*Scientific paper*

# Photooxidation of Salicylic Acid with $TiO_2$ and Metal Coated $TiO_2$

**Tecush Mohammadi* and Asghar Zeini Isfahani**

*Chemistry Department, Isfahan University, Isfahan, Iran*

** Corresponding author: E-mail: tecush@gmail.com*

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## Abstract

Photooxidation of Salicylic Acid with bare $TiO_2$ and metal-modified $TiO_2$ has been studied in a stirred photochemical reactor that was cooled by a water system by irradiation with a 400 W high-pressure mercury lamp. The effects of the amount of copper and silver coated on $TiO_2$ and of the temperature on the rate of oxidation have been investigated. An optimum loading of 5% Ag or 5% Cu was observed for photooxidation of salicylic acid.

**Keywords:** Photooxidation; salicylic acid; metal coated

## 1. Introduction

Over the last thirty years, one particular water purification technique that has received much attention is heterogeneous photocatalysis. Photocatalysis can be used for the treatment of polluted waters containing toxic organic compounds and metal ions. An excellent feature of this technique is that complete mineralization of organics to carbon dioxide, water and simple mineral acids may be achieved when the reactions are performed in the presence of oxygen.[1–11]

It is expected that loaded Cu or Ag may improve photocatalytic activity of $TiO_2$, since the work function of Cu is quite similar to the $TiO_2$ conduction band and to the standard reduction potential of oxygen, which is considered to be a probable electron acceptor in $TiO_2$.[4,7,11,12–17]

The photocatalytic process involves the illumination of metal oxide semiconductor particles such as titanium dioxide ($TiO_2$) by near-ultraviolet light. Titanium dioxide is a popular choice as a photocatalyst since it is cheap and photostable. In addition, $TiO_2$ particles are non-toxic, insoluble under most conditions and re-usable. Provided that the illumination light energy equal to or greater than the band gap energy of the semiconductor ($\lambda < 380$ nm for $TiO_2$), negatively charged electrons residing in the filled valance band of the semiconductor are exited into the empty conduction band. The vacancies created in the valance band are positively charged and are known as holes. After separation, holes and electrons can migrate to the surface of the semiconductor particle where they can initiate oxidation and reduction reactions. Alternatively, holes and electrons can recombine, leaving them unavailable for participation in redox reactions. In aqueous semiconductor suspensions, species which may be oxidized are organic molecules, water molecules and hydroxyl ions. Dissolved oxygen and metal ions are example of species which can undergo reduction.[1,4,9,10,14,17,18]

One drawback of photocatalytic reactions is the low efficiency or quantum yields achieved. The efficiency of photocatalytic reactions is governed by how effectively electrons and holes are channeled into oxidation and reduction reactions before recombination takes place. Increasing the efficiency of photocatalytic processes is important for applications of this technique in the future. To improve the efficiency of $TiO_2$-mediated photoelectrons, the lifetimes of electrons and holes in $TiO_2$ particles must be increased, before recombination take place.[4,10,19–21]

Various strategies have been applied to improve the photoactivity of $TiO_2$ particles. One method is the modification of pure $TiO_2$ particles by partially coating the $TiO_2$ surface with metal islands using noble metals such as silver, gold, platinum and palladium. Some publications report that surface modification of $TiO_2$ particles can improve the activity of the particles considerably,[1,22–25,28] while others report that a detrimental effect results.[1,24–28] The enhanced activity of metal/$TiO_2$ particles is said to be due to the better separation of electrons and holes. Metal deposits behave as sites where electron can accumulate and improve the quantum yields of $TiO_2$ reactions by accelerating the removal and transfer of electrons from the particles through accelerating their transfer to molecular oxygen.[1,4,16,19,29,30] The reduction of molecular oxygen is proposed to be the rate-limiting step in organic photooxidation reactions.[31]

In this study pure and surface-modified titanium dioxide particles were used for the photocatalytic oxidation of salicylic acid. The objective of this study was to improve the activity of $TiO_2$ using surface modification and to compare the activity of photocatalyst before and after surface modification with metallic silver and copper deposits. Also the efficiency of Cu and Ag as catalyst's surface modifiers for the salicylic acid degradation was compared.

## 2. Experimental

Salicylic acid was oxidized with oxygen at 85 °C, 42 °C and 15 °C in a stirred reactor at 2 bars pressure, in the presence of $TiO_2$ powder and metal coated on $TiO_2$ as photosensitizer irradiating with a 400W mercury lamp.

### 2. 1. Reaction Equipment

The reactor was round-bottomed glass tank connected to an SH-12 type stirrer, a water thermostat (Haake model F-122), an oxygen gas inlet system, and a 400 W high-pressure mercury lamp. The set up of the photooxidation experiments is shown in Fig. 1.

### 2. 2. Materials

Salicylic acid, glacial acetic acid, ethanol and isopropanol were of analytical grade from Merck. $TiO_2$ anatase and rutile, with surface areas of 50 and 47 $m^2\ g^{-1}$, respectively, they had a mean particle sizes of 30 nm, and commercially $TiO_2$ (anatase 70% and rutile 30%) with surface area of 48 $m^2\ g^{-1}$; were purchased from Aldrich. The $Ag/TiO_2$ 2, 4, 5, 6, and 8% catalysts were prepared according to the following experimental procedure: 0.5 g of $TiO_2$ in 9, 8, 7.5, 7 and 6 $cm^3$ of ethanol as a hole scavenger, were added to 1, 2, 2.5, 3 and 4 $cm^3$ of a 0.0927 M $AgNO_3$ solution, $N_2$ was bubbled through the mixtures for 15 min, it was irradiated with a mercury lamp for 45–60 h, then filtered and washed by distilled water, and finally heated to 90 °C for 15 h. The $Cu/TiO_2$ 2, 4, 5, 6, and 8% catalysts were prepared according to the following experimental procedure: 0.5 g of $TiO_2$ in 9, 8, 7.5, 7 and 6 $cm^3$ of ethanol as a hole scavenger, were added to 1, 2, 2.5, 3 and 4 $cm^3$ of a 0.1574 M $CuSO_4$ solution, $N_2$ was bubbled through the mixtures for 15 min, it was irradiated with a mercury lamp for 45–60 h, then filtered and washed by distilled water, and finally heated to 90 °C for 15 h. Commercially $TiO_2$ was used for all samples ($Ag/TiO_2$ and $Cu/TiO_2$) except for those cases that exactly pointed to the »anatase« or »rutile«.

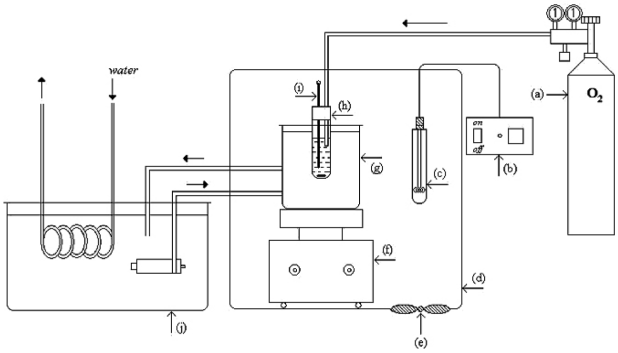

**Fig.1:** The set up of the photooxidation experiments
(a) Oxygen reservoir. (b) on-off switch. (c) High pressure mercury lamp (400 W). (d) Reactor covers. (e) Fan. (f) Heater stirrer. (g) Water tank. (h) Experimental cell. (i) Thermometer. (j) Water thermostat.

### 2. 3. General Procedure for Photooxidation of SA (Salicylic Acid)

20 ml of salicylic acid ($10^{-4}$ M) was charged into the reactor with 0.020 g of catalyst. When the temperature stabilized at the value previously set for the experiment, the oxygen flow (0.4 $cm^3/s$) was set and kept constant during the experiment, and the mercury lamp was switched on. Samples (about 4 $cm^3$) were taken from the reactor at regular intervals (typically 20 min.) during the experiment that lasted when all the salicylic acid is completely oxidized to $CO_2$ and $H_2O$.

### 2. 4. Analysis

Before and after irradiation 4 $cm^3$ of samples were taken through the septum with a syringe and immediately transferred to centrifuge tubings. The solid phase of sample (4 $cm^3$) was separated by centrifugation at 6000 rpm for 8 min.

Absorbance spectrophotometry (Varian CARY 500 2E UV-Vis-NIR spectrophotometer) was used to measure the concentration of salicylic acid in solution. Salicylic acid has maximum absorbance of UV-visible light at a wavelength of 294 nm.[4] The instrument was calibrated using standards prepared in the range 0–200 ppm. A linear calibration curve was obtained for salicylic acid concentrations in the range 0–100 ppm.

## 3. Results and Discussion

### 3. 1. Photooxidation of Salicylic Acid Using Bare and Metal Ion-Modified Titanium Dioxide Suspensions

When photocatalyst (*e.g.* $TiO_2$) particles are illuminated with light of energy equal to or greater than the bandgap energy, valence band electrons are excited into the conduction band, leaving vacant sites or holes in the valence band. Conduction band electrons and valence band holes migrate to the surface of the catalyst where they take part in a series of redox reactions, described by the following equations:

1. Electron-hole pair generation

$$TiO_2 \xrightarrow{h\nu \geq E_g} e^-_{cb} + h^+_{vb} \quad (1)$$

2. Possible traps for holes

(a)Surface-adsorbed hydroxyl ions

$$h^+_{vb} + OH^-_{ads} \rightarrow OH^\bullet_{ads} \quad (2)$$

(b) Surface-adsorbed waters molecules

$$h^+_{vb} + H_2O_{ads} \rightarrow OH^\bullet_{ads} + H^+ \quad (3)$$

$$h^+_{vb} + H_2O_{ads} \rightarrow \frac{1}{2}O_2 + H^+ \quad (4)$$

(c) Electron donor (D) species

$$h^+_{vb} + D_{ads} \rightarrow D^+_{ads} \quad (5)$$

3. Possible traps for electrons

(a) Surface traps (shallow traps)

$$e^-_{cb} + Ti(IV)OH \rightarrow Ti(III)OH \quad (6)$$

(b) Lattice traps (deep traps)

$$e^-_{cb} + Ti(IV) \rightarrow Ti(III) \quad (7)$$

(c) Electron acceptor (A) species

$$e^-_{cb} + A_{ads} \rightarrow A^-_{ads} \quad (8)$$

4. Recombination

$$e^-_{cb} + h^+_{vb} \rightarrow TiO_2 + energy \quad (9)$$

In bare $TiO_2$ suspensions, the electron donating species are water molecules, hydroxyl ions and salicylic acid molecules. The electron accepting species is oxygen for experiments conducted in the presence of air.

The mineralization and degradation of salicylic acid was conducted under an air-equilibrated environment using $TiO_2$ particles with and without metal surface modification. Salicylic acid absorbs UV-visible light best at a wavelength of 294 nm. The addition of salicylic acid to $TiO_2$ suspensions turns the colloid to yellow, indicating the formation of a titanium(IV)-salicylate charge transfer complex.[4]

The degradation and mineralization of salicylic acid was monitored by quantifying the amount of salicylic acid remaining in solution for a certain period of time.

Two sets of experiments were done, one with irradiation and photosensitization and the other without irradiation, keeping constant the rest of the variables of the reactor (temperature, stirring speed, oxygen flow, reactor tank) constant. Figure 2 shows the remained amount of salicylic acid *versus* time (min) for both experiments. Clearly, the kinetic rate of salicylic acid degradation is much better for the photochemical experiment ($3.33 \times 10^{-8}$ mol dm$^{-3}$ s$^{-1}$) than for the experiment without photocatalysis ($3.51 \times 10^{-13}$ mol dm$^{-3}$ s$^{-1}$).

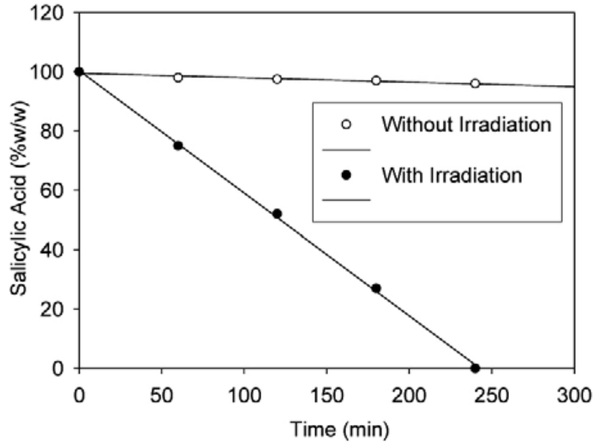

**Fig. 2:** Remained SA (% w/w) vs. time (min), with and without irradiation

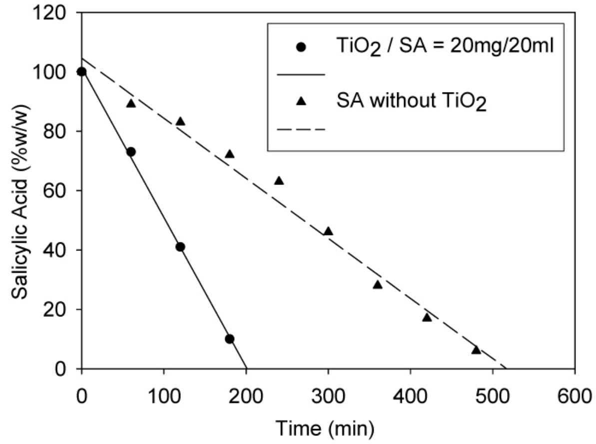

**Fig. 3:** Remained SA (% w/w) vs. time (min), with and without catalyst

An experiment was carried out with irradiation in absence of a catalyst. The results showed that the rate of reaction was very slow. Therefore, in order to get a good kinetic rate the reaction must be carried out photocatalytically (Fig. 2 and 3).

Three experiments were carried out under the same conditions, irradiating externally with the mercury lamp and using 10, 20 and 30 mg of each catalyst to 20 ml of salicylic acid ($10^{-4}$ mol dm$^{-3}$). Results showed that the optimum amount of catalysts (Ag/$TiO_2$ and Cu/$TiO_2$) for 20 ml of salicylic acid $10^{-4}$ M was 20 mg (Fig. 4 and 5). Similar results were obtained for other catalysts (not showed).

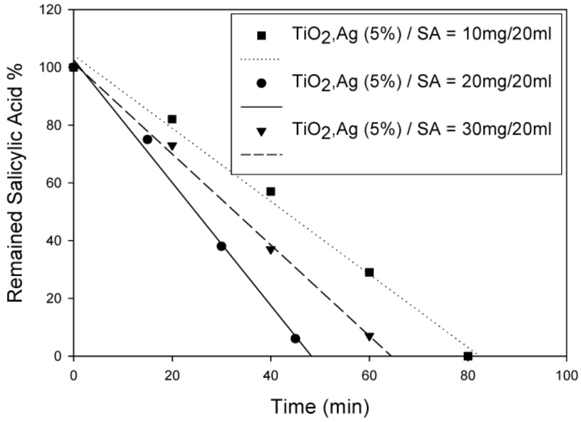

**Fig. 4:** Kinetic plots of remained of SA (% w/w) vs. time (min) for three amount of Ag/$TiO_2$ catalyst (10, 20, and 30 mg) in the proportion of salicylic acid ($10^{-4}$ mol $dm^{-3}$)

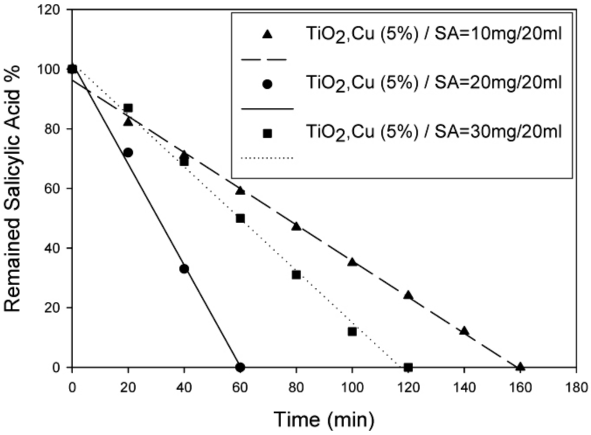

**Fig. 5.** Kinetic plots of remained of SA (% w/w) vs. time (min) for three amount of Cu/$TiO_2$ catalyst (10, 20, and 30 mg) in the proportion of salicylic acid ($10^{-4}$ mol $dm^{-3}$)

Decreasing in the kinetic rate of salicylic acid degradation in those cases of that catalyst ratio to the salicylic acid were 30 mg catalyst / 20 ml SA $10^{-4}$ M, is ascribed to the dirking of solution and decreasing penetrate the light into the solution.

## 3. 2. Effect of Temperature

We tried to keep the thermal initiation process at a minimum level by lowering the temperature and we run experiments with irradiation and photosensitization at 85°, 42°, and 15 °C. Figures 6 and 7 show the kinetic plots of remained amount of the salicylic acid *versus* time (min) for the three temperatures for two catalysts. The kinetic rate of salicylic acid degradation drops at lower temperatures. The influence of temperature on salicylic acid degradation with the Ag coated on $TiO_2$ catalyst was less than with Cu coated on $TiO_2$. By plotting the salicylic acid degradation kinetic rates (mol $dm^{-3}$ $s^{-1}$) *versus* 1/T ($K^{-1}$) we have found the activation energies (kJ $mol^{-1}$) for the oxidation reaction of salicylic acid using different catalysts (Table 1).

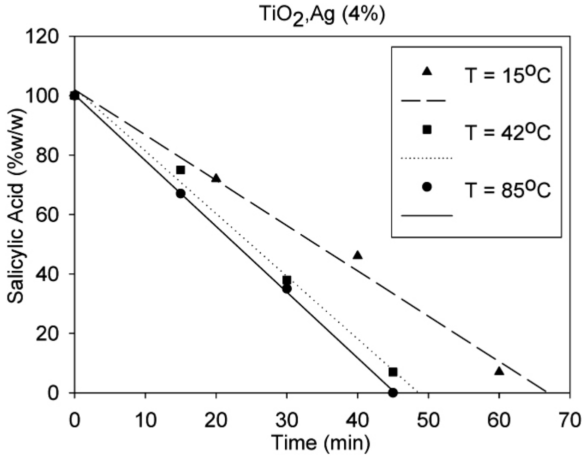

**Fig. 6:** Kinetic plots of SA (% w/w) vs. time (min) for Ag/$TiO_2$ catalyst in three temperatures

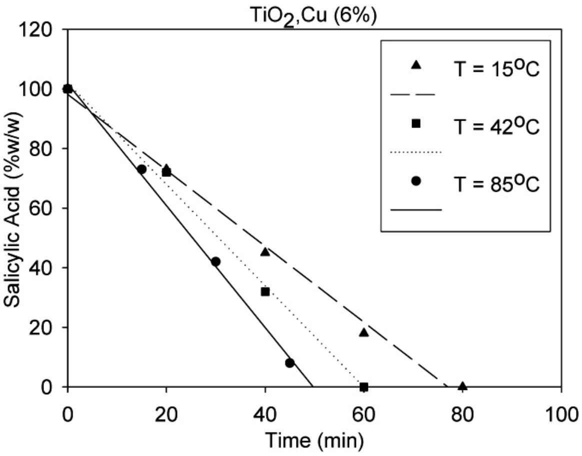

**Fig. 7:** Kinetic plots of SA (% w/w) vs. time (min) for Cu/$TiO_2$ catalyst in three temperatures

Table 1 summarizes the results obtained from the photodegradation of salicylic acid over nonmodified commercially $TiO_2$, anatase, rutile, Ag/$TiO_2$ (2%, 4%, 5%, 6% and 8%) and Cu/$TiO_2$ (2%, 4%, 5%, 6% and 8%). As shown in table 1, surface modification of $TiO_2$ with both of metallic Ag and Cu, was improved the activity of photo catalysts, but as was considered, Ag/$TiO_2$ has more photocatalytic activity than Cu/$TiO_2$. The workfunction of Ag is 4.26 eV. Hence, the energy level of Ag is denoted to –0.24 V in NHE, which is located at slightly higher level than the conduction band of $TiO_2$ (–0.1 V in NHE), and in addition it is close to the electrochemical potential of oxygen reduction in aqueous solution [$o_{2(ap)} + e^- \rightarrow o^-_{2(ap)}$, E° = –0.56 V in NHE] as is described in Fig. 8. Thus it is considered that loaded Ag on $TiO_2$ can promote the transfer of electron in $TiO_2$ conduction band to outer oxygen, which is dissolved in water. The same argument can also be applied to Cu/$TiO_2$ system. The worcfunction of Cu is 4.56 eV, which is relatively close to that of Ag, much differently from other noble metals such as Pt, Ru, or Rh. Therefore, the role of Cu on $TiO_2$ surface is considered to be expedition of electron transfer as Ag dose. Relatively lower photocatalytic activity of Cu/$TiO_2$ than of Ag/$TiO_2$ is ascribed to the location of Cu energy level, which is not so much appropriate in transferring the electrons to outer oxygen as that of Ag (See Fig. 8).[16]

**Table 1:** Activation energies of SA degradation in the presence of catalysts

| Type of catalyst | Ea (kJ mol$^{-1}$) |
|---|---|
| Commercially $TiO_2$ | **44.37** |
| Anatase | **40.59** |
| Rutile | **38.09** |
| Cu/$TiO_2$ (2%) | **42.95** |
| Cu/$TiO_2$ (4%) | **40.39** |
| Cu/$TiO_2$ (5%) | **35.39** |
| Cu/$TiO_2$ (6%) | **45.36** |
| Cu/$TiO_2$ (8%) | **81.37** |
| Ag/$TiO_2$ (2%) | **46.17** |
| Ag/$TiO_2$ (4%) | **42.01** |
| Ag/$TiO_2$ (5%) | **29.11** |
| Ag/$TiO_2$ (6%) | **57.67** |
| Ag/$TiO_2$ (8%) | **89.10** |

Decreasing in photocatalytic in high concentrations of metal loaded on $TiO_2$ (6% and 8%) (Table 1) is ascribed to the covering of catalyst surface by metal and decreasing its surface area.

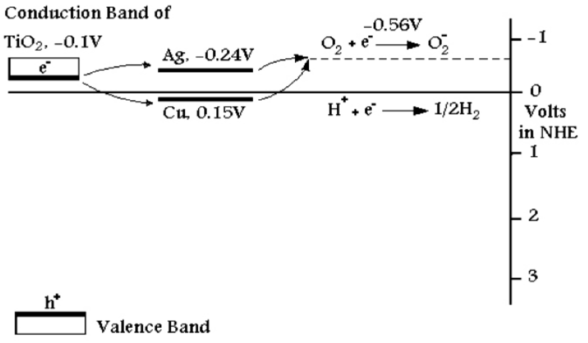

**Fig. 8:** Schematic energy diagram of $TiO_2$, loaded metals and several electrolytes

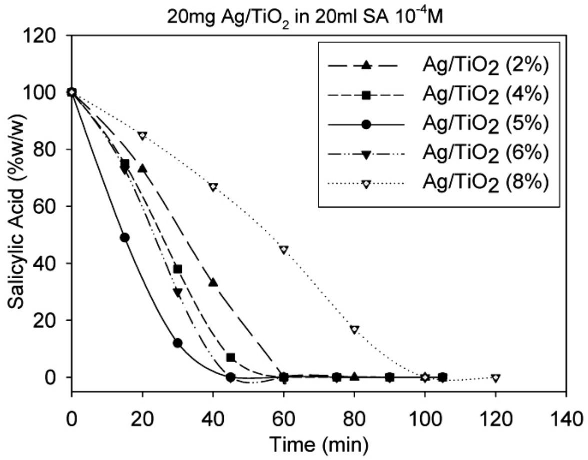

**Fig. 9:** Kinetic plots of remained SA (% w/w) vs. time (min) for five concentration of metal coated $TiO_2$

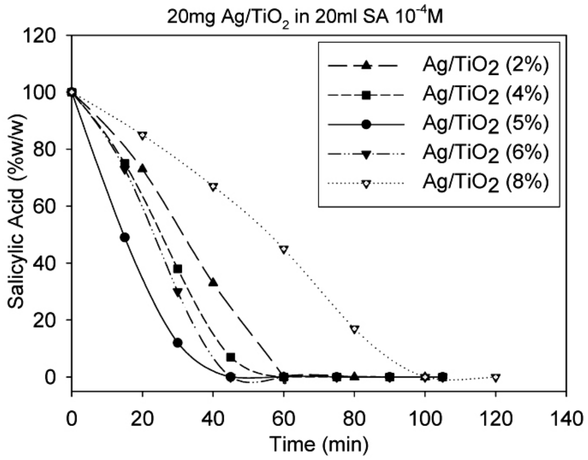

**Fig. 10:** Kinetic plots of remained SA (% w/w) vs. time (min) for five concentration of metal coated $TiO_2$

## 3. 3. Effect of Amount of Photosensitizer

The effect of amount of metals (Ag or Cu) coated on $TiO_2$ on the kinetic rate of salicylic acid degradation (Fig. 9 and 10) shows that the degradation rate of salicylic acid

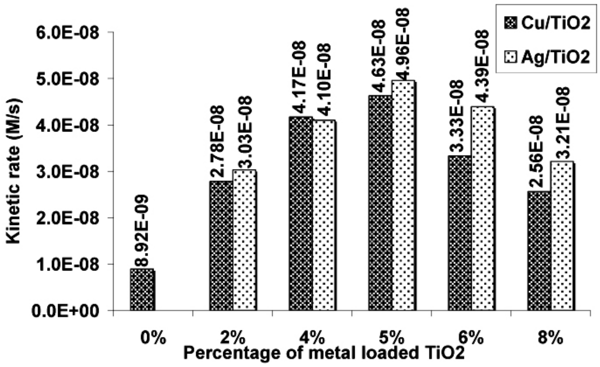

**Fig. 11:** Kinetic rate of degradation of SA for pure $TiO_2$ and five concentration of metal coated $TiO_2$ at 85 °C

is increased by increasing the amount of Cu coated on $TiO_2$ up to 5% Cu. By increasing the amount of Ag up to 5% the rate of degradation of salicylic acid is increased.

Fig. 11 compare the kinetic degradation rate of salicylic acid for nonmodified $TiO_2$, five concentrations of Ag coated on $TiO_2$ and five concentrations of Cu coated on $TiO_2$ at 85 °C. Increasing in the rate of reaction with $Ag/TiO_2$ (2%), $Ag/TiO_2$ (4%), $Ag/TiO_2$ (5%), $Ag/TiO_2$ (6%) and $Ag/TiO_2$ (8%) compared to pure $TiO_2$ were determined to be 240%, 360%, 456%, 392% and 260%, respectively. Increasing in the rate of reaction with $Cu/TiO_2$ (2%), $Cu/TiO_2$ (4%), $Cu/TiO_2$ (5%), $Cu/TiO_2$ (6%) and $Cu/TiO_2$ (8%) compared to pure $TiO_2$ were determined to be 212%, 367%, 419%, 273% and 187%, respectively. The activity of $Ag/TiO_2$ (5%) particles compared to $Cu/TiO_2$ (5%) particles was slightly higher (7%).

The intermediate products of salicylic acid degradation, which require further oxidation to decompose to $CO_2$, have been identified as catechol and a mixture of dihydroxybenzoic acids (DHBAs). Catechol is formed by a photo-Kolbe type decarboxylation reaction and DHBAs by hydroxyl radical addition. The prompt evolution of $CO_2$ during salicylic acid mineralization indicates that other unstable intermediates are formed which are rapidly mineralized to $CO_2$.[4]

## 4. Conclusions

The photocatalytic oxidation of salicylic acid to carbon dioxide and water was performed with the 400 W mercury lamp and using bare and metal-modified $TiO_2$ as catalysts. Reaction was carried out in photochemical reactor and cooled by water system. The effects of temperature and amount of catalyst modifiers on the salicylic acid conversion and its kinetic rates were investigated. Two sets of experiments were done, one set of experiments with irradiation and catalysts modification, and the other set without irradiation, keeping constant the rest of operating variables of the reactor (temperature, stirred speed, oxygen flow and reactor tank) constant. The results showed that the kinetic rate of salicylic acid removing is much better for the photocatalyzed experiment than the experiment without irradiation.

Experiments were carried out with irradiation and catalysts modification at 15°, 42° and 85 °C temperatures. Results showed that the salicylic acid degradation kinetic rates drop as the temperature decreases. Results showed that the photooxidation of salicylic acid is first order and the optimum amount of catalyst for 20 ml salicylic acid $10^{-4}$ M was 20 mg. The best percentage of Cu and Ag coated on $TiO_2$ was 5%. The photocatalytic activity of Ag coated on $TiO_2$ has more advantages than Cu.

Metal deposits on the $TiO_2$ surface behave as sites where electron accumulates. Better separation of electrons and holes on the modified $TiO_2$ surface, allows more efficient channeling of the charge carriers into useful reduction and oxidation reactions rather than recombination reactions.

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## Povzetek

V mešalnem fotokemičnem reaktorju smo zasledovali fotooksidacijo salicilne kisline s čistim $TiO_2$ in $TiO_2$ prevlečenem z različno količino bakra ali srebra. Ugotovili smo, da optimalna fotooksidacija salicilne kisline poteče, če je $TiO_2$ prevlečen s 5 % srebra ali 5 % bakra.