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EFFECTS OF Ag AND Pd MODIFICATIONS OF TiO_2 ON THE PHOTOCATALYTIC DEGRADATION OF p-CHLOROPHENOL IN AQUEOUS SOLUTION

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ABSTRACT

Photocatalytic degradation of p-chlorophenol was studied using Ag and Pd modified Degussa P25 TiO_2 *photocatalysts prepared by impregnation – reduction method. Series of catalysts containing Ag, respectively Pd, between 0,1 and 0,5 mass % were prepared. The results show that the presence of silver or paladium on the* TiO_2 *surface improves his photocatalitic activity, the best results being obtained with 0,5 % Ag/*TiO_2*. The calculation of the adsorption and kinetic parameters shows that the photocatalytic degradability of p-chlorophenol is directly related to its adsorption capacity. The adsorption experiments showed that* TiO_2 *Degussa has the highest adsorption capacity but according to the kinetics it has the lowest activity. This phenomenon could be explained with modification of the adsorptive site caused by the UV-irradiation.*

Keywords: photocatalytic degradation, TiO_2*, Ag modified* TiO_2*, Pd modified* TiO_2*, adsorption, kinetics.*

INTRODUCTION

Various compounds that are commonly used in industry, agriculture and daily life such as halogenated aromatics, aliphatics, phenols, herbicides, pesticides, surfactants and others, cause contamination of environment. Although many organic compounds are in principle biodegradable, resistant compounds may be found or formed as intermediates during the degradation process.

TiO_2 photocatalysts has been improved by numerous investigations in recent years, particularly due to its application for the complete mineralization of almost all organic contaminants to CO_2, H_2O and inorganic constituents. However, photooxidation processes carried in presence of TiO_2 have not been widely applied in water treatment industries due to some limitations. Probably the most important reason for that is the low rate of electron transfer to oxygen and the high recombination rate of electron-hole pairs limit the rate of photooxydation of organic compounds on the surface of a catalyst.

The photocatalytic reaction may drastically be promoted or retarded by doping TiO_2 photocatalyst with different metals. Many investigations have reported that the addition of metals from VIII group or transition metal ions to TiO_2 based photocatalysts are two of the most effective ways to enhance the photocatalytic reaction rate. The noble metals like gold, silver and platinum were usually used to produce the highest Schotty barrier among the metals, which facilitate the electron capture. Choi et al. [1] presented the results of a systematic study on the effects of 21 different metal ion dopants on the photochemical activity of quantum sized TiO_2. Enhanced photocatalytic activity was found in the TiO_2 matrix after doping Fe^{3+}, Mo^{5+}, Ru^{4+}, Re^{5+}, V^{4+} and Rh^{3+} at 0.5 % molar level. However, there was no promoting effect on the photocatalytic decomposition of phenol in the presence of silver ion [2].

Many reports are available on metal-doped TiO_2 preparations, which efficiently decompose toxic compounds. Several of the preparations showed positive effects [3-5], while others presented negative ones [3, 4, 6-8]. In the meantime, several researchers investigated the interaction between the impurity and the supporting materials, and explored the mechanism of the enhancement of photoacatalytic activity of the metal-TiO_2 or metal ion-TiO_2 catalysts. UPS, XPS and AES techniques have been widely applied to provide the evidence for electron transfer from the supports to the metals or metal ions [8-10].

In most of the studies, Langmuir-Hinshelwood model was used to describe the degradation rate expressions in terms of disappearance of compounds or the formation of CO_2. Several kinetic models have been published in literature [11-14], but none of them could completely account for all possible variables affecting the degradation rate. Almost all these studies investigated the effects of various parameters on the initial degradation rate rather than the degradation rate during the whole photocatalytic process.

The aim of this study was to investigate the applicability of the synthesized Ag and Pd dopped TiO_2 catalysts for the photocatalytic decomposition of p-chlorophenol in aqueous media.

EXPERIMENTAL

Catalysts preparation

The Ag and Pd modified Degussa P-25 TiO_2 were prepared by wet impregnation method. The mixtures of previously calculated amounts of TiO_2, $AgNO_3$ and $PdCl_2$ were left for aging for 24 h. After that the liquid was evaporated in a vacuum drier and the mixtures were calcined for 5 hours at 450°C for Ag/TiO_2 and 2 hours at 200°C for Pd/TiO_2. The resulting catalysts were reduced in hydrogen flow for 2 hours at 200°C.

The surface areas of all prepared catalysts were measured by using a surface area analyzer FlowSorb 2300, Micromeritics. The catalyst sample was outgassed at 150°C for 1 h before starting the measurements in order to remove the humidity and volatile compounds adsorbed on its surface. The results are shown in Table 1.

Table 1. Specific surface area of the catalysts.

No	Composition, [% mass]	Specific surface area, [$m^2 g^{-1}$]
1	TiO_2 Degussa P-25	56
2	0.5 % Ag/TiO_2	47
3	0.25 % Ag/TiO_2	52
4	0.1 % Ag/TiO_2	51
5	0.5 % Pd/TiO_2	51
6	0.25 % Pd/TiO_2	52
7	0.1 % Pd/TiO_2	51

The photocatalytic degradation process was carried out in a quartz batch reactor. The upper part of the reactor was sealed with a Plexiglass lid. The light source was a vertical germicidal UV lamp Philips-Osram with the maximum light intensity at 254 nm. Both the reactor and the lamp were enveloped with aluminium foil in order to enhance the irradiation of the catalyst.

Photocatalytic reaction experiments

Model aqueous solutions with three different initial concentrations of 50, 100 and 200 mg dm^{-3} p-chlorophenol were used for the study of the photocatalytic activity of the prepared catalysts. The photocatalytic experiments were conducted using 0,4 g of catalyst, suspended in 400 ml of p-chlorophenol solution. A magnetic stirrer at the bottom of the reactor was rotated during the reaction at 300 rpm in order to ensure an effective mixing. At the beginning of the reaction samples for analysis were collected at 30 and 60 min, afterwards a sample was taken each hour up to 5 hours.

The degradation rate of p-chlorophenol was measured by a gas chromatograph Hewlett-Packard 5890, equipped with capillary column (DB-5) and FID detector.

RESULTS AND DISCUSSION

Fig. 1 shows the patterns of the photocatalytic degradation of p-chlorophenol with initial concentration 50 mg dm^{-3} using TiO_2 Degussa P-25 and three Ag modified catalysts. The photooxidation of p-chlorophenol is completed after 180 min of the beginning of the experiment in the case of 0.5 % Ag/TiO_2 and 0.1 % Ag/TiO_2. For 0.25 % Ag/TiO_2 the complete degradation is

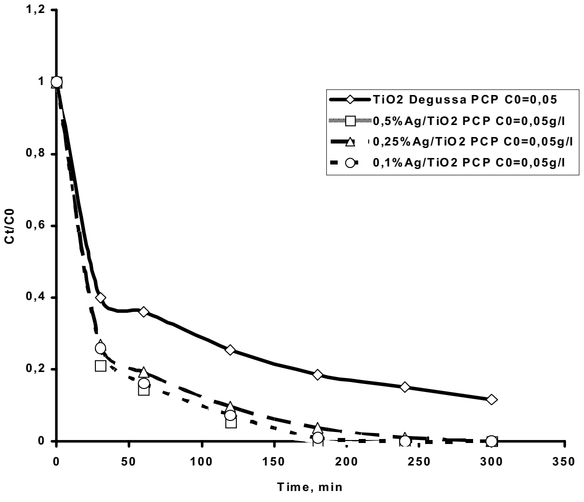

Fig. 1. Photocatalytic activity of Ag doped TiO_2.

achieved after 240 min. The degradation rate of unmodified TiO_2 is about 90 % at the end of the experimental time but the trend of the curve shows a possibility for higher conversion in case of longer reaction time.

Fig. 2 shows the patterns of the photocatalytic degradation of p-chlorophenol with initial concentration 50 mg dm^{-3} using TiO_2 Degussa P-25 and three Pd modified catalysts. The trends of the curves are generally the same as in the case with Ag modified catalysts – faster reaction and higher degradation rate for 0.5 % Pd/TiO_2 and 0.1 % Pd/TiO_2. In all the reactions Ag modified catalysts show higher photocatalytic activity than Pd modified TiO_2.

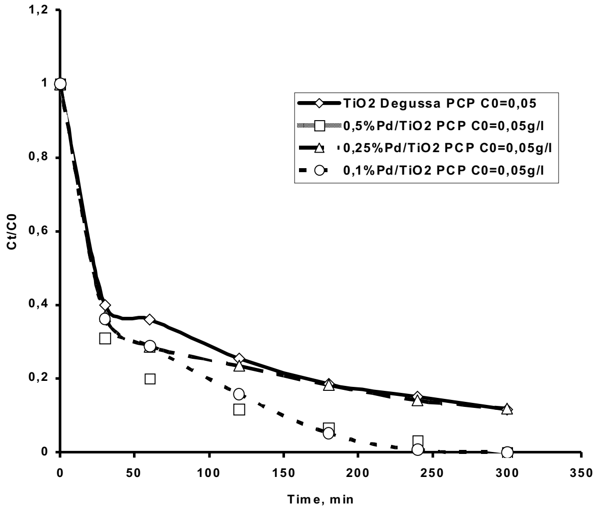

Fig. 2. Photocatalytic activity of Pd doped TiO_2.

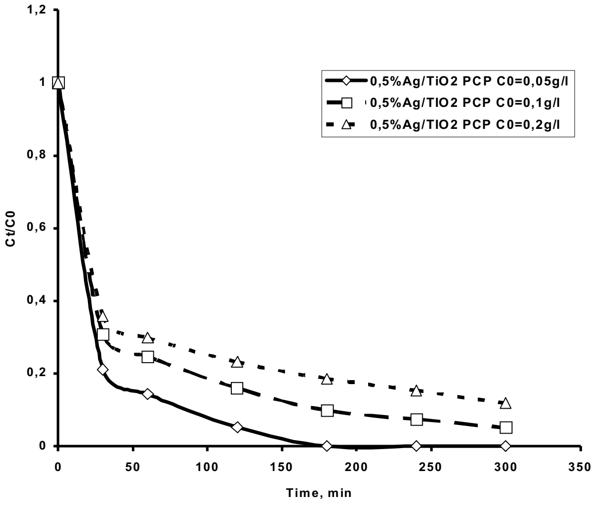

Fig. 3. Influence of the initial concentration of p-chlorophenol on the photocatalytic activity of Ag doped TiO_2.

The improved activity of Ag and Pd modified TiO_2 particles is due to better charge separation and therefore, to slower recombination. The nanosized silver and palladium deposits on Degussa P25 particles act as sites of electron accumulation where the reduction of adsorbed species such as oxygen occurs. The enhanced reduction of oxygen through better electron-hole separation in Ag/TiO_2 and Pd/TiO_2 particles compared to pure TiO_2 increases the rate of p-chlorophenol degradation.

The influence of the initial concentration of p-chlorophenol is most distinguished in the case of TiO_2 Degussa. The conversion is about 90 % for the lowest initial concentration, but it is barely over 60 % for the highest. The same pattern is shown also by the Ag and Pd modified TiO_2 but in lesser degree – for the highest initial concentration the conversion is between 85 and 90 %.

Preliminary adsorption in the dark

A series of experiments were carried out in the dark to study the adsorption isotherms of p-chlorophenol on the various catalysts surfaces. The isotherms were determined by shaking 50 cm^3 model solutions with 10 – 500 mg dm^{-3} concentrations of p-chlorophenol and definite catalyst quantity in screw cap jars for 24 hours which was more than ample time for adsorption equilibrium. Fig. 4 shows that the quantity adsorbed (q_e) at the adsorption equilibrium (C_e) increases with the p-

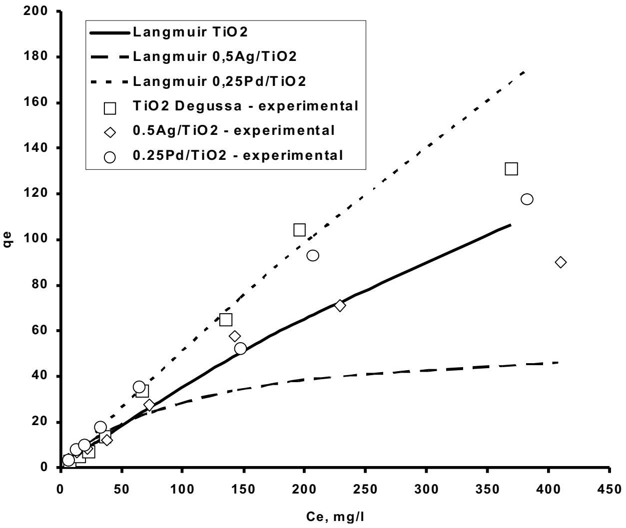

Fig. 4. Langmuir adsorption isotherms of p-chlorophenol.

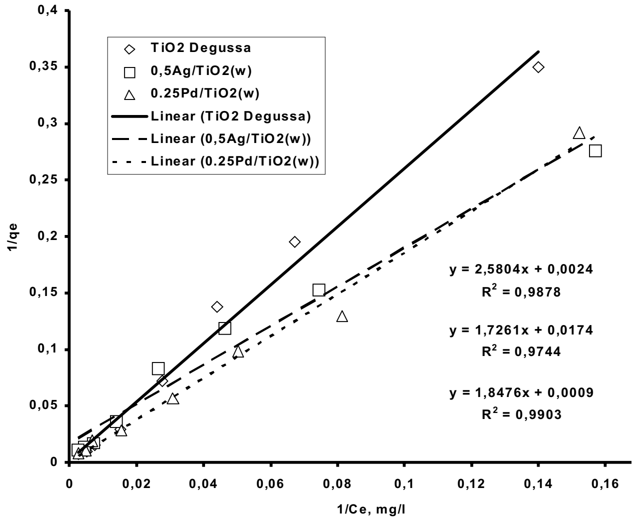

Fig. 5. Linearized Langmuir isotherms.

chlorophenol concentration. This behaviour obeys the classical Langmuir adsorption model, followed by numerous compounds in aqueous suspension given by equation (1):

$$\theta = \frac{q_e}{q_{\max}} = \frac{K_{ads} C_e}{1 + K_{ads} C_e} \tag{1}$$

where θ is the catalyst surface coverage, q_e the adsorbed quantity, q_{max} the maximal adsorbable quantity, C_e the concentration of p-chlorophenol at the adsorption equilibrium and K_{ads} the Langmuir adsorption constant (specific of the pair compound/catalyst).

The linear transformation of the Langmuir adsorption model can be expressed as a function of $1/q_e = f(1/C_e)$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_{ads} C_e} \tag{2}$$

The linear transforms for different experimental isotherms are given in Fig. 5. The ordinate at the origin is equal to the reciprocal of q_{max}, whereas K_{ads} can be calculated from the slope α $(1/q_{max}K_{ads})$. It appears that the adsorption coverages are small for Ag and Pd modified TiO_2 and vary for the different catalysts. In particular, TiO_2 Degussa P25 exhibits higher adsorptive capability compared to the modified species.

Kinetic model of Langmuir-Hinshelwood

Even if some authors consider that the Langmuir-Hinshelwood model is not sufficient to describe the whole photocatalytic process, this model is widely used because it enables one to correlate the degradation rate to the instantaneous concentration according to the expression:

$$r = k_{LH}\theta = k_{LH} \frac{(K_{LH} C)^{\alpha}}{1 + (K_{LH} C)^{\alpha}} \tag{3}$$

where r is the rate of photocatalytic degradation, k_{LH} - the rate constant, C - the p-chlorophenol concentration, K_{LH} - the Langmuir-Hinshelwood adsorption constant and α is the kinetic order. At low value of $(K_{LH}C)^{\alpha}$ it can be neglected with respect to 1 and the result is the simplified expression:

$$r = k_{LH}\theta = k_{LH} (K_{LH} C)^{\alpha} \tag{4}$$

Generally, the photocatalytic degradation of organic compounds in water follows a first-order kinetic low. In the case of the modified catalysts it was observed that the first-order rate did not remain constant when varying the initial p-chlorophenol concentration or the type of catalyst, even if the linear form of kinetics describes the experimental data well. In order to determine the kinetic order of the photocatalytic reaction, a series of kinetic experiments have been carried out varying the initial concentration of p-chlorophe-

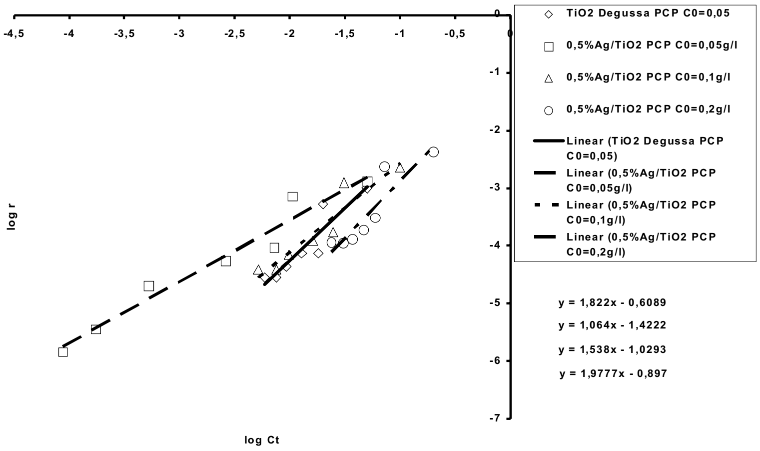

Fig. 6. log-log of the rate of photocatalytic degradation of p-chlorophenol as a function of the concentration.

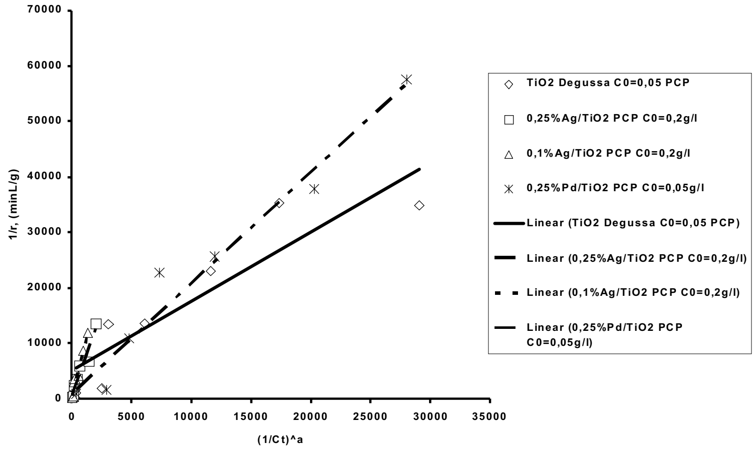

Fig. 7. Linearized Langmuir-Hinshelwood isotherms.

nol for each catalyst. The photocatalytic degradation rate r of the p-chlorophenol can be expressed as a function of the concentration according to:

$$r=\frac{-dC}{dt}=kC^{\alpha} \tag{5}$$

The log-log plot of r = f(C) gives a straight line ($\log r = \log k + \alpha \log C$) of which slope is equal to the kinetic order.

As it is shown on Fig. 6 the kinetic order of the photocatalytic reaction in general increases with the increasing of the initial p-chlorophenol concentration. It also varies for the different catalysts. In the case of Ag modified catalysts it does not depend from the amount of Ag supported on TiO_2 and it varies from 1 to 2 with increasing the initial concentration. There is no such pattern for the Pd modified catalysts – the kinetic order varies for the different catalysts and with the variation of the initial concentration (increases with increasing C_0 except for 0.25 % Pd/TiO_2). TiO_2 Degussa shows second kinetic order for the lowest initial concentration and third for the other two.

The linear form of Langmuir-Hinshewlood model becomes:

$$\frac{1}{r}=\frac{1}{k_{LH}}+\frac{1}{k_{LH}\,(K_{LH}C)^{\alpha}} \tag{6}$$

In Fig. 7 are presented the linearised forms of Langmuir-Hinshelwood model for four different catalysts. The linear plot confirms the Langmuir-Hinshelwood relationship.

As shown in the previous section the calculated adsorption constants were very different from K_{LH} values (K_{LH} is much higher than K_{ads}). These differences do not seem surprising for a Langmuir-Hinshelwood model since K_{LH} does not really reflect the adsorption affinity of p-chlorophenol for the catalyst surface; K_{ads} and K_{LH} should not be identical. There have been several studies reporting that K_{LH} could be substantially higher than K_{ads}: 280 times for metobromuron [15], 13 times for benzylic alcohol [16], 220 times for 2-chlorophenol [17]. Various suggestions have been formulated: i) a photoadsorption would happen [18]; ii) the reaction would take place not only at the surface but also in the bulk solution [19, 20]; iii) the number of adsorption sites would not be enough numerous to initiate the reaction [21]; or iv) UV-illuminations would change electronic properties of the catalyst surface [22]. A recent study [16] has proven the influence of the light intensity on the variability of K_{LH}. The results show that irradiation modifies adsorptive sites, and the consequence is that K_{LH} measured under irradiation is different from K_{ads} measured in the dark.

CONCLUSIONS

Six different types Ag and Pd modified titania catalysts were prepared. All samples have shown increased photocatalytic activity towards the degradation of p-chlorophenol in aqueous solutions comparing to Degussa P-25. Generally Ag modified catalysts show higher activity than Pd modified TiO_2. In the case of silver doped catalysts, the activity increases with the amount of the silver impregnated on the surface of titania. However for Pd modified catalysts dependence is not observed.

The kinetic calculation confirms that the Langmuir-Hinshelwood model describes well the experimental data. Although TiO_2 Degussa shows the highest adsorption capacity it has the lowest photoactivity with respect to p-chlorophenol.

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