USE OF ZnO AS SEMICONDUCTOR IN PHOTOELECTROCATALYTIC DEGRADATION OF PICRAMIC ACID

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ABSTRACT

Photoelectrocatalytic degradation of picramic acid was investigated using a two–electrode system. The decomposition of the substrate was observed to be affected by photo–characteristics. Kinetics of the reaction was found to be affected by parameters like concentration of substrate, pH, amount of semiconductor, light intensity, cell voltage, radical quencher and band gap, etc. Probable mechanism for the photoelectrocatalytic degradation of picramic acid has been proposed.

Key words : Photoelectrocatalytic, Picramic Acid, ZnO, Semiconductor

INTRODUCTION

The rate of reaction, which is thermodynamically allowed, increases in the presence of an irradiated solid in heterogeneous phase. This is due to the creation (under these conditions) of some new reaction paths involving photocreated species and a decrease in the activation energy. The solid comes in contact with the reactants and electron and/or holes, which are generated within the solid by photons of energy equal or higher than the band gap of the solid. Many reactions can be driven under favorable conditions in the presence of a photocatalyst, it has opened new avenues of research in the field of photoelectrochemistry.

Photoelectrocatalytic decolorization and COD removal from simulated waste waters containing reactive dye has been carried out[1]. The electric and photoelectric properties of the electrolyte–semiconductor interface in the chains formed by metal auxiliary electrode electrolyte–multinary–layered semiconductors have been investigated[2]. The humic acid (HA) dissolved in an aqueous medium undergoes a photoelectrocatalytic process (removal in presence of UV_{254}) and the degradation of color (in presence of Vis_{400}) and it followed pseudo–first order kinetics[3]. Preparation, characterization and photoelectrocatalytic properties

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of nanocrystalline Fe_2O_3/TiO_2, ZnO/TiO_2, and $Fe_2O_3/ZnO/TiO_2$ composite film electrodes for pentachlorophenol degradation have been carried out[4]. The effect of particle size of TiO_2 on photocatalytic degradation of methylene blue in aqueous suspension has been studied[5]. The photocatalytic decoloration and degradation of methylene blue in TiO_2 suspension has also been observed by Li and Gu[6]. Minero et al.[7] have studied photocatalytic transformation of organic compounds in the presence of inorganic ions, competitive reactions of phenol and alcohols on a titanium dioxide fluoride system. Photocatalytic oxidation of n–butane at a steady rate over Rb–modified vanadium oxide supported on silica have been investigated[8]. Photocatalyzed oxidation of cyclohexane by $W_{10}O_{32}^{4-}$ irradiated with natural sunlight has been studied[9]. Electrochemically assisted photocatalysis using TiO_2 particulate film electrodes for photocatalytic degradation of 4–chlorophenol has been reported[10]. Synergestic effect in degradation of formic acid using a new photoelectrochemical reactor has been observed[11]. Feasibility study of photoelectrochemical degradation of methylene blue aqueous solutions with three dimensional electrodes in photocatalytic reactor has been carried out[12]. Picramic acid is used in the manufacture of azo dyes. Sometimes it is also used as an indicator (Yellow in acids and red in alkalies) and also as a reagent for albumin.

EXPERIMENTAL

Zinc oxide (Merck) was used and other chemicals were of AR grade. Double distilled water was used throughout. A 25 mL solution (0.03 mM) of picramic acid was taken in a 100 mL beaker and 200 mg of photocatalyst (ZnO, 60 Mesh powder) was added to it. Then this solution was exposed to a 500 W halogen lamp from the top of a beaker and simultaneously, an electric current was passed in the solution.

When a halogen compound is included inside the tungsten bulb, its purpose is to combine with the tungsten evaporated from hot filament. This forms a compound that is electrically attracted back to tungsten filament[13]. Thus it prevents evaporated tungsten from condensing on the envelope and darkening it. The tungsten halogen lamps develop a larger amount of ultraviolet radiation than general service lamps[14]. The progress of photoelectro catalytic reaction was observed by measuring absorbance (ABS) at 350 nm using spectrophotometer (Spectronic–20D+) in a glass cuvette with path length 1 cm. A graph of 2 + log ABS versus exposure time was drawn and its slope was determined. This graph was plotted according to the linear least squares method[15].

RESULTS AND DISCUSSION

The results of typical run for photoelectrocatalytic degradation of picramic acid are showns in Table 1 and graphically represented in Fig.1. The reaction rate constant was determined using expression k = 2.303 x slope. The photoelectrocatalytic degradation of picramic acid was found to be a one step reaction.

$$k = 2.303 \times \text{slope}$$
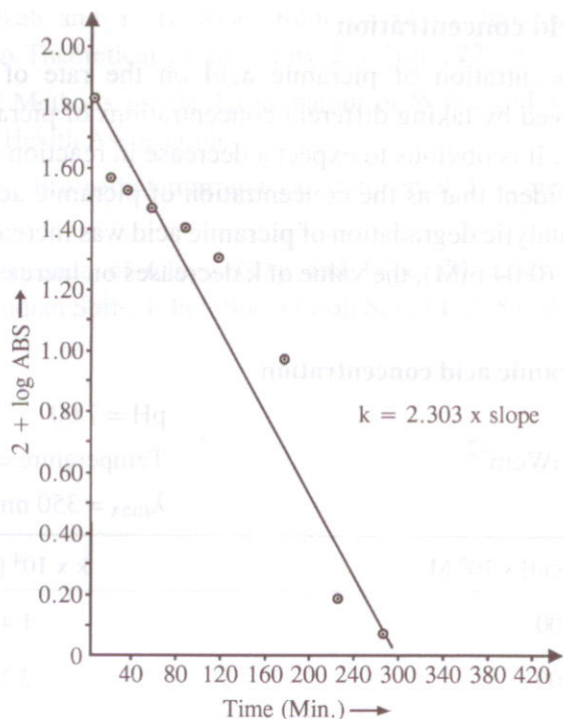
Fig. 1 : A Typical Run

Table 1 : Typical run

Zinc oxide = 0.20 mg   pH = 7.00

Light Intensity = 1.82 mWcm^{-2} Temperature = 300 K

[Picramic Acid] = 3.00 x 10^{-5} M λ_{max} = 350 nm

Cell Voltage = 30 V

Time (min)	ABS	2 + log ABS
0.0	0.396	1.5977
20.0	0.372	1.5705
40.0	0.330	1.5185
60.0	0.297	1.4727
90.0	0.250	1.3979
120.0	0.200	1.3010
180.0	0.092	0.9638
240.0	0.015	0.1761

$$k = 2.26 \times 10^{-4} \text{ sec}^{-1}$$

Effect of picramic acid concentration

The effect of concentration of picramic acid on the rate of photoelectrocataytic degradation was observed by taking different concentrations of picramic acid. The results are reported in Table 2. It is obvious to expect a decrease in reaction rate on increasing the concentrations. It is evident that as the concentration of picramic acid was increased, the rate of photoelectro–catalytic degradation of picramic acid was increased but after reaching a certain concentration (0.04 mM), the value of k decreases on increasing the concentration further.

Table 2 : Effect of picramic acid concentration

Zinc oxide = 0.20 g   pH = 7.00

Light Intensity = 1.82 mWcm^{-2} Temperature = 300 K

Cell Voltage = 30 V λ_{max} = 350 nm

[Picramic Acid] x 10^5 M	k x 10^4 (sec^{-1})
2.00	1.42
3.00	2.26
4.00	2.36
5.00	1.87
6.00	1.43

Effect of pH

The effect of pH on the rate of photoelectrocatalytic degradation of picramic acid was investigated in pH range 5.00 to 9.00. The results are tabulated in Table–3. The semiconductor dissolves in highly acidic medium and therefore, photoelectrocatalytic degradation could not be investigated in lower pH range. It has been observed that when pH was increased, the rate of photoelectrocatalytic degradation of picramic acid also increased. It may be attributed to the greater probability of generation of radicals like $^{\bullet}$OH, HO$_2^{\bullet}$ etc. as pH increases. But after reaching a certain value of pH (pH = 7), the value of k decreases on increasing pH.

Table 3 : Effect of pH

Zinc oxide = 0.20 g	Light Intensity = 1.82 mWcm^{-2}
[Picramic Acid] = 3.00 x 10^{-5} M	Temperature = 300 K
Cell Voltage = 30 V	λ_{max} = 350 nm

pH	k x 10^4 (sec^{-1})
5.00	1.67
6.00	1.80
7.00	2.26
8.00	2.18
9.00	1.38

Effect of amount of photocatalyst

The effect of amount of photocatalyst on the rate of photoelectrocatalytic removal of picramic acid was also observed by taking different amounts of semiconductor keeping all other factors identical. The results are reported in Table 4. As indicated from the data, the photoelectro catalytic degradation of picramic acid increases with increase in the amount of semiconductor, but after reaching a certain amount (0.20 g) the rate of photoelectrocatalytic degradation of picramic acid decreases because the surface exposed to irradiation becomes constant.

Table 4 : Effect of amount of photocatalyst

[Pieramic Acid] = 3.00 x 10^{-5} M	pH = 7.00
Light Intensity = 1.82 mWcm^{-2}	Temperature = 300 K
Cell Voltage = 30 V	λ_{max} = 350 nm

Amount of Photocatalyst (g)	k x 10^4 (sec^{-1})
0.10	1.13
0.15	1.21
0.20	2.26
0.25	2.11
0.30	2.05

Effect of light intensity

The effect of light intensity on the rate of photoelectrocatalytic degradation of picramic acid has been observed by varying the distance between the light source and exposed surface of the semiconductor. The results are given in Table 5. As the intensity of light was increased, more photons will be available for excitation at semiconductor surface and in turn, more electron–hole pairs will be generated, thus resulting into enhanced rate of photo catalytic degradation. In the degradation of picramic acid, the value of k was found to increase with increase in light intensity but after reaching a certain value (1.82 mWCm^{-2}), the rate of photoelectrocatalytic degradation of picramic acid was found to decrease with increase in light intensity.

Table 5 : Effect of light intensity

Zince oxide = 0.20 g   pH = 7.00

[Picramic Acid] = 3.00×10^{-5} M   Temperature = 300 K

Cell Voltage = 30 V λ_{max} = 350 nm

Light intensity (mWcm^{-2})	$k \times 10^4$ (sec^{-1})
1.21	1.42
1.51	2.07
1.82	2.26
2.12	1.51
2.42	1.18

Effect of cell voltage

It is well known that the cell voltage plays an important role in enhancing degradation of organic pollutants in photoelectrocatalytic reactor. In other words, cell voltage plays an important role in enhancing degradation of organic pollutants not only by reducing the electron–hole recombination but also by direct electrochemical oxidation at an anodic bias that is higher than the oxidation potential of the organic pollutant. However, there are few reports that discuss this hybrid photoelectrocatalytic technology under higher cell voltage. In this paper, the effect of applied cell voltage on the degradation of picramic acid was observed in the range from 0.0 to 35V and the profile is shown in Table 6. It is evident that as the cell voltage was increased, the rate of reaction also increases, but after reaching a certain voltage (30 V), the rate of photoelectrocatalytic degradation of picramic acid decreases on increasing cell voltage.

Table 6 : Effect of cell voltage

Zinc oxide = 0.20 g   Light Intensity = 1.82 mWcm^{-2}

[Picramic Acid] = 3.00 x 10^{-5} M   Temperature = 300 K

pH = 7.00 λ_{max} = 350 nm

Cell Voltage (in Volt)	k x 10^4 (sec^{-1})
0.0	0.88
5.0	0.90
10.0	0.92
15.0	1.48
20.0	1.51
25.0	1.59
30.0	2.26
35.0	1.46

Effect of radical quencher

When this photoelectrocatalytic reaction was carried out in present of free radical quencher like methanol and ethanol, the rate of reaction was found to decrease to a significant level indicating the active participation of free radicals like ˙OH and others. The results are tabulated in Table 7.

Table 7 : Effect of radical quencher

Zinc oxide = 0.20 g   Light Intensity = 1.82 mWcm^{-2}

[Picramic Acid] = 3.00 x 10^{-5} M   Temperature = 300 K

pH = 7.00   Cell Voltage = 30 V

Quencher	λ_{max}	k x 10^4 (sec^{-1})
–	350 nm	2.26
Methanol (2 mL)	350 nm	0.88
Methanol (3 mL)	350 nm	0.80
Ethanol (2 mL)	350 nm	1.00
Ethanol (3 mL)	350 nm	1.08

Effect of band gap

The exited semiconductor generates hole and electron pair that induce the photoelectrocatalytic reactions and hence, the band gap energy has an important role to play[15]. The effect of band gap on the photoelectrocatalytic degradation was carried out in presence of different semiconductors having different band gaps. It was observed that the value of k decreases as the value of band gap was increased. The results are tabulated in Table 8.

Table 8 : Effect of band gap

[Picramic Acid] = 3.00×10^{-5} M   pH = 7.00

Light Intensity = 1.82 mWcm^{-2} Temperature = 300 K

Cell Voltage = 30 V

Semiconductor (0.20 g)	Band Gap (eV)	k x 10^4 (sec^{-1})
PbS	0.30	5.03
CdS	2.50	2.38
ZnO	3.20	2.26
ZnS	3.80	1.62

MECHANISM

When a semiconductor is irradiated with light having energy (E = hν) equal to or more than the band gap, a heterogeneous photoelectrocatalytic reaction occurs. The semiconductor forms a pair of valence band (VB) hole and conduction band (CB) electron.

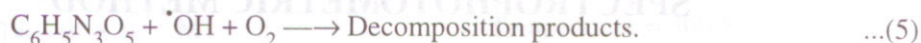$$ZnO + h\nu \longrightarrow h^+(VB) + e^- (CB) \qquad ...(1)$$

The hole generated is capable of oxidizing the substrate and the electron of CB is capable of reducing the substrates. Furthermore, the solution contains species e.g. $^{\bullet}OH$, H^+, $O^{-\bullet}$, $^{\bullet}HO_2$, O_2 etc. which are generated due to the semiconductor–light–water–oxygen interactions. These species are also capable of carrying out redox reactions. The generations of superoxide radical anion $O_2^{-\bullet}$ and $^{\bullet}OH$ radical can be shown as under –

$$h^+ (VB) + H_2O \longrightarrow {^{\bullet}OH}_{ads} + H^+ \qquad ...(2)$$
$$h^+ (VB) + OH^-_{ads} \longrightarrow {^{\bullet}OH}_{ads} \qquad ...(3)$$
$$e^- (CB) + O_{2\ ads} \longrightarrow O^{-\bullet}_{2\ ads} \qquad ...(4)$$

Subscript 'ads' refers to species adsorbed on the surface of semiconductor. It was observed that the products of photoelectrocatalytic degradation of picramic acid in presence of ZnO were

653

colorless gases with virtually no solid residue left in the solution. Hence, probable reactions are proposed as –

$$C_6H_5N_3O_5 + \dot{O}H + O_2 \longrightarrow \text{Decomposition products.} \qquad ...(5)$$

$$C_6H_5N_3O_5 + \dot{O_2^-} + H_2O \longrightarrow \text{Decomposition products.} \qquad ...(6)$$

CONCLUSION

The photoelectrocatalytic degradation of picramic acid was found to be one step reaction. Concentration of substrate, pH of solution, amount of photocatalyst, light intensity etc. affect the reaction rate. This method is useful to degrade picramic acid completely into decomposition products.

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