Photochemical Studies on Degradation of Cetyl Pyridinium Chloride (Cationic Surfactant) in Aqueous Phase Using Different Photocatalysts

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ABSTRACT

The photocatalytic process using semiconductors with a nanostructure is one of the technologies used for the destructive oxidation of organic compounds such as surfactants. In this paper, the photocatalytic degradation of Cetyl pyridinium chloride (CPC), was investigated in aqueous phase using various semiconductors such as titanium dioxide (TiO_2), zinc oxide (ZnO), stannic oxide (SnO_2). The degradation was studied under different conditions including the amount of photocatalyst, pH of the system, initial concentration and presence of anions. The results showed that the photocatalytic degradation of CPC was strongly influenced by these parameters and the best conditions for the photocatalytic degradation of CPC were obtained. The experimental results indicated that maximum degradation (87%) of surfactant occurred when ZnO was used as catalyst. The photodegradation efficiency was enhanced by increasing amount of photocatalyst, and decreases with the increase in the initial concentration of Cetyl pyridinium chloride. Finally, the kinetics process was studied and the photodegradation rate of CPC was found to obey pseudo-first-order kinetics equation represented by the Langmuir–Hinshelwood model.

Keywords: Photochemical degradation; Cationic surfactant; Cetyl pyridinium chloride; ZnO

INTRODUCTION

Surfactants are an abundant class of organic compounds that represent increasing environmental danger. During surfactant production and detergent manufacturing processes a large amount of toxic wastewater may be introduced into aquatic systems. In most countries, researchers are investigating on appropriate treatments for removal of pollutants and impurities. Various chemical and physical processes, such as chemical precipitation and separation of pollutants, electrocoagulation [1, 2], elimination by adsorption on activated carbon [3], etc., are currently used. In recent years, an alternative to conventional methods namely "advanced oxidation processes" (AOPs) is introduced. The method is based on the generation of very reactive species such as hydroxyl radicals that have been proposed to quickly and non selectively oxidize a broad range of organic pollutants [4, 5, 6]. AOPs include photocatalysis systems such as a combination of a semiconductor (TiO_2, ZnO, etc.) and UV light. Due to a faster electron transfer to molecular oxygen, TiO_2 is found to be more efficient for photocatalytic degradation of pollutants [7]. However, widespread use of

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TiO_2 and platinum catalyst is uneconomic for large-scale water treatment operations. However, ZnO appears to be a suitable alternative to TiO_2, since its photodegradation mechanism has been proven to be similar to that of TiO_2 [8, 9]. ZnO has frequently been reported to be more efficient than TiO_2. Its efficiency is particularly noticeable in the advanced oxidation of pulp mill bleaching wastewater [10].

In this study, various semiconductor photocatalysts (TiO_2, ZnO, SnO2) were compared for the degradation efficiency of aqueous solution of CPC. Followed by selection of the most active catalyst, subsequent experiments were conducted to investigate the effects of various process parameters (catalyst weight, pH, and initial surfactant concentration) on the process performance. The obtained results showed a good efficiency of nano-structured materials.

EXPERIMENTAL
Materials
Cetyl pyridinium chloride, CPC (Fig. 1) powder (formula: $C_{21}H_{28}ClN$, molar mass: 358.01g/mol) was purchased from Merk.
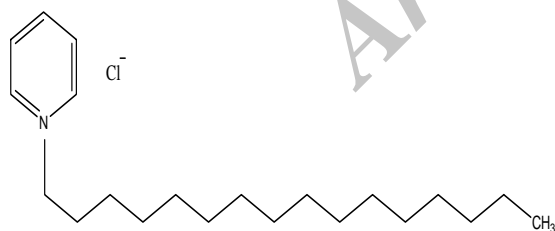

Fig. 1. Chemical structure of Cetylpyridinium chloride (CPC).

Zinc oxide nanopowder (particle size, Ca. 20nm; BET area, 50 m^2/g; 99.5%) was obtained from nanoamor (USA). Other chemicals, TiO_2, SnO_2, $K_2S_2O_8$, Na_2SO_4, $NaNO_2$, Na_2CO_3, NaCl, were also purchased from Merck. The pH of the solution was adjusted to the desired value (2.0-11.0) using dilute solutions of HCl or NaOH.

METHODS
Cetyl pyridinium chloride (CPC), a quaternary ammonium salt, is widely used in industrial and pharmaceutical products, especially in manufacturing of mouth washes, drupes and cosmetics. The photodegradation studies were carried out in a batch reactor system. The setup consisted of a UV chamber made of MDF having dimensions of 90cm×60cm×75cm with a high-pressure mercury vapor lamp (400W), fitted on the top of the chamber. An exhaust fan was fitted on the side wall of the chamber to maintain a constant temperature. The reactor used is cylindrical in shape and made pyrex flask, with a diameter of 2cm and a capacity of approximately 50ml. In a 50 ml flask, 25 ml of the surfactant solution with appropriate concentration was placed and the pH was measured. Then photocatalyst was added to the surfactant and oxidant and the mixture was irradiated with the UV lamp for approximately 8hrs. The aqueous suspension was magnetically stirred (speed of 80 rpm) throughout the experiment. 5ml samples were withdrawn on regular time intervals and centrifuged. Absorbance of the supernatant solution was measured and the sample was returned to the reactor.

The quantitative estimation of the surfactant was carried out using a UV-Vis spectrophotometer (Model Jenway 6405) at λ_{max}=258 nm. The degree of photodegradation (X) as a function of time is given by: X= $(C_0-C)/C_0$. Where, C_0 is the initial concentration of surfactant, and C the concentration of surfactant at time t.

RESULTS AND DISCUSSION
Degradation of surfactant using various photocatalysts
Investigations were carried out with different semiconductors viz., TiO_2, ZnO, SnO_2, in order to select the most effective catalyst for degradation of surfactant. Band positions of these semiconductors are listed in Tab. 1.

Table 1. Band positions of some common semiconductor photocatalysts in aqueous solution at pH 1

Semiconductor	Valence band (V *vs.* NHE)	Conductance band (V *vs.* NHE)	Band gap (eV)	Band gap wavelength (nm)
ZnO	+3.0	−0.2	3.2	387
TiO_2	+3.1	−0.1	3.2	387
SnO_2	+4.1	+0.33	3.9	318

The photocatalysed degradation of a surfactant in solution is initiated by the photoexcitation of the semiconductor, followed by formation of electron–hole pair on the surface of catalyst (Eq. (1)). The high oxidative potential of the hole (h^+_{VB}) in the catalyst permits the direct oxidation of the surfactant to reactive intermediates (Eq. (2)):

$$(MO/MO_2) + hv \rightarrow (MO/MO_2)(e^-_{CB} + h^+_{VB}) \tag{1}$$

$$h^+_{VB} + surfactant \rightarrow surfactant^{\bullet}+ \rightarrow oxidation\ of\ the\ surfactant \tag{2}$$

Another reactive intermediate which is responsible for the degradation is hydroxyl radical ($OH^{\bullet}$). It is either formed by the decomposition of water (Eq. (3)) or by reaction of the hole with OH^- (Eq. (4)). The hydroxyl radical is an extremely strong, non-selective oxidant ($E_0 = +3.06$ V) which leads to the partial or complete mineralization of several organic chemicals [11]:

$$h^+_{VB}+ H_2O \rightarrow H^+ + OH^{\bullet} \tag{3}$$
$$h^+_{VB}+ OH- \rightarrow OH^{\bullet} \tag{4}$$
$$OH^{\bullet}+ surfactant \rightarrow degradation\ of\ the\ surfactant \tag{5}$$

Initially blank experiments were performed under UV irradiation without addition of any catalyst and negligible degradation was observed. Then photocatalytic experiments were carried out using different catalysts, dosage of $K_2S_2O_8$ 3mM, pH values 9 at fixed surfactant concentration (10 mg/l), and catalyst loading of 11mg for 8 h for CPC surfactant. The results indicated that ZnO exhibits higher photocatalytic activity than others, especially TiO_2 for surfactant (Fig. 2.) This was explained as ZnO is having greater quantum efficiency than TiO_2 and others. On the other hand, SnO_2 exhibits less activity, as the wide band gap and light energy is not sufficient to excite this catalyst [12]. The order of degradation efficiency of various photocatalysts is ZnO > TiO_2 > SnO_2 for degradation of CPC. In addition to the higher efficiency, the other advantage of ZnO is its low cost. Therefore, the subsequent experiments were carried out using ZnO.
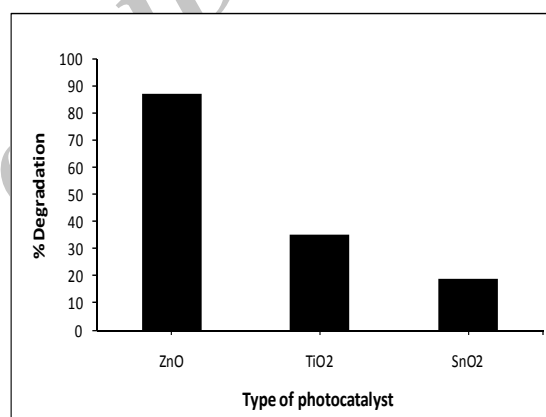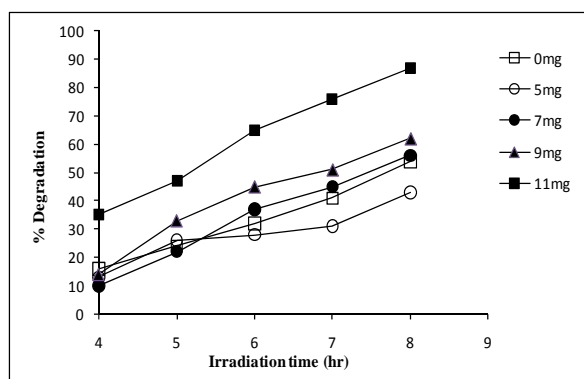

Fig. 2. Type of photocatalyst on the photodegradation efficiency. Irradiation time t = 8hr, surfactant concentration 10mg/l, $K_2S_2O_8$=3mM, pH=9, V=25ml.

Effect of nanocatalyst weight

A series of experiments were carried out by varying the amount of ZnO (0 to 11mg) to establish the effect of photocatalyst loading and to avoid unnecessary excess photocatalyst. The results of experiments performed with different amount of ZnO are presented in Fig.3. It can be observed that the photodegradation efficiency increases with an increase in amount of ZnO up to 11mg. This can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension [13]. The total active surface

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area increases with increasing catalyst weight. It must be stated that degradation of surfactant is inhibited when the irradiation time is less than 4hrs due to the radical attack between molecules that are linked and the pyridine produced. Since the pyridine adsorption on the same wavelength is greater than the initial adsorption to the loss of pyridine, therefore, degradation is not observed [20] .
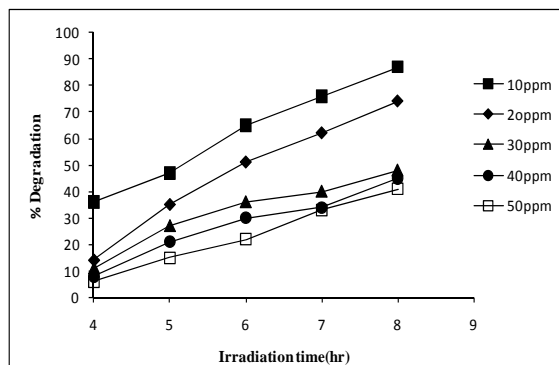

Fig. 3. Effect of catalyst weight on the photodegradation efficiency. Irradiation time t = 8 hr, CPC Concentration = 10mg/L, $K_2S_2O_8$=3mM, pH= 9, V=25ml.

Effect of initial surfactant concentration
The influence of initial surfactant concentration on degradation was examined in the range of 10–50mg/l at 11mg catalyst loading and $K_2S_2O_8$ (3mM) under UV irradiation. A representative concentration-time profile is shown in Fig. 4. It was observed that the rate of surfactant photodegradation decreased at higher concentrations. With increasing the amount of cationic surfactant, more surfactant molecules were adsorbed on the surface of the photocatalyst and the active sites of the catalysts were also reduced. Therefore, with increasing occupied sites of catalyst surface, the generation of hydroxyl radicals will be decreased. On the other hand, increasing concentration of surfactant can lead to decreasing the number of photons arrived to the surface of catalysts. By increasing the intensity of light adsorbed by molecules of surfactant, the excitation of photocatalyst

particles with photons will be reduced leading to diminished photodegradation efficiency [14].

Fig. 4. Effect of initial concentration on the photodegradation efficiency. Irradiation Time t=8 hr, ZnO=11mg, $K_2S_2O_8$=3mM, pH= 9, V=25ml.
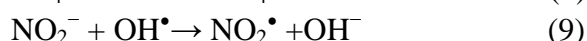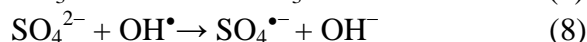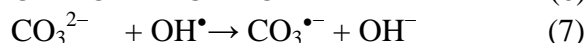
Effect of pH
Photodegradation of surfactant was studied in a pH range of 2.0–11 in the presence of ZnO as catalyst (11mg) and $K_2S_2O_8$ (3mM).The results of 8hrs irradiation are shown in Fig. 5 In all cases, the maximum degradation efficiency was obtained in alkaline pH, i.e. 9.0 for CPC. In presence of ZnO and in pH 9.0, degradation efficiency 87% was obtained. The interpretation of pH effects on the photocatalytic process is a very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction process [15].
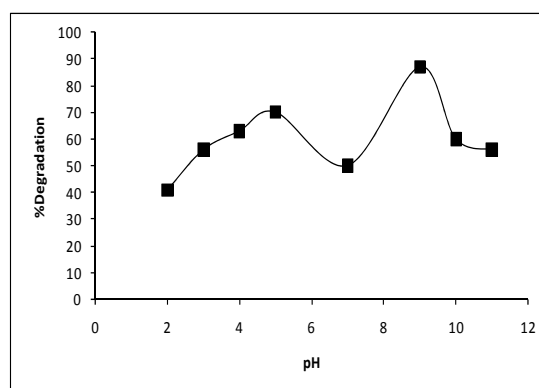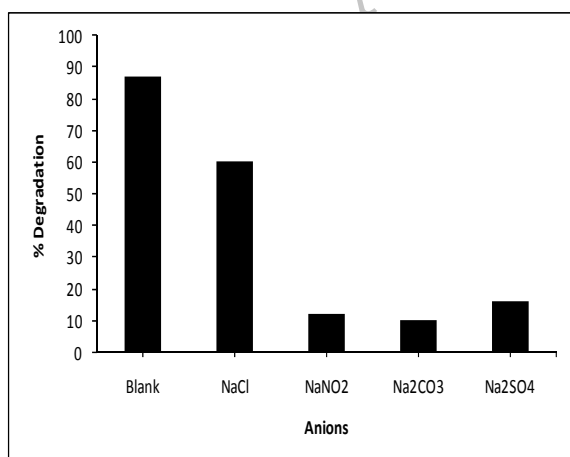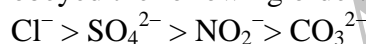

Fig. 5. Effect of pH on the photodegradation efficiency. Irradiation time t =8hr, surfactant Concentration = 10mg/L, $K_2S_2O_8$=3mM, ZnO=11mg, V=25ml.

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Effect of anions

Anions such as NO_2^-, CO_3^{2-}, Cl^-, SO_4^{2-} are often found in wastewater. They may influence the photocatalytic reactions for removal of organic pollutants. These substances may compete for the active sites on a ZnO surface or deactivate the photocatalyst and, as a result, cause a decrease in degradation of targeted surfactant. Generally, anions like carbonate, nitrite, chloride and sulfate ions retard the degradation of organic compounds by scavenging the hydroxyl radicals to form the respective anion radicals, according to the following reactions [16-19]:

$$Cl^- + OH^\bullet \rightarrow Cl^\bullet + OH^- \qquad (6)$$
$$CO_3^{2-} + OH^\bullet \rightarrow CO_3^{\bullet -} + OH^- \qquad (7)$$
$$SO_4^{2-} + OH^\bullet \rightarrow SO_4^{\bullet -} + OH^- \qquad (8)$$
$$NO_2^- + OH^\bullet \rightarrow NO_2^\bullet + OH^- \qquad (9)$$

To consider how the presence of dissolved inorganic anions may affect photo catalytic degradation rate of CPC, we selected $NaNO_2$, Na_2SO_4, Na_2CO_3 and NaCl salts. Similar amounts (0.025M) of these salts were used (pH 9, ZnO:11mg). Fig.6 shows that photo catalytic degradation rate of drug obeyed the following order:

$$Cl^- > SO_4^{2-} > NO_2^- > CO_3^{2-}$$

Fig. 6. Effect of anions on the photodegradation efficiency. Irradiation time t =8hr, surfactant Concentration = 10mg/l, $K_2S_2O_8$=3mM, anions=0.025M, ZnO=11mg, V=25ml, pH=9.

Kinetic study

To estimate the kinetic parameters (k and n), and order rate, an equation of the from – $r_{surfactant}=-dc/dt=K.C^n$ was used, where K is the degradation rate constant, 1/min the first –order kinetic model (n=1) was shown as follows:

$$-Ln=C/C_o=Kt$$

Fig.7. shows $-Ln\ C/C_o$ of LABS versus irradiation time. It is clear from Fig.7 that decreasing the surfactant concentration obeys a linear pattern towards the elapse of irradiation time. This means that the pseudo-first-order kinetics relative to surfactant is operative.
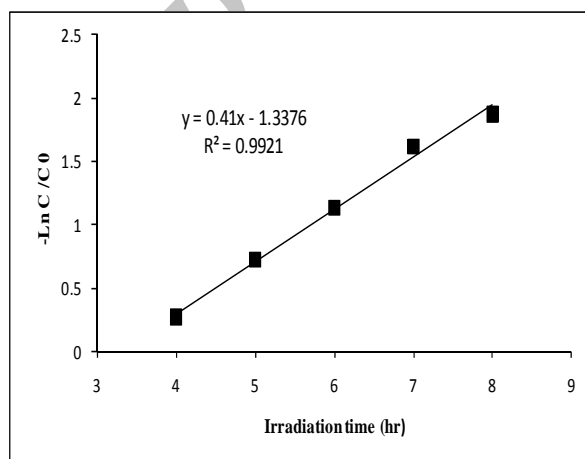
Fig. 7. Kinetic analysis of CPC under optimized conditions. Irradiation time t =8hr, surfactant Concentration = 10mg/L, $K_2S_2O_8$=3mM, ZnO=11mg, pH=9, V=25ml.

CONCLUSIONS

(1)Comparison of photocatalytic activity of different semiconductors has clearly indicated that the ZnO is the most active photocatalyst for degradation of CPC.

(2) The optimal degradation conditions of Cetyl pyridinium chloride are: 11mg catalyst, pH 9.0 and 3mM $K_2S_2O_8$. Under optimal degradation conditions of Cetyl pyridinium chloride, the photo degradation percent of the CPC was 87% when the solution was irradiated by the 400w high pressure mercury vapor lamp for 8 hrs.

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(3) The anions such as SO_4^{2-}, Cl^-, NO_2^-, CO_3^{2-} had an inhibitory effect on the photo degradation percent of CPC in the following order:

$Cl^- > SO_4^{2-} > NO_2^- > CO_3^{2-}$

Therefore, these anions should be tried to be eliminated before the catalyst is added in the practical application.

(4) Kinetic studies showed that the amount of surfactant photocatalytic degradation can be fitted with pseudo-first -order model.

ACKNOWLEDGMENT

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