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Study on the Catalytic Activity of Cerium/Cadmuim Mixed Oxide Catalysts for the Photo catalytic Degradation of Orange G Dye

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Abstract

The Mono and binary-mixed oxide catalysts were prepared by precipitation and co-precipitation method and investigated for the photocatalytic decolorization of orange G dye which was used as a pollutant model in this study. The structure of the synthesized catalysts were characterized by the X-ray diffraction (XRD), bonding by fourier transfer infrared (FTIR), morphology by scanning electron microscope (SEM) and reflection using UV-VIS diffuse reflectance spectra. The XRD results revealed that the mono oxide catalysts confirm well the cubic phase of cadmium and cerium oxide and that their mixed oxide catalyst i.e. 50Ce/25Cd show the same characteristic peaks of pure cerium oxide with slight shift to higher wave lengths for two crystalline peaks at 33.15° and 56.15° respectively. The FTIR spectra of 50Ce/25Cd mixed oxide catalyst improved the combination between both pure cadmium and cerium oxide catalyst. The diffuse reflectance showed a blue shift towards lower wave length and that the energy gap was increased with an increase in cerium content. Different reaction variables such as, effect of metal content, pH values, amount of hydrogen peroxide and effect of catalyst amount were studied to estimate their effect on the decolorization efficiency of orange G dye. The maximum catalytic activity achieved was 91% at a solution pH of 2.1, catalyst dosage of 1.5 g/L, 0.15 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: Mixed oxide catalyst; photocatalytic reaction; Cerium oxide; Cadmium oxide

1. Introduction

In textile industries, azo dyes have been widely used for dyeing purposes that create great hazardous effects to the human health and environment [1]. These dyes have high resistance to the conventional treatment process because of their high stability that makes their biodegradation limited. [2]. Thus advanced oxidation processes (AOPs) such as photocatalytic process has become one of the most promising technologies for waste management, particularly for decomposition of organic pollutants such as dyes.

The photocatalytic activity of the process can be improve by the combination between photolysis irradiation and heterogeneous catalyst thus, more hydroxyl radicals are generated.. Different types of heterogeneous catalysts have been widely investigated for the photocatalytic degradation of organic dyes such as metal oxides heterogeneous catalyst which play an important role in catalytic reactions in addition to their different applicable areas in chemistry, physics and materials science [3]. The major advantage of using metal oxides as a catalyst is due to their low metal leaching during the catalytic reaction thus avoiding secondary metal contamination to the treated wastewater [4]. A number of metal oxide catalyst have been explored for the visible-light driven photocatalytic degradation of pollutants such as WO_3/ZnO [5], Zn/Fe [6], Mg/TiO_2 [7] mixed oxide photocatalysts.

Recently, ceria has been attracting much attention in the oxidative catalysis research due to its high oxygen storage capacity and redox properties [8]. However, the band gap of ceria is about 3.1 eV that limited the absorbing of light to only UV light. Therefore the mixed oxides systems have the ability to obtain structures in combinations with the properties that neither individual oxide possesses [9].

The selection of suitable metal is an important step since the efficiency of the catalyst is qualified by the capacity of electron - hole pairs generation in addition to radical production [10]. Furthermore, the properties of binary mixed oxide catalyst are strongly dependent on the type of preparation methods i.e. conventional solid state mixing, hydrothermal, co-precipitation and sol-gel [6]. Amongst these methods, the precipitation method is the most simple and cost effective method for controlling textural and surface characteristics to produce homogenous materials.

In literature, the work that shows the potential use of ceria with other metal oxide for the degradation of dyes is scarce as such, this work is focusing on the synthesis of cerium/ cadmium mixed oxide catalyst for the photocatalytic degradation of orange G dye which was used as a pollutant model in this study. The selection of cadmium was due to its important properties as p-type semiconductor with a direct band gap of 2.2 to 2.5 eV and an indirect band gap of 1.36 to 1.98 eV. It has been reported that the heterounions between semiconductors of p-type and n-type (ceria metal) exhibit an increase in photocatalytic activity [11]. As such, the mixed oxide catalysts were synthesized using co-precipitation method. The products were characterized by the Fourier transform infrared (FT-IR), X-ray diffraction (XRD), UV-VIS diffuse reflectance spectra and scanning electron microscopy (SEM). Finally, the optimum reaction variables such as amount of metal loading, pH of solution, amount of catalyst loading and H_2O_2 concentration were investigated in addition to the mechanism of reaction.

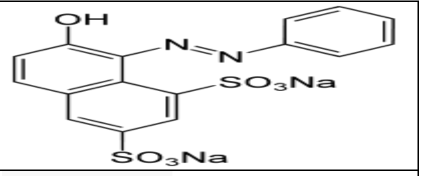
2. Materials and Methods

The pure metal cadmium and cerium nitrate purchased from GPR and BDH respectively. Meanwhile, hydrogen peroxide (30% analytical grade) was supplied from R&M chemicals. The sodium carbonate as a precipitating agent was purchased from Merck. The pollutant model Orange G dye was obtained from Fluka and its properties are listed in Table 1.

2.1 Preparation method

Pure ceria and cadmium oxide were prepared by precipitation method while their mixed oxides were prepared by co-precipitation technique [9]. The sodium carbonate was used as a precipitating agent at room temperature. 0.1M of cerium nitrate and /or cadmium nitrate was taken to prepare the mono-oxide samples. However, for mixed oxide Samples, 0.1 M of cerium nitrate and cadmium nitrate were mixed together and the volume of mixing solution was changed with each sample i.e. 25 ml of Ce/25 ml of Cd, 35 ml of Ce/25 ml of Cd, 50 ml of Ce/25ml of Cd, 35ml of Cd/25 ml of Ce and 50Cd/25Ce.

Table 1: The structure and properties of Orange G dye

Molecular structure	
Other names	Acid Orange 10
Molecular weight	452.38 g/mol
Color Index	16230
λmax	478 nm

In typical experiment, a known volume of pure or mixed oxide was taken individually and Na_2CO_3 of 0.25 M were added into the pure or mixed solution until the pH reached to 9. At that pH, a precipitate solid was formed then the products were collected by filtration, washed several times with distilled water, and dried at 110 °C. Finally, the dried samples were calcined at 500 °C for 4 h.

The prepared catalysts were denoted as CeO_2 and CdO for mono oxide catalysts. Meanwhile for mixed oxide samples, the catalysts were denoted according to their volume ratio i.e. 25Ce/25Cd, 35Ce/25Cd, 50Ce/25Cd, 35Cd/25Ce and 50Cd/25Ce.

3. Characterization techniques

Different analytical techniques were used to characterize the synthesized catalysts. Among various catalysts loadings, the best catalyst was demonstrated by activity of 50Ce/25Cd. 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 morphology for the prepared catalyst was detected by SEM system (Oxford INCA/ENERGY-350) system. Meanwhile, the reflection spectra of the solid samples were measured using the diffrection spectrophotometer by (Perkin Elmer) with a wavelength range between 190 and 1,300 nm.

3.1Reaction procedure and analytical method

The photo-efficiency of all synthesized catalysts was tested towards degradation of orange G dye which was used as a pollutant model in this reaction. The experimental runs were carried out in a 250 mL conical flask as a reactor equipped with continuous mechanical stirrer. Thereafter, the dye solution was exposed to UV light with constant stirring for 1 h after the addition of solid catalyst and hydrogen peroxide . The samples were taken at periodic intervals i.e. (10 min).

The maximum absorption of the dye was detected using spectrophotometric analysis with maximum absorption of the dye at 478 nm. The concentration of the dye solution was calculated based on the maximum absorbance wavelength using Beer-Lambert law. The catalytic activity represented by the color removal was calculated based on equation [7]:

$$\text{Decolorization Efficiency } \% = \left[\frac{C_0 - C_t}{C_0}\right] \times 100 \quad \ldots (1)$$

Where, C_o is concentration of dye in (mg/L), C_t is the concentration of dye in (mg/L) at different reaction time and t (min).

4. Result and Discussions

4.1 X-ray diffraction

Fig.1 shows the indexed XRD pattern for the prepared samples of CdO, CeO_2 and mixed oxide catalyst 50Ce/25Cd catalyst. All the prepared samples show high crystalline structure of peaks that confirms the formation of cubic phase CdO and CeO_2 samples. The d-spacing values of the cadmium and cerium oxide samples matches well the standard code of 98-018-1224 and 98-062-1718 respectively. It was notice that CdO appears with higher crystalline peaks compared to that of cerium oxide. Furthermore, the peaks of CdO were much sharper than that of cerium oxide (smaller particles size) thus, it is expected to enhance the properties of the prepared samples consequently, affect the catalytic activity. Tadjarodi (2013) reports the diffraction peaks of cadmium oxide were at 32.9°, 38.2°, 55.2°, 65.8° and 69.2°. Similar result was detected with our prepared high crystalline sample of CdO. Meanwhile, the crystalline single phase peaks of CeO_2 were observed at 28.65°, 33.15°, 47.55° and 56.15° respectively . Similar results were detected with Chelliah (2012) . For the case of mixed oxide prepared catalyst 50Ce/25Cd, the crystalline structure show the almost the same characteristic peaks of pure cerium oxide (due to its higher content) with slight increase in the crystalline structure. Furthermore, the peaks at 28.65°, 33.15° and 56.15° were slightly shifted to higher angles at 28.75° 33.25° and 56.45° respectively. This shifting could be ascribed to the entrance of CdO within the structure of CeO_2 during the preparation method.

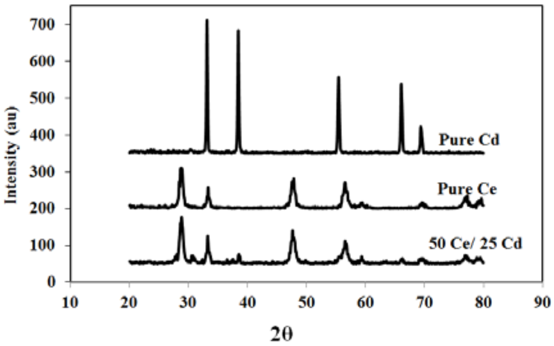


Figure 1: The XRD pattern of different types of prepared catalysts

4.2 UV-VIS diffuse reflectance spectra

The UV-VIS diffuse reflectance spectra for the prepared mixed oxide catalyst are shown in Fig. 2 compared to bare cerium and cadmium oxide catalyst as a reference. The sudden fall in the reflectance at a certain particular wave lengths indicated the presence of an optical band gap for the prepared sample. However, the mix between two different materials can generally change the energy gap of the produced sample to cause a shift in the reflection spectra towards higher or lower wave length. In Fig. 2, all the prepared samples showed a blue shift towards lower wave length with maximum shifting of 410 nm in comparison to bare cerium oxide reference sample which shows reflectance spectra of about 454 nm. Meanwhile the bare cadmium oxide catalyst shows very high wave length of about 820 nm. Similar result was detected with Tadjarodi (2013).

The energies band gap for the prepared samples were calculated from their reflection spectra as in Table 2. The band gap values were determined from the extrapolation of the straight line for the graph figured between the [Ln [(R_{max}-R_{min})/(R-R_{min})]]^2 versus h*v* (as abscissa) kumar (1999).

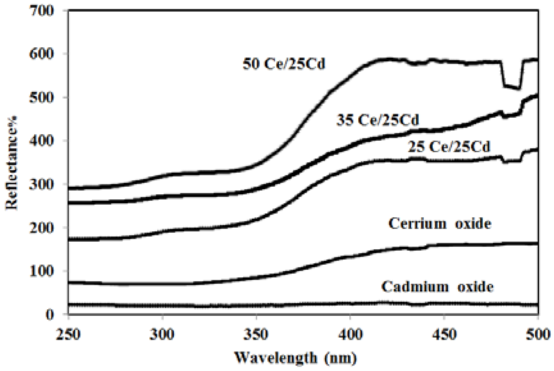


Figure 2: UV-VIS diffuse reflectance spectra for pure and mixed oxide catalyst

From Table 2, it can be seen that the band gap energies of the samples with higher cerium content were increased compared to that bare cerium oxide sample. Meanwhile, as the cadmium content was increase, the band gap energies of the catalysts were decreased. Channei (2013) concluded that the energy gap was reduced with an increase in concentration and thickness of CeO_2 film. On the other hand, Sri dev (2014), Ali and Devadason (2011) founds that the energy band gap of the prepared films increase with an increase in cerium content. It seems that the change in the energy distribution cannot have a general rule such as band gap will decrease after introducing the impurities. As such controlling the chemical composition, synthesis method, reaction temperature, and the particles size affected directly on the structure of the produced samples thus affected their optical properties [18]. As a conclusion, the change in the energy band gap of the produced samples indeed refers to the successful mixing between cerium and cadmium oxides thus, the structure of each oxide was well introduced.

Table 2: Band gap energy and reflection spectra of the prepared samples.

Type of catalyst	Band gap energy(eV)	Wavelength (nm)
Ce	3.4	454
Cd	2.3	820
25Ce/25Cd	3.8	428
35Ce/25Cd	3.9	420
50Ce/25Cd	4.2	410
35Cd/25Ce	3.4	436

4.3 Fourier Transforms Infrared Spectrophotometry

The FTIR spectra of the prepared catalyst i.e. pure CdO, CeO_2 and mixed oxide 50Ce/25Cd catalyst are shown in Fig. 3 and the results are compared to uncalcined raw materials i.e. cadmium and cerria nitrate.

All the absorption spectra of cerium oxide calcined at 500 °C shows a reduction in peaks intensity compared to uncalcined raw material (cerria nitrate). It can be observed that the characteristic absorption bands of the prepared cerium oxide appeared at (3383.1 cm^{-1}) which is attributed to water absorption, while the peak at (1056 cm^{-1}) was related to N-O bond. This band was slightly shifted to higher wave number compared to uncalcined raw material (1047 cm^{-1}). This shifting could ascribe to the increasing in particle size or degree of aggregation due to the effect of calcination temperature [19]. The peaks ranging from 750 to 400 cm^{-1} was related to Metal-O stretching vibration [20].

On the other hand the pure cadmium oxide calcined at 500° C did not show any clear organic functional groups compared to uncalcined raw material (Cadmium nitrate). This could be due to the complete dissociation of cadmium nitrate to cadmium oxide at 500 °C. Similar results were detected with Tadjarodi (2013). Furthermore, during the preparation method the color of this catalyst was converted to redish brown after calcination which consider as evidence to the presence of CdO phase. For the case of mixed oxide catalyst the FTIR spectra show combination between both pure cadmium and cerium oxide spectra as in Fig.3.

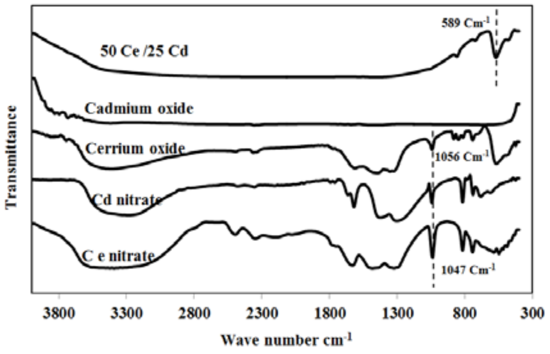


Figure 3: FTIR of different prepared samples compared to their raw materials

4.4 Scanning electron microscopy

Fig. 4 show the SEM image of the prepared mixed oxide catalyst 50 Ce/25 Cd compared to the pure cadmium and cerium oxide catalyst. It can be notice that cerium oxide (image (a)) did not show any regular shape compared to pure cadmium oxide catalyst (image (b)) that show different morphology with almost spherical agglomerated particle. Although all the prepared catalysts have been prepared with the same preparation method however, this difference in the morphology between cadmium and cerium oxide catalyst certainly refers to the chemical properties of each metal. Image (c) almost shows the same characteristic morphology of image (a) due to the higher amount of cerria nitrate used in preparation method compared to that of cadmium nitrate. This result was in good agreement with the XRD result. However, some small spherical particles of cadmium oxide can be notice that did not exist in image (a).

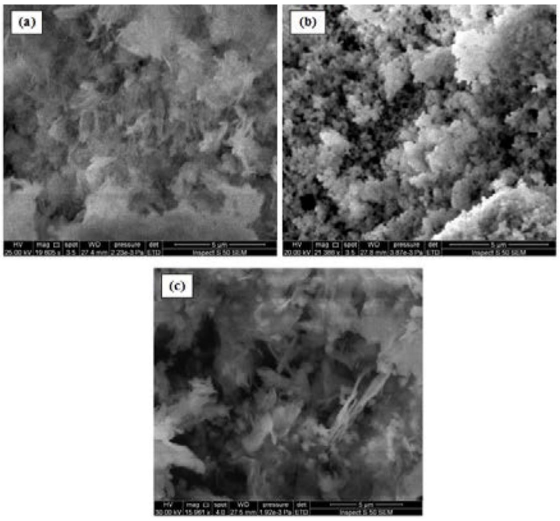


Figure 4: Scanning electron microscopy of (a) pure cerium oxide (b) pure cadmium oxide and (c) 50Ce/25Cd mixed oxide catalyst.

5. Photoreaction

Photocatalytic degradation experiments were carried out in a 100 ml Pyrex-glass cell in the UV chamber equipped with UV light source namely high pressure lamp of (1000 W lwasa ki electric Co. Ltd., Japan)). A magnetic stirrer was used to ensure uniform mixing of solution in vessel. Prior to irradiation the dispersions were magnetically stirred in dark for 30 min to ensure the establishment of adsorption/desorption equilibrium. The pH of solutions was measured using pH-BP3001 Trans instruments digital pH meter. The spectra were taken with UV–VIS spectrophotometer (Shimadzu UV-1650 PC).

5.1Control experiment

The photocatalytic activity for the color removal of orange G dye was investigated under UV irradiation. The absorption capacities of each mixed oxide catalyst compared to pure cerium and cadmium oxide were assessed by monitoring in dark under continuous stirring with dye solution for 30 min as in Fig 5 a. The results revealed that the absorption rate increase with an increase in cerium content reaching its maximum rate to 65% for 50Ce/25Cd mixed oxide catalyst. Meanwhile the absorption rate was decrease with an increase in cadmium content up to 1.79% for 50Cd/25Ce mixed oxide catalyst. These results were compared with the absorption rate of pure cerium and cadmium oxide catalyst which shows a maximum absorption rate of 37% and 6% respectively after 30 min of mechanical stirring.

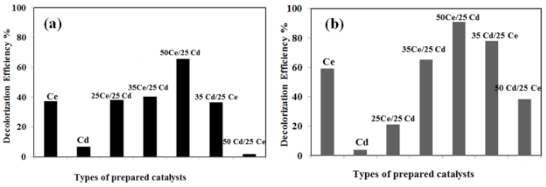


Figure 5: Control experiment for pure and mixed oxide catalysts (a) absorption study (b) photocatalytic reaction

The photocatalytic activity of the prepared catalyst using different vol% of metal content compared to pure cadmium and cerium oxide sample has been investigated for the photodecolorization of orange G dye under UV irradiation as in Fig.5b. Pure cadmium and cerium oxide shows very low decolorization efficiency i.e. 4% and 59% respectively compared to the mixed oxide catalyst. However with gradual increase in cerium metal content, the photocatalytic activity increases from 21% for 25Ce/25Cd to 65% for 35Ce/25Cd reaching maximum photocatalytic activity of 91% for 50Ce/25Cd mixed oxide catalyst. Meanwhile, a reduction in phtocatalytic activity was occurred with an increase in cadmium metal content i.e. 78% and 38% for 35Cd/25Cd and 50Cd/25Ce, respectively.

According to the above results, it seems that the cerium oxide and all the prepared samples with higher cerium content were preferred due to their higher decolorization efficiency. It should be highlighted that the increase in energy gap for the samples with higher cerium content did not affect negatively on the catalytic activity. Instead, the absorption ability of the prepared catalysts seems to play an important role in this reaction. The cerium oxide and all the prepared catalysts with higher cerium content i.e 25Ce/25Cd, 35Ce/25Cd and 50 Ce/25Cd shows high absorption capacities compared to those samples with higher cadmium content. This indeed will facilitate the reaction between the molecules of reaction mixture with catalyst surface resultant in enhancing the generation of hydroxyl radicals and super oxide ions thus, improve the photocatalytic activity [21]. Furthermore, the photocatalytic activity with different cerium content of mixed oxide catalyst was not only relates to the surface absorption ability, but also relates to the influence of metal concentration on structure and oxygen vacancies [22]

Ji (2009) studied the absorption of azo dye Acid Orange 7 on CeO_2 in relation to its photocatalytic activity and concluded that superior absorption properties of CeO_2 in comparison with TiO_2 cause its better photo degradation efficiency.

5.2Effect of pH

The pH parameter plays significant role in both the characteristics of textile wastes and generation of hydroxyl radicals. The catalytic activity based on color removal of orange G dye was investigated within the pH range of 2.1 to 7.0 under photocatalytic reaction as in Fig. 6. The desire pH for the reaction solution was adjusted using 0.1 M NaOH or HCl with an initial dye concentration of 10 mg/L, 0.15 ml of H_2O_2/100 ml of reaction volume and 1.5 g/L catalyst loading for up to 60 min.

Before the starting of the photocatalytic reaction, 30 min of mechanical stirring was carried out between the catalyst and the dye solution until the adsorption-desorption equilibrium was obtained as presented in Fig.6 The absorption rate of the dye reached its maximum rate to about 65% at pH 2.1. However, with an increase in pH values, the catalyst shows a reduction in absorption ability owing to the repulsive forces between the dye and the catalyst surface.

It is well known that the absorption capacity of any catalyst is based on its zero point charge. The electrolyte medium of any reaction is responsible about identifying the surface charge of the solid catalyst. hus, in this reaction, the acidic medium give the catalyst surface its positive charged meanwhile, the sulfonic groups of Orange G dye balancing the positive charges on the of the catalyst surface. Akpan and Hameed (2009) reported that the degradation rate of azo dyes increases with a decrease in pH values meanwhile, the dye molecules are negatively charged in alkaline media, hence, the absorption rate decreased due to coulombic repulsion between the dyes molecules and the catalyst surface.

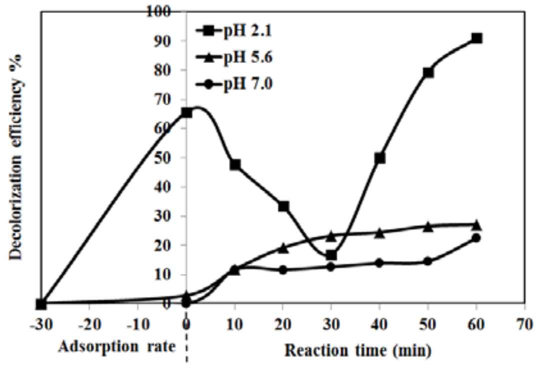


Figure 6: Effect of pH on the decolorization efficiency orange G dye at initial dye concentration 10ppm, 0.15 g/l catalyst loading and 0.15 mlH_2O_2/100ml reaction volume.

Next, after the end of adsorption-desorption mechanical stirring, the decolorization efficiency of orange G dye was investigated under photocatalytic reaction. It was found that the decolorization efficiency reached its maximum rate with about 91% at pH 2.1. However, with an increase in pH of the dye solution, the decolorization efficiency decrease to 27% and 22% at pH 5.6 and 7, respectively.

During the experimental run and when the photocatalytic reaction was started, it was noticed that some of the highly absorbed dye i.e. at pH 2.1 was desorbed from the catalyst surface into the reaction media due to the color change (the dye solution become darker) at the first 30 min of reaction. This was because of the addition of H_2O_2 that slightly affect the pH of solution. However, as the reaction time was increased more $^{\bullet}OH$ radicals were generated thus enhance the catalytic activity.

According to the above results, the higher absorption rate at pH 2.1caused higher photocatalytic activity this is because three possible reaction mechanisms can contribute to dye degradation, namely, hydroxyl radical attack, direct oxidation by the positive hole, and direct reduction by the electron in the conducting band.

5.3 Effect of catalyst loading

The amount of the photocatalyst added to the reaction is most essential parameter that affects the rate of photocatalytic degradation and also affect the economic cost of the whole process. As such, the experiments were carried out using 50Ce/25Cd mixed oxide catalyst at a fixed dye concentration (10 mg/L), pH 2.1, 0.15 H_2O_2 and different loading of catalyst (0.1 to 0.25) g/l at 60 minute of irradiation as in Figure 7. The results revealed that the rate of dye absorption increase with an increase in catalyst loading reaching its maximum to 94% at 0.25 g/l of catalyst loading. This increase in absorption ability of the catalyst was indeed referring to the availability of more active sites on the catalyst surface [24]. Consequently, this will increase the decolorization efficiency up to 100% for 0.2 g/l of catalyst loading within 30 min. Meanwhile an increase in catalyst loading up to 0.25 g/l also achieved the complete decolorization efficiency of 100% but within 60 min of reaction time. This deceleration in speed of reaction was ascribed to the effect of light scattering due to an increase in solid particles [25].

Although higher catalytic activity i.e. 100% was achieved with both catalyst loading (0.2 and 0.25 g/l). However, during the experiment run, both catalysts showed very high absorption rate greater than their catalytic activity. Thus, the decolorization efficiency of 0.15 g/l catalyst loading is the best choice with maximum rate of 91% after 60 min of reaction time besides being more cost effective, it is better to use less amount of catalyst to minimize the cost of the process. Ameta (2014) also reported an optimum value for their prepared catalyst at 0.03 g/50 ml of dye and any increase above this value cause a reduction in photocatalytic activity

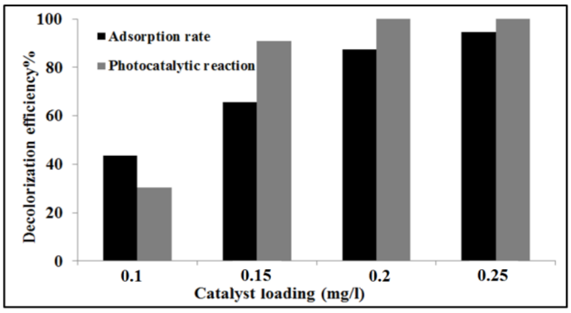


Figure 7: Effect of catalyst loading on the decolorization efficiency orange G dye at initial dye concentration 10 ppm, pH 2.1 and 0.15 mlH_2O_2/100ml reaction volume.

5.4 Effect of H_2O_2 Concentration

The catalytic activity based on color removal of orange G dye as a function of different H_2O_2concentration was studied at 10 mg/l initial concentration of dye, 1.5 g/l of catalyst loading, pH of the dye about 2.1 with different concentrations of H_2O_2 of (0.1, 0.15 and 0.2) ml/100 ml of reaction volume. The decolorization efficiency was found to increase from 60 % to 91 % with an increase in the concentration of H_2O_2 from 0.1 to 0.15 ml as presented in Fig. 8. The certain amount of H_2O_2 added into the reaction was likely because it enhance the radicals generated during the reaction. However, with an increase the amount of H_2O_2 above 0.15 ml, the decolorization efficiency was decreased to 47% at 0.2 ml of H_2O_2concentration after 60 min of reaction. This fall in the catalytic activity was referred to the extra amount of H_2O_2 molecules that act as scavengers to •OH radicals as in eq. below [26]:

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + {}^{\bullet}OOH \quad \ldots \quad (3)$$

$${}^{\bullet}HO_2 + {}^{\bullet}OH \longrightarrow H_2O + O_2 \quad \ldots \quad (4)$$

Aravindhan (2006) reported that the catalytic activity can be negatively affect by the additional amount of hydreogen peroxide added into the reaction system due to the scavenging of ${}^{\bullet}OH$ radicals.

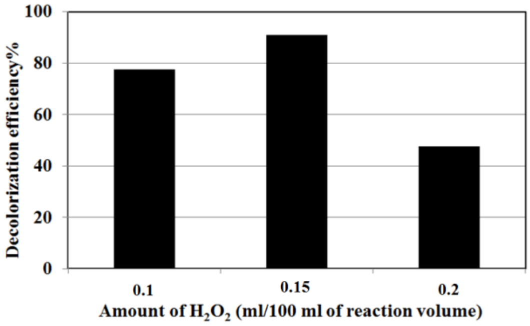


Figure 8: Effect of H_2O_2 on the decolorization efficiency orange G dye at initial dye concentration 10 ppm, 0.15 g/l catalyst loading and pH of 2.1.

6. Mechanism of reaction

In photocatalytic reaction, the absorption of pollutant on the surface of catalyst is an important factor that enhance the reaction pathway. Semiconductor photocatalysts generally absorb different colour light depending on their band gap energy and used as photocatalysts because of their interesting electronic configurations, light absorption ability, charge carrier transport property, and excited-state lifetimes. Primarily, the catalyst can be excited directly by the absorption of UV light that generated the e^--h^+ pair. The excited electron transfer from the valance band of Ce (n-type) to its conduction band which then transfer to the conduction band of cadmium. However, cadmium has full d-block electron configuration therefore, the electron will immediately migrate and react with absorbed oxygen creating oxygen radicals ($O^{\bullet}_2$, $O^{\bullet}$). The presence of Cd could be effective in producing a catalyst that has a delay in electron–hole recombination, thus increasing the lifetime of the electron–hole separation and support the charge carrier transfer to the catalyst surface. On other hand, oxidation of water or OH^- by the hole generated in the valance band of prepared catalyst produces the hydroxyl radical (${}^{\bullet}OH$), a powerful oxidant. These radicals ($O^{\bullet}_2$,$O^{\bullet}$ and $OH^{\bullet}$) present extremely strong oxidizing properties. The principal reaction mechanism of a semiconductor photocatalyst is described as in Fig. 9:

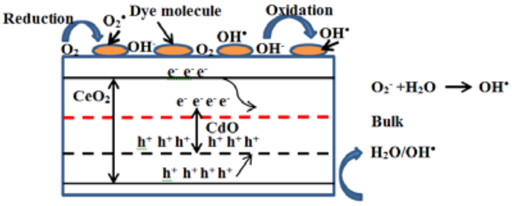


Figure 9: Mechanism of the photocatalytic reaction

It seems that the mix between the cerium and cadmium oxide generated a promise mixed oxide catalyst in UV region. This enhancement in properties of the prepared catalyst could be ascribed to oxygen vacancies generated within catalyst, higher ability for absorption and the prevention of electron –hole recombination. Furthermore, although the higher efficiency of the mixed oxide catalyst has the higher energy gap however, the absorption ability seems to be the most controlling step in this reaction compared to that of energy gap.

Conclusion

The heterogeneous catalyst of cerium/cadmium mixed oxide has been synthesized successfully by simple precipitation and co-precipitation method. The XRD results showed that the prepared mixed oxide catalyst 50Ce/25Cd has almost the same crystalline structure of pure cerium oxide. Meanwhile the UV-VIS diffuse reflectance revealed that the energy gap of the prepared catalysts increased with an increase in cerium content. The SEM result was in good agreement with XRD result that 50Ce/25Cd has the same characteristic morphology of cerium oxide due to the higher amount of cerria nitrate used in preparation method compared to that of cadmium nitrate.The process behaviors of the catalysts were also successfully elucidated. The optimum conditions for the highest decolorization efficiency (91%) were achieved at 10 mg/L of orange G dye, catalyst loading of 1.5 g/L, pH 2.1 and 0.15 mL H_2O_2. Hence, the prepared catalyst under photocatalytic reaction was proven to be a highly potential environmental catalyst and can become an alternative choice of treatment method for organic dyes in effluents.

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دراسة كفاءة العامل المساعد لخليط اوكسيد الكادميوم/سيريوم في تحطيم صبغة الاورانج ج بواسطة عملية التشعيع

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الخلاصة :

تهدف الدراسة الى تحضير خليط اوكسيد الكادميوم/والسيروم كعامل مساعد عن طريق عملية الترسيب والتحقق من كفاءته في ازالة صبغة الاورانج ج والذي استخدم كملوث في هذة الدراسة . تم تشخيص بنية المادة المصنعة باستخدام عدة تقنيات ومنها اشعة الحيود السينية ال XRD، المجهر الالكتروني الماسح SEM ، تشخيص الاواصر الرابطة باستخدام FTIR وقياس فجوة الطاقة بواسطة diffuse reflectance spectra . وجدت نتائج اشعة الحيود السينية ان قمم الحيود للاكاسيد الاحادية متطابقه مع طوراوكسيد الكادميوم والسيريوم بينما كانت قمم خليط اوكسيد الكادميوم/سيريوم مشابهه لقمم اوكسيد السيريوم مع زحف قليل للقمم باتجاه منطقة الترددات الاعلى ل33.15° ، 56.15° على التوالي. أظهرت نتائج diffuse reflectance spectra حيودا باتجاة الطيف الموجي القصير وقد ادى الى زيادة فجوة الطاقه بزيادة نسبة السيروم.

بعد استكمال عملية التشخيص للعامل المساعد المصنع تم دراسة العديد من متغيرات التفاعل التي لها تأثير مباشر على كفاءة ازالة اللون خلال وقت التفاعل ومنها نسب المعدن في العامل المساعد ، الاس الهيدروجيني، كمية الهيدروجين بيروكسايد، كمية العامل المساعد. وكانت اعلى كفاءة للعامل المساعد قد وصلت الى 91% حيث كانت قيمة الاس الهيدروجيني 2.1، وكمية العامل المساعد 1.5غم/مل، 0.15 مل هيدروجين بيروكسايد/100 مل من حجم التفاعل مع تركيز ابتدائي للصبغه 10 ملغ/ليتر خلال 60 دقيقة من وقت التفاعل.