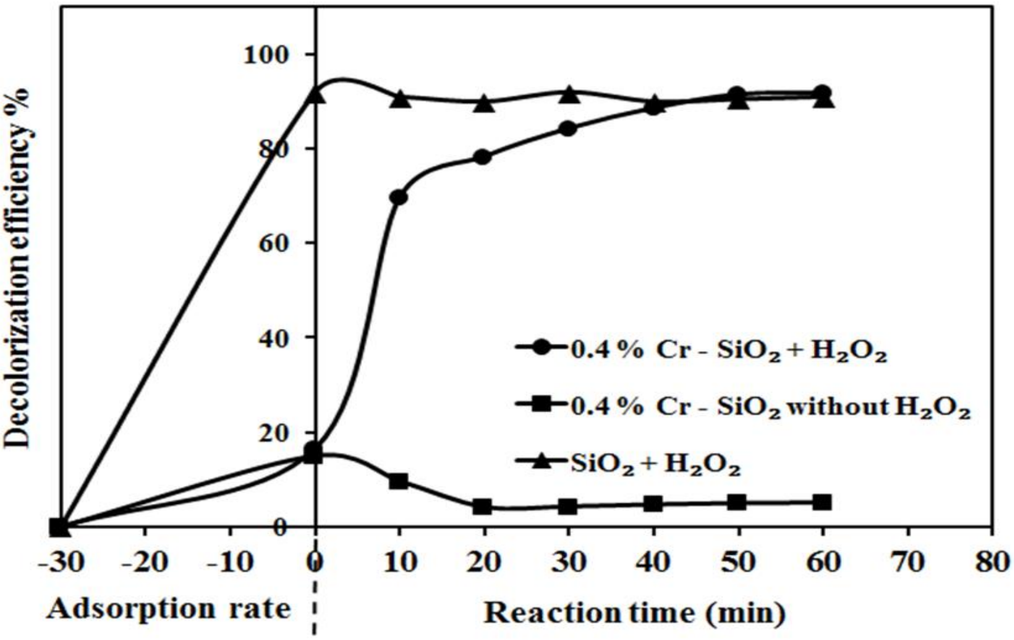


Fig. 5. The control experiment study for decolorization of neutral red dye under various conditions. (Initial dye concentration 10 mg/L, catalyst loading 1.5 g/L, reaction temperature of 60 °C and original pH).

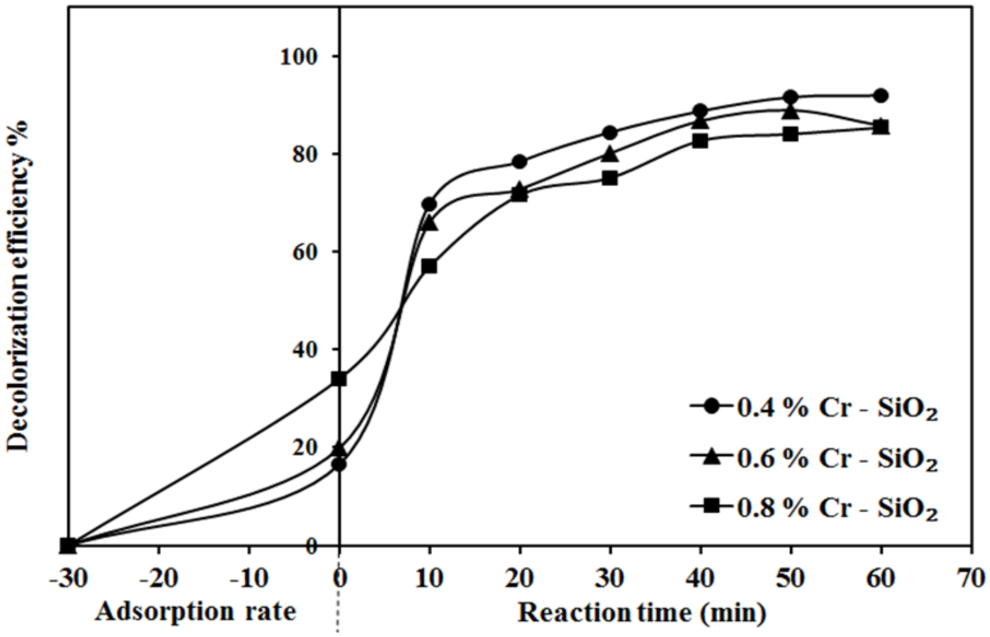


Fig. 6. Effect of Cr loading for decolorization of neutral red dye under various conditions. (Initial dye concentration 10 mg/L, catalyst loading 1.5 g/L , pH 5.5, 0.1 mL H_2O_2 and reaction temperature of 60 °C).

stirring was carried out for 30 min before starting the reaction as presented in Fig. 6. The adsorption of the dye was found to increase with increasing the loading of Cr ions due to an increase in the active sites of catalyst reaching its maximum to 34 % with Cr loading of 0.8 wt. %. The catalytic activity for the decolorization of neutral red dye was investigated after the end of 30 min of the adsorption-desorption equilibrium. The results showed that the maximum decolorization efficiency was 92% for 0.4% Cr loading after 60 min of reaction time.

The higher catalytic activity of the catalyst could be attributed to the continuous production of the active radical $^{\bullet}OH$ [17] as in the following Eqs.

$$Cr^{+3} + H_2O_2 \rightarrow Cr\text{-}OOH^{+2} + H^{+} \quad (1)$$

$$Cr\text{-}OOH^{+2} \rightarrow Cr^{+2} + HO\bullet_2 \quad (2)$$

$$Cr^{+2} + H_2O_2 \rightarrow Cr^{+3} + {}^{\bullet}OH + OH^{-} \quad (3)$$

On the other hand, the catalytic activity was decreased with increasing Cr loading to about 85 % for both 0.6 and 0.8wt.% of Cr ions after 60 min of reaction. This reduction in catalytic activity could be ascribed to the excess number of $^{\bullet}OH$ radicals formed during the reaction led to the recombination of the $^{\bullet}OH$ radicals as in the following eqs.

$$Cr^{+2} + {}^{\bullet}OH \rightarrow Cr^{+3} + OH^{-} \quad (4)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO^{\bullet}_2 + H_2O \quad (5)$$

$$2Cr^{+2} + H_2O_2 + 2H^{+} \rightarrow 2Cr^{+3} + 2H_2O \quad (6)$$

The above mechanism shows that Cr^{+3} species located at the surface of the catalyst reacts with the hydrogen peroxide and leads to the formation of various active intermediates to produce hydroxyl and perhydroxyl radicals to decompose the organic dye. Consequently, Cr^{+2} species formed in the reaction process also reacts with H_2O_2 to generate Cr^{+3} species and hydroxyl radical which are capable to degrade the neutral red dye.

4.1.2Effect of pH

The effect of initial pH of the solution on decolorization efficiency of neutral red dye was investigated at different initial pH levels (2.7, 3.5 and natural pH (5.5)) without any further pH control during the oxidation reaction. The reaction parameters were fixed at an initial dye concentration of 10 mg/L, catalyst loading of 1.5 g/L, reaction temperature at 60 °C and H_2O_2 concentration of 0.1 mL.

Prior to the oxidation reaction, the solution was first stirrer for 30 min at room temperature to maintain a good dispersion between catalyst and the dye solution. In Fig. 7, the catalyst showed an adsorption rate between 20-30 % at pH range from (2.7-5.5). However, during the experimental run and when the oxidation reaction was started, some of the absorbed dye was desorbed from the catalyst surface into the reaction at the first 10 min due to the addition of H_2O_2 that slightly affect the pH of solution. At the end of reaction, the maximum decolorization efficiency was 92% at natural pH 5.5 followed by 87 % and 78% at pH 2.5 and 3.5 respectively. The lower catalytic activity of the catalyst at pH 2.7 and 3.5 could be attributed to the fact that chromium ions (III) may accept an electron from the decomposition of hydrogen peroxide and as a consequence, corresponding chromium (II) complex is formed along with generation of proton and hydroxyl radicals [16].

These complexes will undergo throw a series of reaction until the formation of radicals. This behavior explains the slow activity of the catalyst at the first 10 min of reaction for pH 2.7 and 3.5, respectively. However, as the reaction time was increased, the catalytic activity become faster at pH 2.7 compared to that of 3.5. The solution pH has a significant effect on various reaction factors and consequently affected the decolorization efficiency such as the protonation/de-protonation of dye molecules and the decomposition rate of H_2O_2.

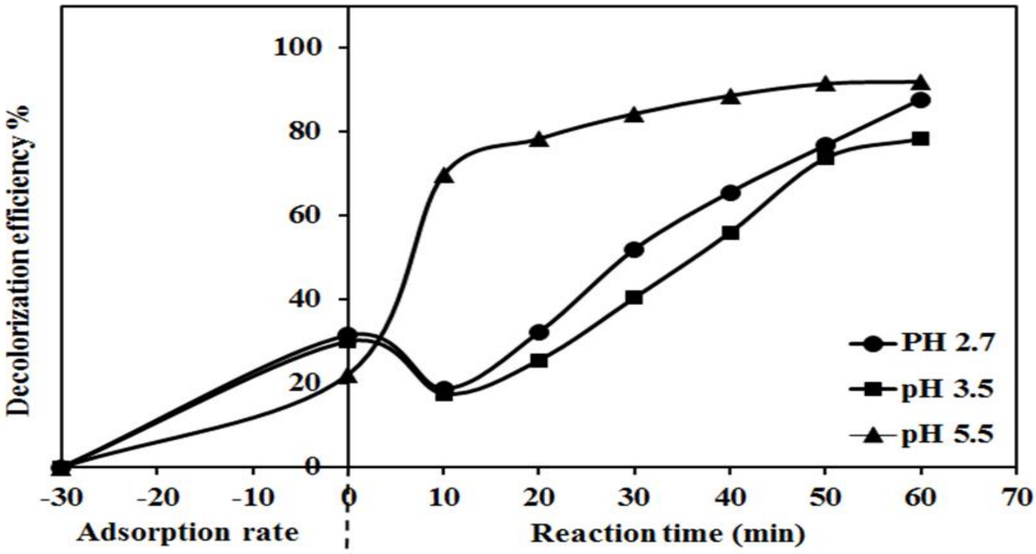


Fig. 7. Effect of pH solution on the decolorization of neutral red dye under various conditions. (Initial dye concentration 10 mg/L, catalyst loading 1.5 g/L, 0.1 mL H_2O_2 and reaction temperature of 60 °C).

According to the above results, the higher catalytic activity at pH 5.5 depends strongly on the pH of the solution. As such, the decolorization efficiency at pH 5.5 seems to prevent or slow down the formation of chromium complexes.

4.1.3Effect of calcination temperature

Fig8 shows the decolorization curves of neutral red dye catalyzed by 0.4% Cr-SiO_2 calcined at 200-600 °C. It can be observed that the adsorption rate between the catalyst and dye molecules after 30 min of mechanical stirring was increased with increasing the calcination temperature reaching its maximum to about 59 % for 0.4%Cr-SiO_2 calcined at 600 °C.

Next, the reaction between the catalyst and dye solution was started after the addition of H_2O_2 and the results showed an increase in catalytic activity with increasing the calcination temperature i.e. 22 % and 66 % for 0.4% Cr-SiO_2 catalyst calcined at 200 °C and 300°C.

It should be highlighted that the catalyst at this temperature showed very high adsorption rate for the dye solution on the catalyst surface. Wang *et al*. [23] also reported the synergetic effect between the adsorption rate andcalcinations temperature and their effect on catalytic activity of Cr doped TiO_2-Zeolite. However, in this reaction, the reduction in catalytic activity at the end of reaction might be ascribed to the rapid capturing of H_2O_2 by the adsorbed dye molecules on the catalyst surface. Ganesan *et al*. [10] reported that the heterogeneous oxidation of the organic matter occurs after the adsorption and decomposition of hydrogen peroxide on the solid's surface. As such, less amount of $^{\bullet}OH$ radicals could be formed in bulk solution caused this reduction in catalytic activity

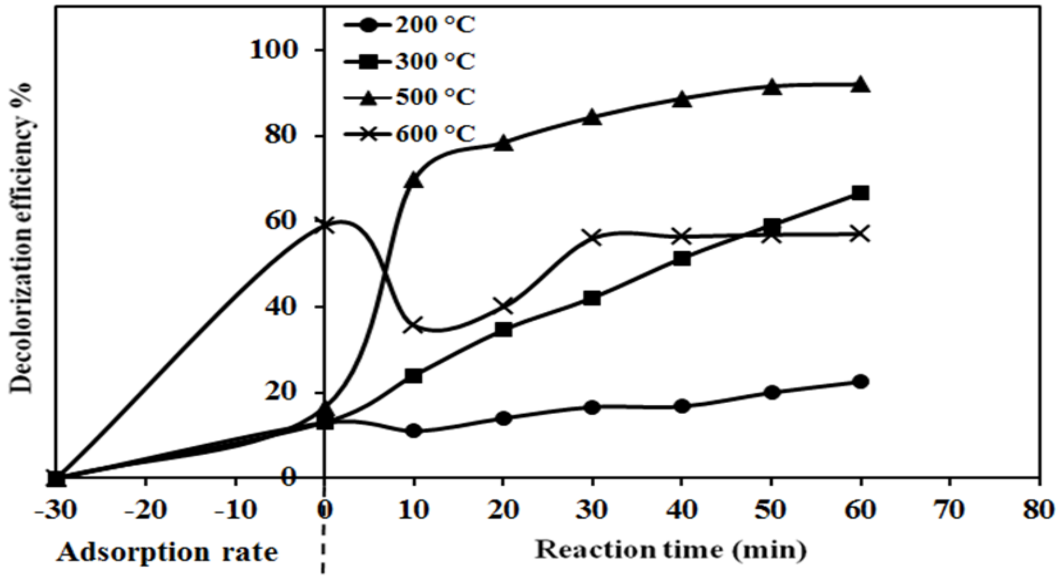


Fig. 8. Effect of calcinations temperatures on the decolorization of neutral red dye under various conditions. (Initial dye concentration 10 mg/L, catalyst loading 1.5 g/L, pH 5.5, 0.1 mL H_2O_2 and reaction temperature of 60 °C).

4.1.4Effect of H_2O_2 concentration

The decolorization efficiency of neutral red dye as a

function of different H_2O_2 concentration was investigated at initial dye concentration of 10 mg/L, 1.5 g/L of catalyst loading, original pH of the dye about 5.5, temperature rate of 60 °C and with different concentrations of H_2O_2
From (0.05 – 0.2) mL/100 mL of reaction volume. After allowing 30 min of adsorption – desorption stirring by the dye solution and catalyst, the adsorption rate was about 16 %. Next, as H_2O_2 was added into the solutions and the reaction was started, the decolorization efficiency was
found to increase from 84 % to 92 % with increasing the concentration of H_2O_2 from 0.05 to 0.1 mL as presented in Fig. 9. The increase in decolorization of dye by the addition of H_2O_2 was due to the production of hydroxyl radical.

$$H_2O_2 \rightarrow \bullet OH + \bullet OH \qquad (7)$$

$$\bullet OH + Dye \longrightarrow Intermediate\ products \longrightarrow Final\ Products \quad (8)$$

Further increase in H_2O_2 above 0.1 mL, the decolorization efficiency was decreased to 84 % at 0.2 mL of H_2O_2. This reduction in catalytic activity with increasing the amount of H_2O_2 was attributed to the excess amount of H_2O_2 molecules act as scavengers to hydroxyl radicals to generate perhydroxy radicals which have lower oxidation potential than the hydroxyl radicals [19].

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + {}^{\bullet}OOH \ (9)$$

$${}^{\bullet}HO_2 + {}^{\bullet}OH \longrightarrow H_2O + O_2 \qquad (10)$$

Neamtu, *et al.* [19] reported the effect of heterogeneous catalyst contain the redox sites on its surface i.e. (Cr^{+3} ions in our study). The radicals generated at the inner and outer surface of the solid catalyst can carry out the electrophilic attack to the aromatic ring of the substrate and break the large molecule into smaller fragments. As such, the presence of heterogeneous catalyst can be considering an effective factor that effect on the amount of H_2O_2 added into the reaction. In section 4. the catalytic activity of 0.4% Cr-SiO_2 without the addition of H_2O_2 was 5% only after 60 min of reaction thus, only 0.1 mL was needed to enhance the catalytic activity to 92% and that no desirable effect in the color removal was observed with the addition of higher concentration of H_2O_2.

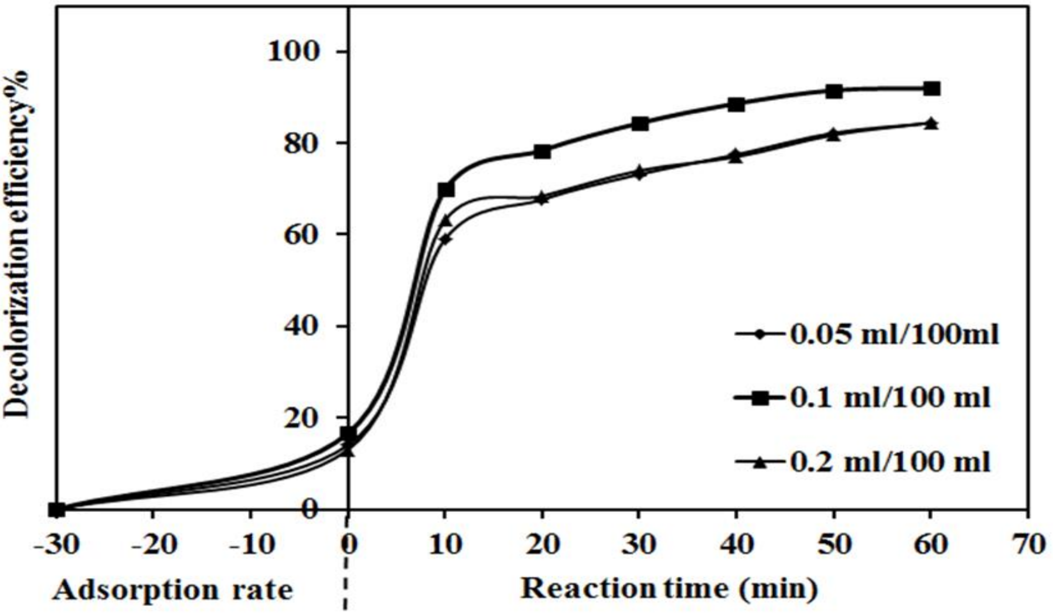


Fig. 9. Effect of H_2O_2 addition on the decolorization of neutral red dye under various conditions. (Initial dye concentration 10 mg/L, catalyst loading 1.5 g/L, pH 5.5 and reaction temperature of 60 °C).

4.1.5 The influence of the reaction temperature

The influence of temperature on the removal of neutral red dye using 0.4% Cr-SiO_2 catalyst was studied at 30, 45, and 60 ˚C as in Fig. 10. The results indicated that the decolorization of neutral red dye was significantly influenced by the reaction temperature and that the decolorization rate was accelerated from 50 to 92% by a rise in temperature from 30 ˚C to 60 ˚C. This enhancement in catalytic activity at higher temperature was ascribed to an increase in the reaction rate between hydrogen peroxide and the active site of catalyst, thus increasing the generation of oxidizing species i.e. radical. In addition, higher temperature can provide more energy for the reactant molecules to overcome reaction activation energy [19]. Similar result was also reported by Hameed and Lee [9]. Fig. 11 presents the absorbance spectrum of neutral red dye solution during the process catalyzed by 0.4% Cr/SiO_2 using oxidation reaction. The absorbance spectrum was measured with 10 mg/L of initial dye concentration, pH 5.5, H_2O_2

concentration of 0.1mL/100 mL of reaction volume and 1.5 g/L for catalyst loading at 60 °C. At the end of 60 min, the dye color was almost disappeared with maximum catalytic activity of 92%.

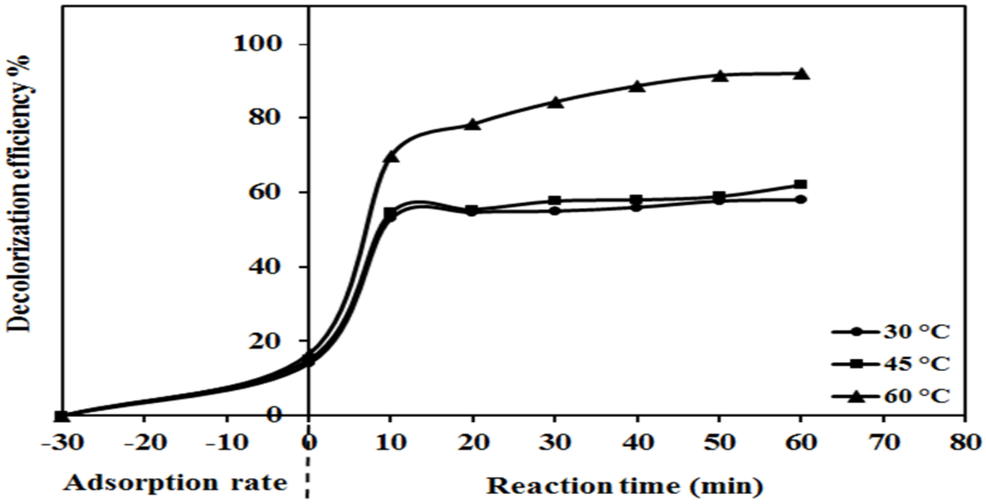


Fig. 10. The effect of reaction temperature on the decolorization of neutral red dye under various conditions. (Initial dye concentration 10 mg/L, catalyst loading 1.5 g/L, pH 5.5 and 0.1 mL H_2O_2).

4.2 Mechanism of reaction for neutral red dye

Advanced oxidation process (AOP) are based on powerful oxidant such as radical species $^{\bullet}OH$ and they are formed, basically, when H_2O_2 is reacted in the presence of transition metal ions, UV light, an alkali or acid [20]. The general decolorization of neutral red dye by oxidation reaction is represented by [Eq.11-12]. In this reaction, the Cr^{+3}/ H_2O_2 is the main active sites responsible about the formation of $^{\bullet}OH$ radicals. The possible mechanism of oxidation reaction is mainly related to the dissociation of H_2O_2 and the formation of chromium complexes [Eq. 13] to form various reaction series [Eq. 13- 18] until the formation of radicals which consider as the most active species for the decolorization process. Furthermore, the radicals can be formed by the oxidation/ reduction of chromium ions with the oxygen molecules adsorbed on the catalyst surface as in [Eq. 19- 21]]. However, the scavenger of $^{\bullet}OH$ radicals in the system might also take place during the reaction with 3 pathways as represented by[Eqs.23-25] [7]. In this case, the radicals will react with H_2O_2 to produce less reactive hydroperoxyl (•OOH) radicals, reacting with •OOH radicals or undergoing self-recombination to form H_2O_2. All the three reactions led to a significant decrease in the reaction rate as observed in this study

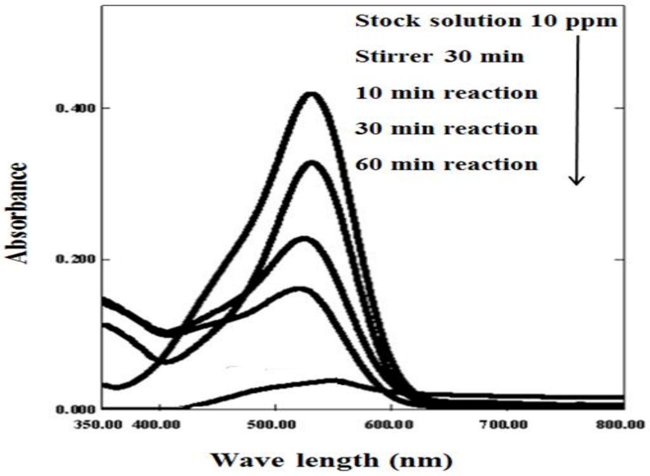


Fig.11 The absorption spectra of neutral red dye at Initial dye concentration 10 mg/L, catalyst loading 1.5 g/L, pH 5.5 and 0.1 mL H_2O_2.

$S+Dye \rightarrow S\text{–}Dye+[Dye]bulk$ (11)

$S\text{–}Dye+[Dye]_{bulk}+\bullet OH \rightarrow$ [Intermediate products] $\rightarrow$ Products (12)

$Cr^{+3} + H_2O_2 \rightarrow Cr - OOH^{+2} + H^+$ (13)

$Cr - OOH^{+2} \rightarrow Cr^{+2} + HO_2^{\bullet}$ (14)

$Cr^{+2} + H_2O_2 \rightarrow Cr^{+3} + \bullet OH + OH^-$ (15)

$Cr^{+3} + H_2O_2 \rightarrow Cr^{+2} + HO_2^{\bullet}\ H^+$ (16)

$Cr^{+3} + HO_2^{\bullet} \leftrightarrow Cr^{+2} + H^+ + O_2$ (17)

$Cr^{+3} + OH^- \rightarrow Cr^{+2} + \bullet OH$ (18)

$Cr^{+2} + O_{2(ads)} \rightarrow Cr^{+3} + \bullet O_2^-$ (19)

$\bullet O_2^- + H^+ \rightarrow HOO^{\bullet}$ (20)

$HOO^{\bullet} + H_2O \rightarrow H_2O_2 + \bullet OH$ (21)

$Cr^{+2} + \bullet OH \rightarrow Cr^{+3} + OH^-$ (22)

$H_2O_2 + \bullet OH \rightarrow HO_2^{\bullet} + H_2O$ (23)

$\bullet OH + HO_2^{\bullet} \rightarrow HO_2 + O_2$ (24)

$\bullet OH + \bullet OH \rightarrow H_2O_2$ (25)

According to the above mechanism the synergic between Cr^{+3}/H_2O_2

produces a strong oxidant capable of oxidizing (large and small) organic pollutants in mild conditions and this approach can be applied in wastewater treatment. **Comparative study between the modified catalyst and other heterogeneous catalysts.**

Metal ions doped solid supports have been widely investigated in photocatalytic reactions. A dopant ion may act as an electron trap or hole trap. This would prolong the lifetime of the generated charge carriers, resulting in enhancement in photocatalytic activity. Among these transition metal ions, Cr^{+3} has attracted considerable attention because its introduction can extend the visible light absorption. However, no report is available on the use of these types of heterogeneous catalysts in oxidation process applications. In the current study, the incorporation of Cr^{3+} with silica resulted in a catalyst with high catalytic activity for the decolorization of dye in short reaction time.

Meanwhile, the photocatalyst reactions could suffer from the aggregation of the catalyst particles at long reaction time that will consequently reduce the catalytic activity. **Table2** presents comparison between the prepared catalyst used in this study (0.4%Cr/SiO_2) and different heterogeneous catalyst of chromium supported solid support that have been reported in photocatalytic reaction. The results showed that the produced catalyst in this study under oxidation reaction showed high decolorization efficiency in short reaction time compared to those catalyst in the of photocatalytic reaction.

5. Conclusion

XRD results revealed the crystallinity properties of the prepared catalyst after calcination. The FTIR results improved the existence of Cr^{+3} within the structure of silica due to the shifting of peaks to higher wave numbers. The TGA/DSC analysis showed the significant influence of temperature on the chromium phases supported silica. The superior properties of 0.4% $Cr\text{-}SiO_2$ catalyst led to significant enhancement in the decolorization of neutral red dye in aqueous solution. Process behaviors of the catalysts were also successfully elucidated. The optimum conditions for the highest decolorization efficiency (92%) were achieved at 10 mg/L of neutral red dye, catalyst loading loading of 1.5 g/L, pH 5.5, reaction temperature of 60 °C and 0.1 mL H_2O_2. Hence, the prepared catalyst under oxidation reaction was proven to be a highly potential environmental catalyst and can become an alternative choice of treatment method for organic dyes in effluents.

Table 2. Comparative study between the performance of the synthesized catalyst and different types of catalysts reported in photocatalytic reaction

Composition of catalyst	Reaction condition	Irradiation time	Degradation	Reference
10mol%Cr- TiO_2/zeolite	0.2g/100ml catalyst loading, 10mg/L dye concentration, 40 W UV lamp	5hr	41.73%	[7]
TiO_2/Cr/MCM-41	1g/L Catalyst loading, pH 5, 20 mg/L dye concentration, 20 W UV-VIS	5 hr	97%	[24]
Cr_2O_3-CNT/TiO_2	0.05g/L Catalyst loading, pH 5, 1.0×10^{-5}mol/L dye concentration, 8 W UV-VIS	2 hr	-	[5]
0.05 wt. %Cr - TiO_2/SiO_2	Not mention	5hr	95%	[8]

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سلوك العامل المساعد المكون من الكروم ي المدعوم بالسيليكا لإزالة اللون من الصبغة الحمراء المتعادلة باستخدام تفاعل الأكسدة

أثيل حسن علوش
جامعة النهرين- كلية العلوم
قسم علوم الكيمياء-بغداد/العراق

الخلاصة

تم دراسة العامل المساعد غير المتجانس المكون من الكروم المدعوم بالسيليكا والذي تم نحضيره بطريقة النقع لازالة الصبغه الحمراء المتعادلة والتي استخدمت كملوث في هذه الدراسة. اظهرت نتائج الاشعه السينية وجود منحنيات جديدة لأوكسيد الكروم في درجة 24.6 ، 32.92 °، 40.8 °، 41.4 ° و 44 °. كما اثبتت نتائج FTIR وجود الكروم الثلاثي داخل هيكل السيليكا بسبب الزحف الحاصل لقمم الامتصاص في منطقة الترددات العالية. بينما كشفت نتائج DSC / TGA التأثير الكبير لدرجات الحرارة على ظهور اطوارعديدة للكروم المدعومة بالسيليكا. تمت دراسة متغيرات تفاعل مختلفة مثل، تأثير تركيز أيونات الكروم، وقيم الرقم الهيدروجيني، وكمية بيروكسيد الهيدروجين وتأثير درجة الحرارة لتقدير تأثيرها على كفاءة إزالة اللون . وكان الحد الأقصى لنشاط العامل المساعد قد حقق نسبة 92٪ في ازالة اللون عند درجة الحموضة 5.5، كمية محفز 1.5 غرام / لتر، 0.1 مللتر H_2O_2/ 100 مللتر من حجم التفاعل وتركيز الصبغة الأولي من 10 ملغ / لتر بعد 60 دقيقة من زمن التفاعل.