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Inactivated properties of activated carbon-supported TiO_2 nanoparticles for bacteria and kinetic study

LI Youji*, MA Mingyuan, WANG Xiaohu, WANG Xiaohua

College of Chemistry and Chemical Engineering, Jishou University, Hunan 416000, China. E-mail: bcclyj@163.com

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Abstract

The activated carbon-supported TiO_2 nanoparticles (TiO_2/AC) were prepared by a properly controlled sol-gel method. The effects of activated carbons (AC) support on inactivated properties of TiO_2 nanoparticles were evaluated by photocatalytic inactivation experiments of *Escherichia coli*. The key factors affecting the inactivation efficiency were investigated, including electric power of lamp, temperature, and pH values. The results show that the TiO_2/AC composites have high inactivation properties of *E. coli* in comparison with pure TiO_2 powder. The kinetics of photocatalytic inactivation of *E. coli* was found to follow a pseudo-first order rate law for TiO_2/AC composites, and kinetic behavior could be described in terms of a modified Langmuir-Hinshelwood model. The values of the adsorption equilibrium constants for the bacteria, K_c, and for the rate constants, k_r, were certainly depended on TiO_2 content. At 47 wt.% TiO_2 coatings with the highest rate constant, the K_c and k_r were 1.17×10^{-8} L/cfu and 1.43×10^6 cfu/(L·min), respectively. The variety of parameters shows significant effects on inactivation rate. The outer layer of bacteria decomposed first resulting in inactivation of cell, and with further illumination, the cells nearly decomposed.

Key words: inactivation; activated carbon-supported TiO_2; sol-gel method; bacteria

Introduction

Disinfection of water by chlorine or ozone has been carried out for about one hundred years. However, some chlorine residuals in water are toxic to many aquatic organisms, and some byproducts of chlorination in water such as trihalomethane may be carcinogenic. To avoid adding chemicals to the drinking water, disinfection by photocatalysis with titanium dioxide (TiO_2) is generating considerable interest in recent years (Li *et al*., 1996). There are many publications reporting the application of photocatalysis toward water remediation with recent review articles summarizing the photocatalytic removal of organic, inorganic, and microbial pollutants (Salinaro *et al*., 1999; Ollis *et al*., 1991; Heller, 1995; Hoffmann *et al*., 1995, Mills and Hunte, 1997; Blake *et al*., 1999; Fujishima *et al*., 2000). When TiO_2 powder is suspended in water and irradiated with near ultraviolet (UV) light below $\lambda < 385$ nm, electron hole pairs are generated within the metal oxide semiconductor and then are separated between the conductance band and valence band. The valence band hole has a very positive reduction potential and is capable of oxidizing water, or hydroxide ions, to form hydroxyl radicals in water (Mills and Hunte, 1997). Hydroxyl radicals are known to be powerful for both the oxidation of organic substances and the inactivation of bacteria and virus (Rincón and Pulgarin, 2004). Mechanisms for the bactericidal action of TiO_2 photocatalysis have been proposed by a number of authors (Matsunaga *et al*., 1985; Christensen *et al*., 2003; Maness *et al*., 1999; Zheng *et al*., 2000; Sunada *et al*., 1998). The results from the above studies suggest that the cell membrane is the primary site of reactive photogenerated oxygen species attack. Oxidative attack of the cell membrane leads to lipid peroxidation. The combination of cell membrane damage and further oxidative attack of internal cellular components ultimately results in cell death. TiO_2 powder is commonly used in the laboratory in the form of a suspension. This method yields a high catalyst surface area to volume ratio for pollutant hydroxyl radical interaction; however, the catalyst must be removed by a posttreatment separation stage, which may not be cost effective on a large scale. There is an effective way to remove the need for posttreatment separation that the TiO_2 is loaded on a high surface area support, such as activated carbon, exfoliated graphite, and optical fibers (Hammer and Kvande, 2007; Lu *et al*., 1999; Matsunaga and Okochi, 1995). Meanwhile, this method is not associated with a decrease in surface area to volume ratio and mass transfer resulting in a reduction in the pollutant degradation rate. Matos and coworkers prepared carbon-coated TiO_2 with high photocatalytic activity and repeated-use property and investigated influence of different activated carbons (AC) on the photocatalytic degradation of aqueous organic

* Corresponding author. E-mail: bcclyj@163.com.

pollutants (Matos *et al*., 1998, 1999, 2001). But the studies about bacteria inactivation by TiO_2/AC composites and the effects of AC supports on inactivated properties of composites have not been reported. The main purpose of this article was to evaluate and compare photocatalytic inactivation of TiO_2/AC composites and TiO_2 powder. Meanwhile, We investigated that the effects of AC supports on inactivated properties of composites from photocatalytic kinetics. Finally, the inactivated mechanism of bacteria was explained in photocatalytic course in term of photocatalytic characteristics.

1 Experimental

1.1 Preparation of TiO_2/AC composites

Commercially available activated carbon grains from Tianjing, China, which were produced by the vapor activation of coconut shell, were serially treated and then used. Precursor solutions for TiO_2/AC were prepared by the following method. Tetrabutylorthotitanate and diethanoiamine were dissolved in ethanol. The solution was stirred vigorously for 2 h at 20°C, followed by addition of a mixture of distilled water and ethanol. The resulted alkoxide solution was left at 20°C for hydrolysis reaction to produce TiO_2 sol. Then, a desired amount of activated carbon grains was used as the substrates and was added into TiO_2 sol with a certain degree. After this, sol changes to gel; TiO_2 gel coated activated carbon was heat treated at 250°C for 2 h in air and then heating temperature was increased gradually to the end temperature from 300 to 700°C for 2 h in a flow of high purity nitrogen using an electric oven. The amount of coated TiO_2 was adjusted by repeating the cycle from dipping to heat treatment.

1.2 Culture of bacteria and growth media

Escherichia coli (*E. coli*, NCIMB 8277) was grown under aerobic conditions at 37°C overnight in 50 ml of Luria Bertani (LB) medium (pH 7.0) containing tryptone 1%, yeast extract 0.5%, and sodium chloride 1%. Shaking was done to obtain the necessary oxygen transfer into the medium. The cells were centrifuged at 8,000 r/min for 10 min, washed three times in sterilized Milli-Q water, and resuspended in sterilized water.

1.3 Photocatalytic reactor operation

Semiconductor composites or powder was suspended in sterilized water by sonication for 5 min. As shown in Fig.1, inactivated experiments were carried out in a cylindrical pyrex glass vessel on which there was a black light fluorescent lamp to provide the irradiance source. Appropriate dilutions of *E. coli* suspensions were prepared in photocatalytic systems by *E. coli* being inoculated in sterilized water. A bacterial suspension without catalysts was irradiated as a control, and a dark reaction was also carried out. Circulation of reactant was provided with a magnetic stirrer. Samples were withdrawn at regular intervals and each experiment was repeated at least twice. The pH was adjusted to 6, 7, or 8 using a phosphate buffer (KH_2PO_4/NaOH). The resulting phosphate buffer solutions were maintained at approximately 20 mmol/L. Inactivation temperature was maintained at 25, 37, and 45°C by a temperature controller.

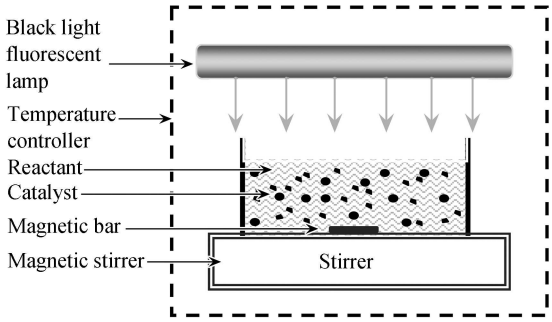

Fig. 1 Experimental apparatus for photocatalytic reaction.

1.4 Determination of viable bacteria

The number of viable cells in the solution was determined by plating samples after suitable dilutions on LB medium supplemented with 20 g/L agar and counting the colonies which appeared after 24 h of incubation at 37°C. Many replicate plates were used and all experiments were repeated more than five times to obtain a mean value applied in kinetics in terms of statistic principle. All the materials were autoclaved for 30 min to ensure sterility.

1.5 Scanning electron microscopy

Bacteria were deposited on TiO_2/AC composites or TiO_2 powder. The samples were subjected to the standard procedure for sample preparation: after being fixed with glutaraldehyde and osmium tetroxide, the samples were drained with ethanol/water in increasing concentrations of ethanol. The absolute ethanol was replaced by dimethoxymethane, and the samples underwent critical point drying with CO_2. The photocatalysts were glued onto stages and metallized with gold. The samples were microscoped and photographed with a scanning electron microscope (JSM-5600LV, JEOL, Japan).

2 Results and discussion

2.1 Characterization of TiO_2/AC

The content of TiO_2 in composite samples per doped cycle, BET surface area, and total pore volume, including the original AC, are summarized in Table 1, together with heat-treatment temperature (HTT) and doped cycle times. Nano-TiO_2 particles have high surface area to increase surface area of hybridization catalyst by doped surface of AC and at the same time, to decrease surface area by blocking the pore entrances on the surface of AC substrate. For 1-doped cycle TiO_2/AC, because the former effect on surface area is stronger than the latter effect, its surface area is larger than the original AC and increased with increasing heat-treatment temperature. However, for TiO_2/AC catalyst with 2-doped cycles or 3-doped cycles, its surface area was decreased markedly and was increased

Table 1 Characteristic of TiO_2/AC composites and original activated carbon (AC) supports

Sample	HTT (°C)	TiO_2 content (wt.%)	Doped cycle (times)	Surface area (m^2/g)	Total pore volumn (cm^3/g)	Crystallite phase	*Escherichia coli* survival rate after 100 min (%)
AC	–	0	–	435	0.08768	Amorphou	92
TA1-300	300	3	1	440	0.08547	Anatase	60
TA1-400	400	4	1	448	0.08469	Anatase	57
TA1-500	500	5	1	456	0.08231	A+R	45
TA1-600	600	9	1	462	0.08075	Rutile	38
TA1-700	700	10	1	478	0.07968	Rutile	32
TA2-500	500	18	2	373	0.074874	A+R	27
TA3-500	500	47	3	279	0.06458	A+R	23
TA4-500	500	63	4	271	0.05364	A+R	30

HTT: heat-treatment temperature; A+R: anatase and rutile.

gradually with increasing heat-treatment temperature, but complete recovery of surface area was not attained. The decrease of surface area is reasonably supposed to be the fact that the effect of nanometer TiO_2 particles on enhancing surface area were fewer than that of its blocking. The total pore volume of original AC is 0.08768 cm^3/g. The total pore volume of TiO_2/AC is smaller than that of original AC and decreases with increasing TiO_2 content, which could indicate that TiO_2 particles had performance of blocking the pore entrances. Therefore, the change tendency of surface area is the same as that of total pore volume with increasing doped cycle times for catalysts at heat-treatment of 500°C as shown in Table 1. Meanwhile, the ratio of anatase to rutile and TiO_2 crystallite phase on TiO_2/AC samples at heat-treatment temperature of 500°C were invariable with changes of TiO_2 content.

2.2 Photocatalytic inactivation of *E. coli*

The time course of viable *E. coli* cells when cell suspensions (10^7 cfu/ml) were irradiated with powder or composites (2 g/L) under lamp light after saturation of adsorption in dark was determined in Fig.2. By the control experiments, the percentage of viable cell counts was observed to be > 95% in the absence of photocatalysts. In contrast, the number of viable cells decreased gradually for powder or composites in illumination. After 250 min illumination, only 60%–70% of *E. coli* were inactivated using TiO_2 powder; however, 99.99% of *E. coli* were inactivated using TiO_2/AC composites. It is obviously found that the TiO_2/AC composites were more effective for *E. coli* inactivation in comparison with powder. The AC effect on inactivated enhancement as observed in photocatalytic course was mainly due to its high surface area, which shows great adsorbing energy to bacteria, as well as organic molecules more than TiO_2 powder. In addition, it is experimentally shown that the carbon in active carbon reduces TiO_2 to form more Ti^{3+} ions (Liu *et al*., 2003). By acting as active center, the Ti^{3+} can trap photogenerated electrons in the conduction band and prevent the recombination of electron-hole pairs; hence, there are more photogenerated holes in composites. The hole in the valence band received an electron from CoA as the donor to form dimeric CoA. Dimerization of CoA inhibited the respiration and caused the death of the cells (Matsunaga *et al*., 1988).

$$2\text{CoA–SH} + 2h^+_{vb} \longrightarrow \text{CoA–S–S–CoA} + 2H^+ \quad (1)$$

Meanwhile, it can be observed from Fig.2 that TiO_2 content affects inactivated properties of composites. The relation between rate of *E. coli* inactivation and TiO_2 content follows the sequence: 47% > 18% > 63% > 5%. The survival rate of the *E. coli* inactivated by the pure TiO_2 was nearly 77% after 250 min. However, the TiO_2/AC that contained 47% TiO_2 has reached almost 100% of the removal of *E. coli* for 175 min.

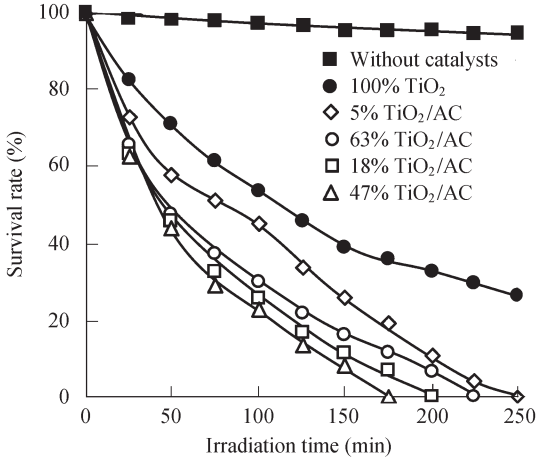

Fig. 2 Time course of changes in the survival rate of *E. coli* caused by photocatalysis with 2 g/L of TiO_2/AC catalyst or without catalysts. *E. coli* content is 1×10^7 cfu/ml.

2.3 Photocatalytic inactivation kinetics of *E. coli* by TiO_2/AC composites

The inactivated curves of *E. coli* by TiO_2/AC are well fitted by a mono-exponential curve, suggesting that a pseudo-first order homogeneous reaction model can be taken into consideration for describing the kinetic behavior. However, in photocatalytic inactivation reaction system, the reactant in solution absorbs light and then lowers its intensity, which results in the decrease of photocatalytic activity. So the initial concentration of *E. coli* has a fundamental effect on the degradation rate, i.e., the kinetic rate constant decreases with the concentration (da Silva and Faria, 2003). In other words, from a practical standpoint, at the same illumination time, the relative amount of *E. coli* inactivated is less for the more high content of bacteria solutions. The inactivated experiments by TiO_2/AC of *E. coli* follow the pseudo-first order kinetics with respect to

E. coli concentration (C) in the bulk solution:

$$-\frac{dC}{dt} = k_{app}C = r \quad (2)$$

Integration of that equation will lead to the expected relation:

$$\ln(\frac{C_0}{C}) = k_{app}t \quad (3)$$

where, k_{app} is the apparent pseudo-first order rate constant and is affected by *E. coli* concentration, C_0 is the initial concentration in the bulk solution after dark adsorption, and t is the reaction time, with the same restriction of $C = C_0$ at $t = 0$.

Generally, the photocatalytic degradation is assumed to occur on the basis of adsorption, so it can be speculated that the inactivation reaction between the surface-adsorbed substrates and the photogenerated oxidants is predominant, although other pathways may exist (Tunesi and Anderson, 1993). We reasonably postulate that photocatalytic inactivation of *E. coli* on the TiO_2 supported on porous AC follows a modified Langmuir-Hinshelwood model, where the oxidation of intermediates competes with that of *E. coli* intact cells. Then, the reaction rate can be written as:

$$r = -\frac{dC}{dt} = k_2\theta_{HO\cdot}\theta_{EC}t \quad (4)$$

where, k_2 is a second-order surface rate constant, $\theta_{HO\cdot}$ is the fractional site coverage by HO· radicals, and θ_{EC} is the fraction of sites covered by *E. coli* cell (EC) at any time t.

Owing to the fact that water is the solvent (i.e., H_2O and OH^- are in large excess) and the oxygen partial pressure remains the same in a given experiment, the fractional site coverage by HO· radicals is also constant, and Eq.(3) can be arranged as:

$$r = -\frac{dC}{dt} = k_r\theta_{EC}t \quad (5)$$

where, k_r is rate constant. $k_r = k_2\theta_{HO\cdot}$ includes the second-order rate constant. On the other hand, the fractional site coverage by the *E. coli* cells is given by

$$\theta_{EC} = \frac{K_C C}{1 + K_C C + \sum_i K_i [I_i]} \quad (6)$$

where, K_C and K_i are adsorption equilibrium constants, and I refers to the various intermediate products of *E. coli* decomposition. If it is assumed that the adsorption coefficients for all intermediates present in the reacting mixture are effectively equal, the following assumption can be made as:

$$K_C C + \sum_i K_i [I_i] = K_C C_0 \quad (7)$$

where, C_0 is the initial concentration of *E. coli*. Now, substitution of Eq.(6) into Eq.(5) results on the expression:

$$r = k_r \times \frac{K_C C}{1 + K_C C_0} = k_{app}C \quad (8)$$

The relationship between k_{app} and C_0 can be expressed as a linear equation:

$$\frac{1}{k_{app}} = \frac{1}{k_r K_C} + \frac{C_0}{k_r} \quad (9)$$

The values of k_{app} can be obtained directly from the regression analysis of the linear curve in Eq.(2) (a plot of $\ln(C_0/C)$ versus t) for all the experiments with different initial bulk concentrations of *E. coli*. In Fig.3, a plot of $1/k_{app}$ versus C_0 for different TiO_2 contents of TiO_2/AC is shown. The values of K_C and k_r were obtained by linear regression of the points calculated by Eq.(8). Fig.4 shows dependence of k_r and K_C determined in this way on the TiO_2 content of TiO_2/AC. By comparing the dependence of the k_r on the TiO_2 content with that of K_C given in Fig.4, rate constant first increases with increasing content of TiO_2, but then decreases; however, absorption equilibrium constant decrease with increasing content of TiO_2. It can be observed that the rate of *E. coli* inactivation for TiO_2/AC catalysts is mostly determined by TiO_2 particles. This may be caused by the fact that *E. coli* cells have to be adsorbed into AC layer and then migrated to the surface of TiO_2 par-

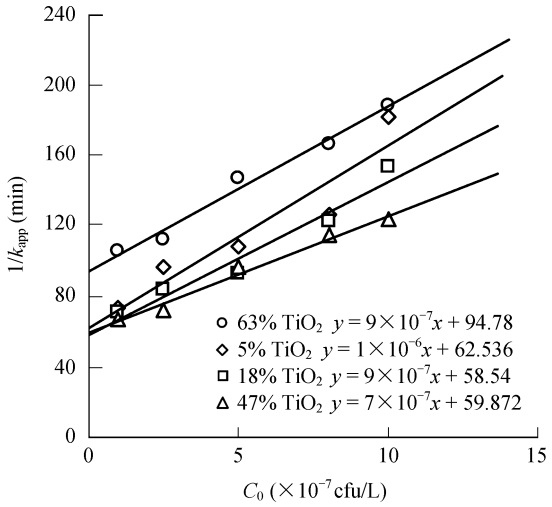

Fig. 3 Relation between $1/k_{app}$ and C_0.

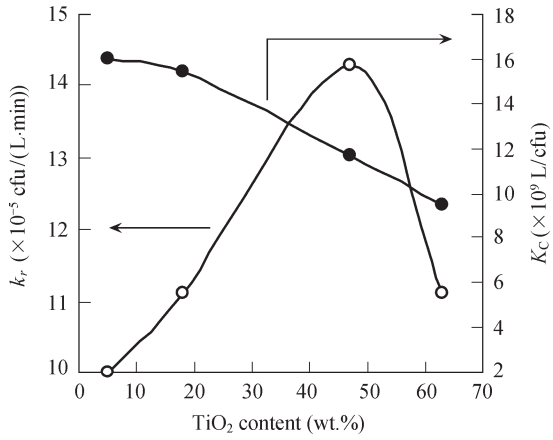

Fig. 4 Rate constant (k_r) of *E. coli* inactivated reaction and the adsorption equilibrium constant (K_C) of *E. coli* as a function of the TiO_2 content in composite catalyst.

ticles. The rate of TiO_2/AC catalysts inactivation depends on the content of TiO_2, k_r being the lower with the smaller TiO_2 content. But absorption strength of substrates is an important factor effecting photoactivity of catalysts. Very high adsorption equilibrium constant for 5% TiO_2 content of catalyst showed a lowered degradation rate presumably due to low TiO_2 content and retardation of easy diffusion of the adsorbed *E. coli* by high absorption strength. The highest rate constant (1.43×10^6 cfu/(L·min)) was observed for the sample, which contained 47% TiO_2 with adsorption equilibrium constants of 1.17×10^{-8} L/cfu. Rate constant appears to increase gradually at a region of TiO_2 content below 47%, which is reasonably supposed to be due to increased amount of TiO_2 particles because of the occurrence of photocatalytic inactivation on TiO_2 particles. After passing a maximum, rate constant decreases with increasing TiO_2 content, which may be due to decreasing amount of adsorbed *E. coli* drastically decreased (low K_C) by reduced surface area. It is obvious that a decrease of the amount of adsorbed substrate resulted in the decrease of the inactivation rate. The inactivation of *E. coli* through hybrid catalysis process by using TiO_2/AC catalysts is mainly determined by TiO_2 particles, but adsorption of *E. coli* cells into AC layer appears to be also important. This may be due to the photon generated by excitation of TiO_2 species can easily contact with *E. coli* and so the process of their recombination could be avoided, giving high yield of photocatalytic activity. In Fig.3, it can be observed that rate constant k_{app} for 5% TiO_2 catalysts with high surface area is higher than that for 63% TiO_2 catalysts. However, rate constant k_r shows inverse result for both. It can be explained by the fact that degradation of *E. coli* occurs on TiO_2 particles.

2.4 Effects of electric power, temperature, and pH on *E. coli* inactivation

To investigate the relation between inactivation rate constant and these parameters including electric power and lamp, temperature, and pH values, a series of experiments was conducted using TiO_2/AC with 47% TiO_2 as catalysts. Light intensity is a major factor in photocatalytic reactions because electron-hole pairs are produced by light energy (Ku and Jung, 2001). The relation between electric power of the fluorescent lamp and its light intensity fits direct ratio when the positions of fluorescent lamp and reactor are invariable in Fig.1, so the electric power of the fluorescent lamp also influences photodegradation of bacteria during photocatalytic process. Table 2 shows that the rate of inactivation increased with increasing electric power of the lamp. For example, the inactivation constant at 400 W was faster than that at 300 and 200 W. This was because higher electric power provides higher flow of photons, which is available not only to directly attack bacteria but also to induce generation of oxidative species on the TiO_2 surface that subsequently attack bacteria, increasing considerably the bacterial inactivation rate. In addition, the selfdefense and autorepair mechanisms of bacteria are insufficient to protect cells at high electric power.

From Table 2, it can be observed that although most of photoreactions are not sensitive to the small variation in the temperature and very few cases have shown an Arrhenius dependence (Herrman *et al*., 1993, Eqling and Lin, 2001), the modifications in the initial temperature in these ranges affect the photocatalytic inactivation of *E. coli* to a significant extent. As the temperature was increased from 25 to 45°C, the rate constant of *E. coli* inactivation was 1.28×10^6 and 1.63×10^6 cfu/(L·min), respectively. This implies that the effect of temperature on *E. coli* inactivation in photocatalytic TiO_2 disinfection is mainly owing to the change in microorganism susceptibility. The relation between temperature and bacteria inactivation is consistent with description by Tang *et al*. (2004).

The pH is an important factor in influencing the photocatalytic process. It was clearly observed that pH 7 is an advantage for the photocatalytic inactivation of *E. coli* (Table 2). The weak acid or alkali is not available for *E. coli* inactivation, it is owing to the fact that the amount of hydroxy absorption and hydroxy produce on TiO_2 is influenced by pH in solution (Chen *et al*., 2001). So pH value affects photocatalytic inactivation process of *E. coli* because high hydroxy content and plentiful *E. coli* cells that are absorbed on TiO_2/AC are available for the photocatalytic inactivation.

2.5 Inactivated mechanism of bacteria

To elucidate the mechanism for photocatalytic inactivation of bacteria cells on TiO_2/AC, the morphology of bacteria cells on TiO_2/AC composites was characterized using SEM with different illumination times as indicated in Fig.5. Before illumination, the surfaces of the cells appeared grainy, smooth, furrowed, crumbled, or dilapidated (Fig.5a). Even after illumination for 1.0 h, no obvious morphological changes were recognized, even though the cells had already lost their viability (Fig.5b). However, the outermost layer that was clearly observed in Fig.5a disappeared after 1.0 h of illumination. In contrast, the outermost layer of the cells on TiO_2/AC before illumination remained intact. Therefore, the disappearance of the outermost layer results from the composites photocatalysis. Furthermore, the observation reflects the change in concentration of the cell wall components and also demonstrates that cells on illuminated TiO_2/AC are decomposed from the outside of the cell. Along with illumination time, bacteria cells lose the smooth and tight surface. As

Table 2 Effects of parameters change on reaction constant k_r

Kinetic constant	Electric power of lamp[a] (W)			Temperature[b] (°C)			pH[c]		
	200	300	400	25	37	45	6	7	8
$k_r \times 10^6$ (cfu/(L·min))	1.43	1.61	1.87	1.28	1.43	1.63	1.26	1.43	1.39

[a] At 37°C and pH 7; [b] at 200 W and pH 7; [c] at 200 W and 37°C.

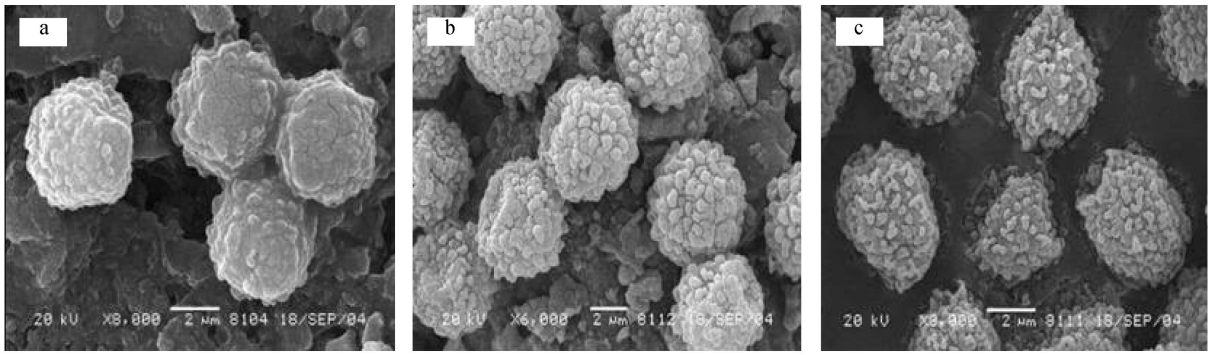

Fig. 5 SEM photographs of bacteria on TiO_2/AC in course of photocatalytic inactivation before inactivation (a), inactivation for 1.0 h (b), and inactivation for 2.0 h (c).

shown in Fig.5c, the outer layer of the spherical-shape cells disappeared completely and the inner membrane dissolved after 2.0 h of illumination, indicating the damage of bacteria cells and starting of decomposition of dead cells.

3 Conclusions

The use of AC adsorbents as a support for TiO_2 is effective in getting high inactivated rates of bacteria in water phase. These merits are summarized as follows: (1) the adsorbent supports make a high concentration environment of bacteria around the loaded TiO_2 by adsorption, and then the rate of photocatalytic inactivation is improved; (2) the bacteria are inactivated on the photocatalyst surfaces and then further decomposed. High inactivation efficiency of composite is available to prevent the repair of cells. The amount of TiO_2 in catalysts may play a significant role on the photoefficiency of the hybrid catalysts. The *E. coli* inactivation process well fits a pseudo-first order kinetic equation. The photocatalytic inactivation processes can be explained in terms of a modified Langmuir-Hinshelwood model for the surface reaction between the bacteria and the oxidizing agent. The values of K_C and k_r were certainly dependent on the TiO_2 coatings. At 47 wt.% TiO_2 coatings with the highest rate constant, K_C and k_r was 1.17×10^{-8} L/cfu and 1.43×10^6 cfu/(L·min), respectively. The electric power of lamp, pH values, and temperature show significant effects on inactivation rate of *E. coli*. The scanning electron microscopy measurements of bacteria cells on illuminated TiO_2/AC showed that the outer layer decomposed first resulting in inactivation of cell, and with further illumination, the cells nearly decomposed. These results suggest that the inactivated reaction is initiated by a partial decomposition of the outer wall, followed by dissolving of inner member, and then it resulted in cell death.

Acknowledgments

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