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SIGNIFICANT EFFECT OF pH ON PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS USING SEMICONDUCTOR CATALYSTS

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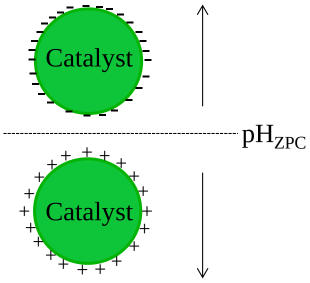
Graphical abstract



Abstract

Photocatalytic is one of the inexpensive and non-toxic techniques for degradation of organic pollutants into harmless substances such as water and carbon dioxide. In this study, simple electrolysis method was used in preparation of Ag/TiO_2 and α-Fe_2O_3/HY catalysts. The physicochemical properties of the catalysts were studied using XRD, FTIR, FESEM-EDX and surface area analysis. The pH of solution plays an important role in the photocatalytic degradation of organic pollutants which influences the surface-charge properties of the catalysts. Ag/TiO_2 and α-Fe_2O_3/HY were used as catalyst on degradation of 2-chlorophenol (2-CP) and methyl orange (MO), respectively. The effect of pH on degradation of 2-CP and MO were investigated over a pH range from 2 to 9. Higher degradation of 2-CP and MO were obtained at pH 5 (74%) and pH 2 (80%), respectively. This finding might be explained by the amphoteric performance of the catalyst using point zero charge *(pH_{ZPC})*. The *pH_{ZPC}* for Ag/TiO_2 and α-Fe_2O_3/HY was found to be at pH 6.3 and pH 7.2, respectively. Hence, the activities of the catalysts may have been affected by the existence of a strong electrostatic field between the positively charged catalysts surface and negatively charged 2-CP and MO caused a pH value lower than their *pH_{ZPC}* give greater degradation.

Keywords: pH, Ag/TiO_2, α-Fe_2O_3/HY, 2-chlorophenol, methyl orange.

Abstrak

Fotopemangkinan adalah salah satu teknik yang murah dan tidak beracun untuk degradasi bahan pencemar organik kepada bahan-bahan tidak berbahaya seperti air dan karbon dioksida. Dalam kajian ini, kaedah elektrolisis yang mudah telah digunakan dalam penyediaan Ag/TiO_2 dan pemangkin α-Fe_2O_3/ HY. Ciri-ciri kimiafizikal daripada pemangkin dikaji menggunakan XRD, FTIR, FESEM-EDX dan analisis kawasan permukaan. pH larutan memainkan peranan yang penting dalam degradasi fotopemangkinan bahan pencemar organik kerana ia mempengaruhi sifat caj permukaan bagi pemangkin. Ag/TiO_2 dan α-Fe_2O_3/ HY masing-masing digunakan sebagai pemangkin untuk degradasi 2-klorofenol (2-CP) dan metil jingga (MO). Kesan pH ke atas degradasi 2-CP dan MO telah disiasat dengan mempelbagaikan nilai pH 2 hingga 9. Degradasi tertinggi untuk 2-CP dan MO masing-masing telah diperolehi pada pH 5 (74%) dan pH 2 (80%). Penemuan ini mungkin dapat dijelaskan oleh prestasi amphoteric mangkin dengan menggunakan titik caj sifar *(pH_{ZPC})*. *pH_{ZPC}* untuk Ag/TiO_2 dan α-Fe_2O_3/ HY telah didapati masing-masing pada pH 6.3 dan pH 7.2. Oleh itu, aktiviti pemangkin mungkin telah dipengaruhi oleh kewujudan medan elektrostatik yang kuat antara permukaan pemangkin yang bercas positif serta 2-CP dan MO yang bercas negative telah menyebabkan nilai pH kurang daripada pH_{ZPC} mereka memberikan degradasi yang lebih tinggi.

Kata kunci: pH, Ag/TiO_2, α-Fe_2O_3/HY, 2-klorofenol, metil jingga

1.0 INTRODUCTION

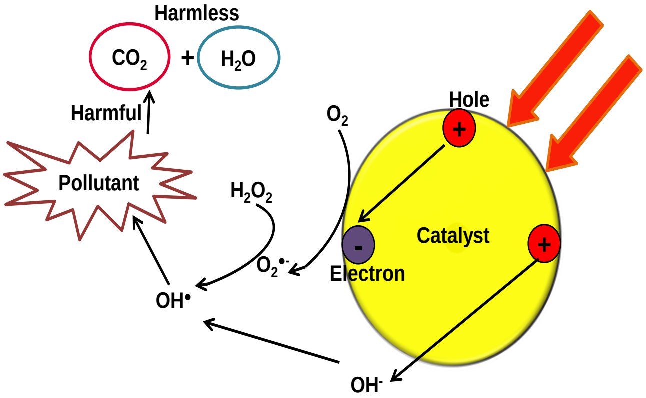
Industries like plastic, cleaning agents, biocides, preservatives and textile use organic compound like chlorophenols and dyes in their processes which caused serious problem owing to their toxicity, persistence and growth in the environment [1, 2]. Chlorophenols include in one of the most important group in ecotoxins which those com-pounds commonly used as components and pre-cursors of many chemicals [3]. Besides that, chloro-phenols emit high toxicity, including genotoxic, mutagenic and carcino-genic activity which caused infections, dermatitis, irritation of digestive tract and strong exhaustion. The tri, tetra- and penta-chlorophenol recognized as odorants in corks and wine besides as the precursors for formation of chloroanisoles, while nitrophenols are produce from vehicle exhausts by photochemical process in the atmosphere.

While, dyes have natural characteristic which gives colour, they become the first pollutant that easily observed by human eyes even at 1 ppm. There are difficulties in treating and handling the effluent because there are many complex structures that exist in the dye molecules. The dissolved oxygen in the watercourse is consumed when wastewater containing dyes undergoes biological and chemical reaction that affect the aquatic life [4]. Dyes molecules have potential to react with metal ion creating microtoxicity to aquatic life such as fish.

The discharged of a large amount wastewater by these industries have a drawback effects which is non-biodegradable, high toxicity and patiently carcinogenic caused numerous health disorder and harmful to aquatic life [5]. Among the various wastewater treatment methods, advanced oxidation process (AOPs) including photocatalysis become a famous method to be used due to the ability of this method to convert the pollutants to a stable inorganic compounds such as carbon dioxide and water without producing secondary pollutant [6].

Photocatalytic degradation is based on the generation of electron-hole pairs by means of band-gap radiation with the species adsorbed on the surface of catalyst [7]. When the generated electron reacts with oxygen molecule (O_2), the peroxide radical will be formed. The reaction occurs during formation of hydroxyl radical ($^{\bullet}OH$) and existence of strong oxidation agent such as hydrogen peroxide (H_2O_2) would help to increase the formation of $^{\bullet}OH$ as shows in Scheme 1. In photocatalytic degradation of organic pollutant, formation of $^{\bullet}OH$ is important to measure the effectiveness of the photocatalyst.

This process uses non-toxic semiconductors such as TiO_2, ZnO, a-Fe_2O_3 and ZrO_2, which lead to total mineralization of organic compound to CO_2, water and mineral acids [8]. Moreover, semicon-ductors also potentially can prevent recombination if the suitable surface defect site and scavenger is available to trap the electron or hole. TiO_2 has a good potential as catalyst but has a wide band gap (~3.2 eV) and high electron-hole recombine-tion. The used of noble metal such as Au, Ag, Pt and Pd for doping with TiO_2 is an effective way to enhance the photocatalytic activity. Among the noble metal, Ag has shown the potential to enhance the electron-hole separation by decrease the electron recombination and band gap. Besides TiO_2, a-Fe_2O_3 with band-gap 2.3 eV is another good candidate to be used as a catalyst. However, a-Fe_2O_3 tends to form a suspension for the oxidative abatement of toxic compounds. This disadvantage can be overcome by using zeolite like HY as a support due to its low polar surface, large surface area and its high adsorption capacity for organic pollutants.



Scheme 1 Illustration of photocatalytic processes on the photo-catalyst.

The pH of solutions is an important controlling parameter in the evaluation of aqueous phase for photocatalytic degradation reaction. It affects the adsorption and dissociation of substrate, catalyst surface charge, oxidation potential of the valance band and other physiochemical properties. Semiconductor oxides usually have amphoteric behavior which influence the surface-charge properties of catalysts when the rate of reaction taking place on the surface of semiconductor [9]. In this study, the catalysts properties were determined by XRD, FTIR, FESEM-EDX and surface area analysis. The significant effect of pH was studied to determine the influence on surface-charge properties of the catalysts when the reactions occur on the surface of the catalysts toward Ag/TiO_2 and a-Fe_2O_3/HY as semiconductor catalysts for degradation of 2-CP and MO, respectively.

2.0 METHODOLOGY

2.1 Materials

The TiO_2 powder catalyst JRC-TiO_2-2 was supplied by the Catalysis Society of Japan and Zeolite Y with a silica/alumina ratio of 80 was purchased from Zeolyst International. The Ag, Fe and Pt plates of greater than 99% purity were used as electrodes and were obtained from Nilaco, Japan. *N,N*-dimethylformamide (DMF), methyl orange, and perchloric acid were purchased from MERCK, Malaysia and 2-CP from Alfa Aesar, Germany with 99% purity. Naphthalene and tetraethylammonium bromide solution were obtained from Fluka Chemical and acetone was purchased from HmbG Chemical. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from QREC™ and methanol was purchased from RPE Reagent pure Erba. Tetraethylammonium perchlorate (TEAP), which was used as a supporting electrolyte in the electrolysis, was prepared accordance with the procedure reported in the literature [10].

2.2 Preparation of the Catalyst

In this study, electrolysis method was used in preparation of Ag/TiO_2 and α-Fe_2O_3/HY catalysts accordance with the procedure reported in the literature [11-14]. For the preparation of Ag/TiO_2, DMF solution (10 mL) was added to a one-compartment cell fitted with a Pt late cathode (2 cm x 2 cm) and an Ag plate anode (2 cm x 2 cm) containing TEAP, naphthalene and TiO_2. The electrolysis was conducted under a N_2 atmosphere with continuous stirring using constant current of 60 mA/cm^2.

Then, the mixture obtained from electrolysis was impregnated in an oil bath at 80°C before dried for overnight at 100°C. Finally, the catalyst was calcined at 600°C for 3 h to give a grey-colored Ag/TiO_2 catalyst. The experimental proce-dure for preparation of α-Fe_2O_3/HY catalyst was similar to the Ag/TiO_2 except that the Ag plate anode and TiO_2 were replaced with Fe plate anode and HY zeolite, respectively. Then, the catalyst was calcined at 550°C for 3 h to give a brown-colored α-Fe_2O_3/HY catalyst.

2.3 Material Characterization

The crystalline structures of the catalysts were conducted by a Bruker Advance D8 X-ray powder diffractormeter (XRD) with Cu Kα radiation (λ=1.5418 Å). FTIR spectroscopy (Perkin Elmer Spectrum GX FTIR Spectrometer) was used to determine the chemical functional groups present in the catalysts. The Brunnauer-Emmett-Teller (BET) was used to calculate surface area and prior to measurement, the catalysts were degassed at 300°C at 0.1 Pa. Field-Emission Scanning Electron Microscopy was conducted to determine topology and elemental composition of catalysts using Energy Dispersion X-ray Spectroscopy (FESEM-EDX, JEOL JSM-6701F).

The pH_{ZPC} of the catalyst was performed using powder addition (PA) method as reported in the literature [15]. Set of pH solution (pH 2, 5, 7, 9 and 11; 40 mL) were prepared by using HCl and NaOH as pH adjuster. The initial pH (pH_i) of every set of solution was taken before an amount of catalyst was added. The final pH (pH_f) was recorded after the solution was stirred for 48 h. Finally, the value of pH_f is plotted vs. pH_i.

2.4 Photocatalytic Degradation Of Organic Pollutants

The photoactivity of Ag/TiO_2 and α-Fe_2O_3/HY were tested on degradation of 2-CP and MO, respectively. The photocatalytic performances were tested in a batch reactor with UV lamp consisting pyrex conical flask and cooling system with magnetic stirrer to uniformly disperse the catalyst into solution. The preparation of 2-CP and MO solution was started by preparing the pH water. The hydrochloric acid (HCl) was added in the distilled water to decrease the pH of water until the desired pH was obtained. In contrast, sodium hydroxide (NaOH) was used to increase the pH of the solution.

The solution and catalyst was keeping stirring in the dark for 1 h to achieve adsorption-desorption before being exposed to the irradiation to start the photocatalytic reaction. During the degradation, 2 mL of solution were taken out at intervals of 30 min and centrifuged in a Hettich Zentrifugen Micro 120. Then, the samples concentrations were determined by measuring the absorbance by UV-Vis spectrophotometry (Agilent Technologies, Cary 60 UV-Vis) before calculated the percentage of photodegradation. The degradation percentage was calculated using the following equation:

$$Degradation(\%) = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

Where C_o and C_t are the initial concentration of 2-CP and the concentration at time *t*, respectively.

3.0 RESULTS AND DISCUSSION

The XRD pattern of Ag, TiO_2 and Ag/TiO_2 are shown in Figure 1A. Two peaks at 37° (111) and 45° (200) (Figure 1A/a) indicated peaks of Ag^0 which consistent with silver metallic peaks (JCPDS file no. 01-087-0717). Figure 1A/b shows a series of TiO_2 anatase phase (JCDPS file no. 00-004-0477) with peaks at 25° (101), 37° (103), 38° (004), 40° (112), 47° (200), 52° (105) and 54° (211). Figure 1B shows the XRD pattern of α-Fe_2O_3, HY zeolite and α-Fe_2O_3/HY. A series of α-Fe_2O_3 peaks were observed at 23° (012), 33° (104), 36° (110), 40° (113), 48° (024) and 53° (116), demonstrated a hematite phase of Fe_2O_3 (JCPDS file no. 33-0664).

It clearly observed that the XRD pattern of Ag/TiO_2 (Figure 1A/c) and α-Fe_2O_3/HY (Figure 1B/c) were similar to TiO_2 (Figure 1A/c) and HY zeolite (Figure 1B/b), respectively. This phenomenon indicated that the introduction of Ag and α-Fe_2O_3 did not affect the structure of the TiO_2 and HY zeolite, respectively [16]. However, the intensity of these peaks slightly decreases maybe because of the change in the crystallinity of the catalysts due to the distribution of the Ag and α-Fe_2O_3 on the support. The same phenomenon was indicated on Ir/Pt incorporated HZSM-5 zeolite which the crystallinity of the zeolite decreased with the addition of Ir/Pt [17].

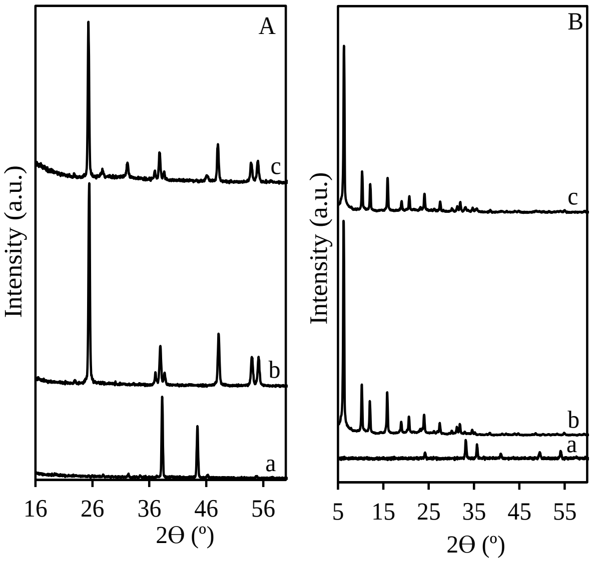


Figure 1 (A) XRD pattern of (a) Ag, (b) TiO$_2$ and (c) Ag/TiO$_2$; (B) XRD pattern of (a) a-Fe$_2$O$_3$, (b) HY zeolite and (c) a-Fe$_2$O$_3$/HY.

In addition, the diffraction spectra of Ag and a-Fe$_2$O$_3$ could not be observed in either Ag/TiO$_2$ or a-Fe$_2$O$_3$/HY, respectively maybe due to the loading of these metals too small to be detected by XRD. Similar result was reported for Pd and Pd-Ag supported on TiO$_2$, in which no XRD peaks for Pd and Ag species were detected, indicated that the strong diffraction peaks of TiO$_2$ support obscured the low amount of metals [18].

The textural properties of the catalyst are summarized in Table 1. Ag/TiO$_2$ and a-Fe$_2$O$_3$/HY showed decreasing in surface area and pore volume after the introduction Ag and a-Fe$_2$O$_3$, respectively; this may be due to the blockage of catalysts pores. The introduction of new metal on the support increased the pore size which probably due to the bigger crystallites aggregates on the pores caused pore blockage [19]. A similar observation was reported when IS-FeOOH loaded on MSN induce the silica removal rate which reduce pore size and increase pore volume of MSN [20].

Table 1 Textural properties determine from nitrogen adsorption-desorption experiments of TiO$_2$, Ag/TiO$_2$, HY zeolite and a-Fe$_2$O$_3$/HY.

Catalyst	Surface Area (m^2g^{-1})	Pore Volume (cm^3g^{-1})	Pore Size (nm)
TiO$_2$	13.5	0.26	31.6
Ag/TiO$_2$	11.7	0.15	36.4
HY zeolite	675	0.425	2.79
a-Fe$_2$O$_3$/HY	634	0.403	2.92

The interaction between support and metal was studied using FTIR shown in Figure 2. Figure 2A shows the interaction of TiO$_2$ framework with Ag in region 1400-410 cm^{-1}. Band at 1604 cm^{-1} was assigned to O-H bond of hydroxyl group, while a sharp band 535 cm^{-1} was attributed to Ti-O-Ti bond of TiO$_2$ anatase phase [21]. However, after the addition of Ag, the intensity of this band decreased and broader indicated that there is possible distur-bance by Ag species to TiO$_2$ framework. The inter-acttion between HY framework and iron (region 2000-400 cm^{-1}) is shown in Figure 2B. The band at 1060 cm^{-1} was corresponding to asymmetric Si-O-Si vibration, while two broad bands at 540 and 475 cm^{-1} were assigned to iron. Conversely, there is no band was observed for interaction between HY and a-Fe$_2$O$_3$ may be due to the small amount of iron added [22].

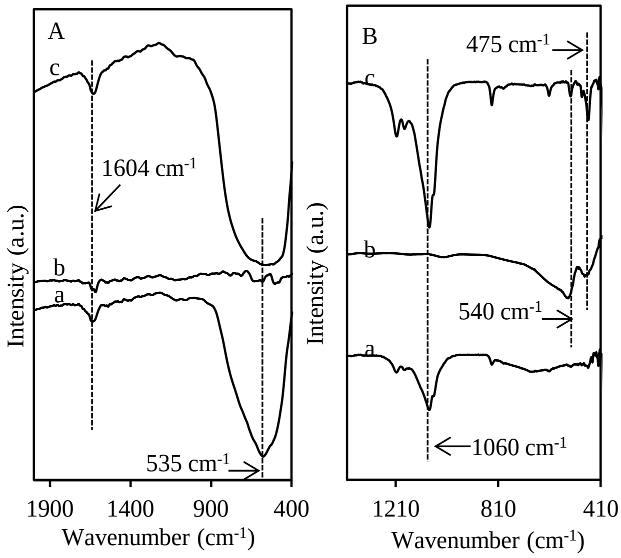
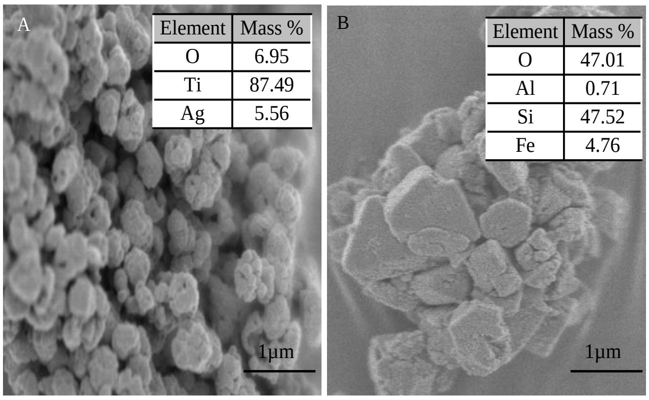


Figure 2 (A) FTIR spectra of (a) Ag, (b) TiO$_2$ and (c) Ag/TiO$_2$; (B) XRD pattern of (a) a-Fe$_2$O$_3$, (b) HY zeolite and (c) a-Fe$_2$O$_3$/HY

The topology and elemental analysis of the catalysts were studied using FESEM-EDX and the images shown in Figure 3. Figure 3A shows the irregular shape of Ag/TiO$_2$ and with rough surface maybe due to the introduction of Ag onto the TiO$_2$. Moreover, the insert table present the weight loading of Ag was approximately 5wt%. While, Figure 3B shows a-Fe$_2$O$_3$/HY with irregular square shape with the insert table present the elemental weight percentage of the catalyst.

The best photocatalytic activity can be achieved by controlling the important reaction parameter and pH is one of it. Effect of pH need to be considered since the pH of industrial wastewater can be either basic or acidic. Points zero charge (pH_{ZPC}) of the catalyst can be used to consider the pH optimum for the reaction. Figure 4A and 4B shows the pH_{ZPC} of Ag/TiO$_2$ and a-Fe$_2$O$_3$/HY, respectively. The pH_{ZPC} for both catalysts were found to be pH 6.3 (Ag/TiO$_2$) and pH
7.2 (a-Fe$_e$O$_3$/HY). The pH higher than this value indicates that catalyst surface is negatively charged and vice versa. Besides, it is important to determine the organic pollutants charge in order to detect a suitable pH reaction.



Element	Mass %
O	6.95
Ti	87.49
Ag	5.56

Element	Mass %
O	47.01
Al	0.71
Si	47.52
Fe	4.76

Figure 3 FESEM images of (A) Ag/TiO_2 and (B) α-Fe_2O_3/HY. Insert table shows elemental analysis of the catalysts.

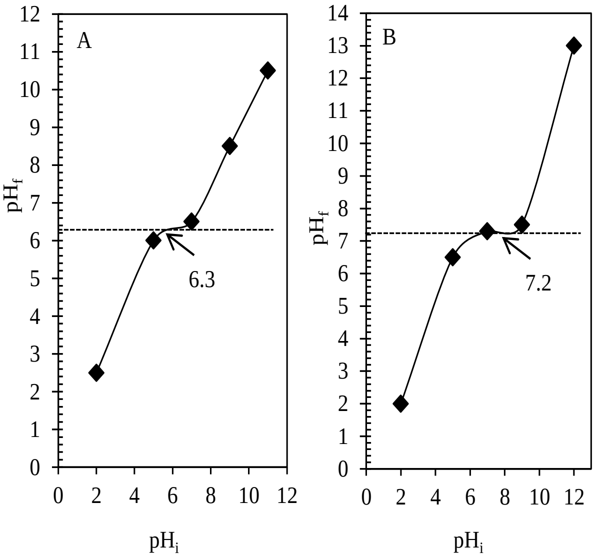


Figure 4 pH_{ZPC} of (A) Ag/TiO_2 and (B) α-Fe_2O_3/HY.

Figure 5 shows the effect of pH on degradation of 2-CP and MO over a pH range from 2 to 9. The highest degradation of 2-CP using Ag/TiO_2 was obtained at pH 5 with 74%, while MO at pH 2 resulted in 80% degradation using α-Fe_2O_3/HY. The catalyst surface in acidic solution was assumed to have positively charged while negatively charged in alkaline solution [23]. Moreover, 2-CP and MO known as the organic materials which carry negative charged. Therefore, this result could explain why the highest degradation was found at acidic pH compared to alkaline pH. The activity of the catalysts might be due to the existence of a strong electrostatic field between the positively charged Ag/TiO_2 and α-Fe_2O_3/HY surface and negatively charged of 2-CP and MO. This finding shows the important role of pH solution in the degradation of organic pollutant.

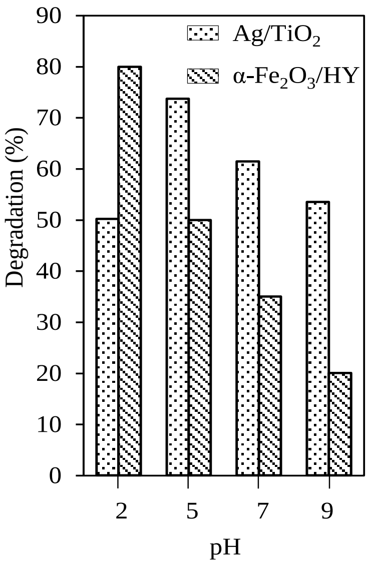


Figure 5 Photocatalytic degradation of 2-CP and MO using Ag/TiO_2 and α-Fe_2O_3/HY, respectively.

4.0 CONCLUSION

In this study, Ag/TiO_2 and α-Fe_2O_3/HY catalysts were successfully synthesize by simple electrolysis method. All the catalysts were characterized using XRD, FTIR, FESEM-EDX and surface area analysis. XRD results reveal that the intensity of TiO_2 and HY zeolite peaks slightly decreases after introduction of Ag and α-Fe_2O_3, respectively maybe because the distribution of the Ag and α-Fe_2O_3 on the support due to the change in the crystallinity. In addition, the surface area for both catalysts also decreased after the introduction of new metal caused by the blockage of catalysts pores.

The effect of pH on degradation of 2-CP and MO were investigated over a pH range from 2 to 9 shows higher degradation of 2-CP and MO were obtained at pH 5 (74%) and pH 2 (80%), respectively. This result can be explained by the amphoteric performance of the catalyst using point zero charge (pH_{ZPC}). It is well known that the amphoteric performance affects the surface charge properties of the catalyst when the photodegradation occurs on the surface of semiconductor which pH higher than pH_{ZPC} value shows that catalyst surface is negatively charged and vice versa.

The pH_{ZPC} for Ag/TiO_2 and α-Fe_2O_3/HY was identified at pH 6.3 and pH 7.2, respectively. Therefore, the existence of a strong electrostatic field between the positively charged catalysts surface and negatively charged 2-CP and MO affect the catalytic activities which the pH value lower than their pH_{ZPC} give greater degradation. This finding will be useful the evaluation of aqueous phase for photocatalytic degradation reaction.

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