

Effect of different type of scavengers on the photocatalytic removal of copper and cyanide in the presence of $TiO_2@yeast$ hybrids

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Abstract Effect of different type of organic or inorganic additions (formic acid, AgNO₃, NaCl) on the photocatalytic reduction of copper and photooxidation of cyanide with illuminated TiO₂@yeast was studied in this work together with the impact of solution pH values and contact time. The results indicated that pH values exhibited a great effect on the adsorption and photocatalytic performance of cyanide and copper because the surface charge of the TiO₂@yeast and the existence form of cyanide and copper are highly pH dependent. The optimal adsorption and photo-oxidation of cyanide was observed at pH 2.0 while the best adsorptive and photocatalytic efficiency for copper was achieved at pH 5.0 within the studied range. The addition of formic acid increased the photo-reduction rate of copper and inhibited the photo-oxidation of cyanide. AgNO₃, as electron acceptor, restrained the Cu(II) reduction from 75.0 to 30.5 %, whereas accelerate the photooxidation of cyanide. Besides, the presence of chloride ions retarded the removal efficiency of both cyanide and copper. The first-order kinetic model well described the experimental data. One possible mechanism of the effect of additives on copper and cyanide degradation was discussed.

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1 Introduction

Currently, cyanide species are broadly generated in various industrial activities such as mining, electroplating and metal finishing etc., for its strong complex formation potential. As a result, the wastewater generated from such processes always contain a mixture of cyanide and metal ions such as copper [1]. The presence of complex cyanides in industrial effluent imposes many environmental problems on the public domain on account of their toxicity even at very low concentrations, and must be destroyed or removed from wastewaters prior to discharge. Efficient and cost-effective treatment technologies for removal of cyanide/copper ions are therefore highly desired. Typically, Felix et al. [2] and Lu et al. [3] have suggested an electrochemical process to destroy cyanide and recover copper at the same time. Xie et al. [4] and Law et al. [5] employed the anion-exchange techniques as a selective recovery method of cyanide-metal complexes from cyanide waste streams. In addition, a copper cyanide recovery process using activated carbon has also been proposed [6, 7]. Unfortunately, these processes do suffer from several limitations such as not efficient and cost-effective enough for practical applications. In recent years, semiconductor photocatalysis, especially using TiO₂ as the photo-catalyst, has been employed for cyanide and copper removal [1, 8–10]. It has been proposed that the TiO₂ photo-catalysis can treat the toxic cyanide and heavy metals simultaneously.

As is well known, photocatalytic reactions are initiated by the photogenerated holes (h^+) and electrons (e^-) when the TiO₂ photocatalyst was illuminated. The holes react with the adsorbed water or hydroxyl groups (OH⁻) on the photocatalyst surface, forming the hydroxyl radicals (OH·), which are generally accepted to be responsible for initiating the oxidation pathway [11–13]. On the other hand, the electrons are responsible for initiating photoreduction reactions. The rapid recombination rate of the photogenerated electrons and holes greatly affects the photoreaction rate. Thus, some techniques have been used to overcome the rapid recombination rate including the addition of a hole or electron scavenger to the reaction system. This technique serves to mediate the photogenerated charge carriers away from the TiO₂ surface and to prolong the lifetime of the holes or electrons, giving them sufficient time to initiate reduction and oxidation reactions, respectively [14]. Wang et al. [15] have investigated the effects of various organic additives such as ethanol, citric acid and EDTA on the photoreduction of Cr(VI). They found the type of organic is important in determining the rate of Cr(VI) reduction, with ethanol resulting in the fastest reduction rate. Ibadurrohman et al. [16] found that glycerol plays an important role as an effective sink for the photogenerated holes so that the surface charge recombination can be significantly suppressed and, subsequently, the photocurrent is enhanced. Qi et al. [17] used multi-shelled CeO₂ hollow microspheres as superior photocatalysts for water oxidation with AgNO₃ as the electron scavenger; excellent activity and enhanced stability for O₂ evolution are achieved.

In the previous work, we fabricated the novel $TiO_2@$ yeast microsphere with raspberry-like morphology based on the hydrothermal method. In the present work, as a continual job, the prepared hybrid raspberry-like $TiO_2@$ yeast microspheres were further used as photocatalyst for removal of copper/cyanide in wastewater. The current work aims to investigate the effects of pH value and various scavengers on the photoreduction of copper and photooxidation of cyanide. The scavengers investigated in this study are formic acid, AgNO₃ and NaCl. The kinetic study was also performed and the mechanism of photocatalytic oxidization of cyanide anions and reduction of copper cations was discussed.

2 Materials and methods

2.1 Materials

Yeast powder was purchased from Angel Yeast Co. Titanium tetrachloride (TiCl₄), sulphuric acid (H₂SO₄), sodium hydroxide (NaOH), formic acid(HCOOH), silver nitrate (AgNO₃) and sodium chloride (NaCl) were provided by Xi'an Chemical Agent Corp. All chemicals were analytical grade and used without further purification. Deionized water was used throughout all the experimental procedures.

2.2 Analysis of cyanide and copper

deionized water. Copper ions in solutions were analyzed by Atomic Absorption Spectrophotometer (Aanalyst 800, Perkin Elmer Instrument, Norwalk, CT). Cyanide ions concentration was analyzed by colorimetry followed the pyridine–barbituric acid procedure as described in standard methods [18]. The color was measured by using a UV– visible spectrophotometer (HP-8452A, Germany) at a wavelength of 578 nm. The photoreduction rate (η , %) was calculated from the following equation:

$$\eta = (C_0 - C)/C_0 \times 100\%$$
(1)

where C_0 and C are the concentration of AF aqueous solution before and after irradiation, respectively.

2.3 Photocatalytic experiments

Batch adsorption experiments on $TiO_2@$ yeast were conducted in the dark to reach equilibrium. The pH values of the solutions were adjusted with 0.1 mol/L NaOH and 0.1 mol/L HClO₄, respectively, and measured with a Sartorius PB-10 pH meter.

Photocatalytic experiments were performed as follows: a specific amount of the prepared $TiO_2@$ yeast powders (0.75 g/L) was dispersed in a beaker containing 200 mL of copper and cyanide aqueous solution with a concentration of 10^{-4} mol/L. After pH adjustment, the suspensions were magnetically stirred in the dark for 30 min at room temperature to reach an adsorption–desorption equilibrium. Irradiation was provided by a UV-light lamp placed 7 cm above the beaker. During the irradiation, aliquots of the solution were collected at regular intervals and the solid samples were removed by centrifuging. Then the supernatant was analyzed with respect to the remaining metal ions and cyanide concentration. After each analysis, samples were returned into the reactor immediately.

2.4 Zeta potential

In order to investigate the surface properties of the samples, the ζ potential values of yeast, TiO₂ and TiO₂@yeast suspensions with different pH values were measured by a Brookhaven Zeta Plus zeta potential analyzer.

3 Results and discussion

3.1 Effect of pH on the adsorption of cyanide and copper

In order to investigate the adsorption and selectivity behavior of the TiO_2 @yeast hybrid microspheres for both cyanide and copper, a set of parallel experiments in the dark at different pH values of 2.0, 5.0 and 8.0 were executed. The adsorption behavior was evaluated in terms of a distribution coefficient (K_d) and the adsorption selectivity was assumed by the selectivity coefficient (K_I) . A dynamic equilibrium was established in the aqueous solution according to Eq. (2), thus the distribution coefficient (K_d) can be defined as the ratio of the percentage of pollutants adsorbed onto the adsorbent to those remain in aqueous solution (Eq. (3)). Besides, the selectivity coefficient, K_I , for the binding of a specific metal ion in the presence of competitive species can be obtained according to Eq. (4) [19]:

$$M_{(\text{solution})} + I_{(\text{adsorbent})} \rightarrow I_{(\text{solution})} + M_{(\text{adsorbent})}$$
 (2)

 $K_{\rm d}$ = percentage on the adsorbent

/percentage in aqueous solution

(3)

$$K_{\rm I} = K_{\rm d}(M) / K_{\rm d}(I)$$

= [I]_{solution} · [M]_{adsorbent} / [M]_{solution} · [I]_{adsorbent} (4)

where M represents copper, I stands for cyanide and $K_{\rm I}$ represents the ratio of the value of $K_{\rm d}$ of copper to $K_{\rm d}$ of cyanide in copper/cyanide mixtures. Table 1 summarized values for the distribution coefficient ($K_{\rm d}$) and selectivity coefficient ($K_{\rm I}$) of TiO₂@yeast hybrid microspheres toward copper and cyanide. The adsorption of both cyanide and copper on the TiO₂@yeast hybrid surface reached saturation within nearly 30 min, which agreed basically with the adsorption principle of dead microorganism and nano-TiO₂, and such behavior was also observed in previously research [20–22].

It can be seen from Table 1 that the fraction of cyanide adsorbed by TiO₂@yeast hybrid particles decreased from 61.1 to 26.2 % with the increasing of solution pH values from 2.0 to 8.0. The adsorption of copper on TiO₂@yeast hybrid has a peak value of 55.2 % when pH = 5.0, and lower values at both pH = 2.0 and pH = 8.0. Table 1 also provides a comparison between the selectivity coefficients (K_I) of TiO₂@yeast toward copper and cyanide obtained in equimolar mixtures at different pH values. As can be seen in Table 1, the selectivity coefficient K_I at pH = 2.0 is 4.45, which is almost 4.1 times of that for pH = 5.0 and 5.9 times for pH = 8.0. That means the selectivity behavior of TiO₂@yeast toward copper and cyanide can be modified by simply changing the pH values of reaction system.

The above observation may be attributed to the combined effect of two reasons: one is the surface charge of the $TiO_2@$ yeast hybrid particles, and the other is the existence

form of cyanide at different pH values. In order to investigate the surface charge of the adsorbents, the ζ -potential values of yeast, TiO₂ and TiO₂@yeast hybrid particles suspensions as a function of pH are rendered in Fig. 1. As shown in Fig. 1, the isoelectric point (pI) was approximately 2.4, 5.7 and 4.4 for yeast, TiO₂ and TiO₂@yeast hybrid particles, respectively. Therefore, TiO₂@yeast hybrid particles are positively charged when pH is lower than 4.4. Moreover, the total amount of positive charge decreases gradually with the increasing pH values. When pH is higher than 4.4, the surface of TiO₂@yeast hybrid particles are changed to negatively charged. This could lead to the controllable of electrostatic interactions between the pollutant molecules and the TiO₂@yeast hybrid particles.

In addition, the existence form of copper and cyanide in aqueous solutions are extraordinary complicated for the reason that copper ions can exist in the presence of CN^- to form various Cu–CN complexes in different molar ratio at different pH values. A detailed literature survey had been conducted to have an insight to the copper–cyanide species in aqueous solution of different pH and the reaction equations can be displayed as follows [23, 24]:

$$Cu2+ + 2CN- = Cu(CN)2(unstable)$$
(5)

$$2Cu(CN)_2 = 2CuCN + (CN)_2 \tag{6}$$

$$Cu^{2+} + 2CN^{-} = Cu(CN)_{2}^{-}$$
 (7)



Fig. 1 ζ-potential of yeast, $\rm TiO_2$ and $\rm TiO_2@yeast$ suspensions as a function of pH

Table 1 Distributioncoefficient (K_d) and selectivitycoefficient (k) of cyanide andcopper adsorbed on theTiO2@yeast hybrid composites

рН	Percentage adsorbed (%)		Distribution of	coefficient $K_{\rm d}$	Selectivity coefficient K_{I}
	Cyanide	Copper	Cyanide	Copper	
2.0	61.1	26.0	1.56	0.35	4.45
5.0	57.0	55.2	1.33	1.22	1.08
8.0	26.2	32.5	0.35	0.47	0.75

$$Cu^{+} + 3CN^{-} = Cu(CN)_{3}^{2-}$$
 (8)

$$Cu^{+} + 4CN^{-} = Cu(CN)_{4}^{3-}$$
(9)

Figure 2 shows the existence ions form of cyanide and copper at different pH values at equal CN/Cu(II) molar ratio. It can be seen from Fig. 2 that at equal CN/Cu(II) molar ratio, $Cu(CN)_2^-$ is the only complex species existed. Figure 2 also reveals that at low pH, for example, pH = 2.0, Cu(I) and Cu(II) were the uppermost species, and at the same time, TiO₂@yeast hybrid particles were largely positively charged (Fig. 1). The strong electrostatic repulsive force against Cu(I) and Cu(II) and the electrostatic attraction between CN⁻ and the positively charged TiO₂@yeast hybrid particles lead to a low copper but high cyanide adsorption, which resulted in the highest distribution coefficient (Table 1). When pH = 5.0, the surface of TiO₂@yeast hybrid particles turned into negatively charged and the total amount of negative charge increases gradually with the increasing pH values (Fig. 1). As shown in Fig. 2, the predominant ions species are Cu(I), Cu(II) and Cu(I)-cyano ($Cu(CN)_2^-$). The electrostatic attraction force between positively charged Cu(I), Cu(II) and negatively charged TiO₂@yeast caused a higher copper adsorption and the electrostatic repulsive force against $Cu(CN)_2^-$ can explain the decrease in the adsorption of cyanide well. As depicted in Fig. 2, at pH = 8.0, the $Cu(CN)_2^-$ take the place of Cu(II), i.e. there is about 50 % of Cu(I) and 50 % Cu(CN)₂⁻ in aqueous solution at pH = 8.0 [25]. Intermolecular repulsion between negatively charged $Cu(CN)_2^-$ and TiO₂@yeast hybrid particles resulted in a lower adsorption of cyanide. Thus, it is concluded that the adsorption and selectivity behavior of TiO2@yeast hybrid particles depends to a considerable extent on the pH of the system.



Fig. 2 Copper and cyanide ions species for solution containing cyanide/copper ratios = 1:1 (10^{-4} M) at different pH values

3.2 Effect of pH on the photocatalytic behavior

The pH value of aqueous solution has been recorded to be a critical parameter for chemical reactions, and its affect on the photocatalytic process has been reported quite often [26, 27]. To be specific, some properties of photocatalysts and pollutant molecules, such as the surface charge of photocatalyst, potential of valence and conduction bands and existence species of pollutant molecules, are highly pH dependent [28]. Thus, the photocatalytic removal of copper and cyanide over TiO₂@yeast under different pH conditions was conducted to determine its impact on the photocatalytic efficiency. The pH values of solutions were adjusted to be 2.0, 5.0 and 8.0 respectively before the UV irradiation and not controlled specifically during the photocatalytic reaction.

Figure 3 depicts the results of cyanide (a) and cooper (b) photocatalytic removal efficiency as a function of irradiation time at different solution pH values in the



Fig. 3 Effect of pH on the percent removal of cyanide (**a**) and cooper (**b**) as a function of irradiation time at different solution pH values (photocatalyst = 0.75 g/L, cyanide = copper = 10^{-4} mol/L)

presence of TiO₂@yeast. First of all, it's not difficult to find out from Fig. 3 that the removal efficiency of both cyanide and copper at acidic pH is larger than those of alkaline conditions. This might suggest that an acidic condition was beneficial to the photocatalytic removal of both cyanide and copper over TiO₂@yeast hybrid composite. Besides, for cyanide (Fig. 3a), the optimal pH is 2.0, at which the photocatalytic removal efficiency was more than 90.0 %. With the increase of pH, the photocatalytic elimination was restrained. At pH = 8.0, only about 70.0 % of cyanide was removed. As for copper (Fig. 3b), the maximum photocatalytic removal efficiency (70.2 %) occurred at pH = 5.0, which was nearly twofold of that at alkaline condition (35.4 %).

The interaction between existed pollutant species and TiO₂@yeast plays a significant role in the photocatalytic process. As illustrated in Fig. 1, firstly, the surface of TiO_2 @yeast is positively charged at pH < 4.4 (isoelectric point), but negatively charged when pH > 4.4. Secondly, under different pH conditions, cyanide and copper mixture exist in different form. These two reasons contribute a lot to the adsorption behavior of cyanide and copper onto the TiO₂@yeast particles. The increasing amount of adsorbed cyanide onto the TiO₂@yeastcomposite (Table 1) with an increase in solution pH makes additional cyanide ions available to react with photo-generated holes on the TiO₂ surface and so does the copper [20]. That is why the trend of phtocatalytic efficiency in Fig. 3 is in agreement with the adsorption behavior in Table 1. Furthermore, it is also important to point out that the potentials of both conduction and valence bands of TiO2 follow a Nernstian pH dependence, decreasing 59 mV per pH unit according to Eqs. (10) and (11), and consequently, the ability of electrons and holes to participate in redox processes is determined by the pH of the solution [29].

 $E_{\rm VB} = -3.15 - 0.059 \text{ pH}(\text{anatase at } 25 \,^{\circ}\text{C})$ (10)

$$E_{\rm CB} = -0.05 - 0.059 \text{ pH} \text{ (anatase at 25 °C)}$$
 (11)

The photooxidation of cyanide is favored at more acidic pH, because the potential of the valence band hole shifts to more cathodic potentials with increasing solution pH (Eq. 10), and this enhances the photo oxidation ability of the valence band holes. As depicted in Eq. (11), the potential of the conduction band electrons also shifts to more cathodic potentials with increasing pH. Theoretically, the driving force for Cu(II) reduction by conduction band electrons also increases with increasing pH values. However, from Fig. 3b, we can observe that by increasing the pH from 5.0 to 8.0, the photocatalytic reduction of copper decreases. This surprising phenomenon can be attributed to that the mechanism of the photocatalytic reduction is based on the delivery and receipt of electrons between photo-

excited TiO₂ and copper ions adsorbed onto the TiO₂@yeast particles. Compared with pH = 5.0, fewer copper ions were adsorbed onto the surface of TiO₂@yeast particles when pH = 8.0, i.e. a low substrate concentration was provided to the photaocatalyst. Thus, a bad adsorption behavior may lead to an unsatisfactory photocatalytic performance.

The results above demonstrated that $TiO_2@$ yeast composite catalyst displayed high photocatalytic activity for cyanide and copper, suggesting that the cyanide and copper removal is related to a synergistic effect between the adsorptive ability of yeast and photocatalytic function of TiO_2 . The former one could transfer the existed pollutant ions from aqueous solutions to the active sites of $TiO_2@$ yeast surface by absorption, while the latter one could reduce or oxidize the ions by photocatalytic function. Usually these two procedures take place simultaneously. Many researchers observed that the kinetic data of photocatalytic reduction and degradation of various organics or inorganics over illuminated catalyst based metal oxide fitted the Langmuir–Hinshelwood (L–H) model well [30, 31]:

$$-dC/dt = kKC/(1 + KC)$$
(12)

where *C* is the concentration of the reactant (mol/L), *t* is the illumination time, *k* is the reaction rate constant (min⁻¹), and *K* is the adsorption coefficient of the reactant (L mol⁻¹). When concentration is very low (i.e. KC << 1), Eq. (12) can be simplified to a pseudo-first-order kinetic law [32]:

$$\ln(C_t/C_0) = -k't \tag{13}$$

where C_0 is the initial concentration of the cyanide or copper, C_t is the pollutant concentration at any time *t*, and *k'* is the apparent reaction rate constant, respectively. In order to check whether the reaction rate *k'* accords with the first-order reaction, curves between $\ln(C_t/C_0)$ versus time *t* are plotted in Fig. 4. The regressed pseudo-first-order kinetic constant *k'* and adj.R-square R^2 were tabulated in Table 2.

From Fig. 4a, we could see that a good linear relationship between $\ln(C_t/C_0)$ and t can be observed, revealing that the experimental data of cyanide in this study are in good agreement with Eq. (13). As tabulated in Table 2, the calculated $k'(\min^{-1})$ values of the cyanide at different pH values of 2.0, 5.0 and 8.0 are 12.4×10^{-3} , 8.1×10^{-3} and 6.4×10^{-3} respectively. Obviously, at pH of 2.0, the photocatalytic oxidation of cyanide showed the lowest rate constant k' ($12.4 \times 10^{-3} \min^{-1}$), whereas the rate constant decreased as the pH values increased. In addition, in Fig. 4b and Table 2, the higher rate constant for photocatalytic reduction of copper occurred at lower pH values. Clearly, the pH values of TiO₂@yeast suspensions had a great significant effect on the removal rate of cyanide, and



Fig. 4 First-order kinetics for photocatalytic removal of cyanide (a) and copper (b) at different pH values

Table 2 First-order kinetic constant k' and Adj. R-Square R^2 for removing copper and cyanide at different pH values

pН	Cyanide		Copper		
	k' (min ⁻¹)	R^2	k' (min ⁻¹)	R^2	
2.0	12.4×10^{-3}	0.9010	1.57×10^{-2}	0.5700	
5.0	8.10×10^{-3}	0.9240	1.85×10^{-2}	0.6210	
8.0	6.40×10^{-3}	0.9870	2.40×10^{-3}	0.9230	

the higher pH values both of cyanide and copper achieved lower reaction rate constant, consistent with the previously research of cyanide conducted by Chiang et al. [9] and copper performed by Yeber et al. [33].

3.3 Effect of holes scavenger cyanide and copper removal

Preliminary experiments showed a progressive increase in the amount of cyanide and copper under acidic condition, thus all further experiments were carried out at the pH of



Fig. 5 Effect of formic acid on **a** the photocatalytic removal of cyanide and copper and **b** linear plot of— $\ln(C/C_0)$ versus time

2.0. It is well known that the overall quantum efficiency of photocatalysis is determined by the interfacial electrontransfer rate and the recombination lifetime of the photogenerated electrons and holes [20]. To strengthen the quantum efficiency, the most general way is to trying to delay the recombination of photo-generated holes and electrons. Therefore, filling the valence band holes by the electrons of some kind of reductant may reinforce the photocatalytic efficiency. Formic acid was selected as the holes scavenger in our experiments because, firstly, it is a small molecule, which is easily adsorbed onto the photocatalyst, so that direct oxidation by the hole may occur; secondly, the photo-oxidation products of formic acid are CO_2 and H_2O , which would not lead to environmental issues [34].

Figure 5a illustrates the dramatic effect of formic acid on the photocatalytic removal of cyanide and copper. The figure clearly shows that in the absence of formic acid, the photocatalytic removal rate of cyanide and copper were approximately 69.5 and 79.0 %. With the addition of formic acid, the photocatalytic removal rate of cyanide reduced to 57.0 % while that of copper increased to about 92.0 %. This means the formic acid can accelerate the rate of copper reduction by acting as an efficient holes scavenger during the photocatalytic reaction. However, the photo-oxidiation of cyanide was inhibited because the valence band holes were partially consumed by the formic acid. It should be noted that the absence of formic acid enhanced the selectivity removal of cyanide and copper mixture.

To obtain kinetic information, the experimental results in Fig. 5a were fitted with the pseudo-first-order reaction kinetic equation (Eq. 13). The curves between $\ln(C_t/C_0)$ versus time t are plotted in Fig. 5b. From Fig. 5b, it is obvious that there are two distinct regions (0-20 min and 20-90 min) into which the kinetics would be separated. We could see that a good linear relationship between $\ln(C_t/$ C_0) and t can be observed in both regions, revealing that the experimental data in this study are in good agreement with Eq. (13). The regressed first-order kinetic constant k' and adj. R-square R^2 were summarized in Table 3. As shown in Table 3, the coefficient of linear regression (R^2) was always higher than 90 %. Though both regions follow the first-order kinetics well, the reaction rate decreased after 20 min, which was also in accordance with the trend presented in Fig. 5a.

It can also be seen from Table 3 that the rate constant for copper in the presence of formic acid were 7.092×10^{-2} and $1.493 \times 10^{-2} \text{ min}^{-1}$, which were almost double of those for copper removal in the absence of formic acid. The higher rate constants mean that the addition of formic acid promoted the photo-reduction of cooper by the TiO₂@yeast. Interestingly, the cyanide exhibited the opposite trend that, with the presence of formic acid, the rate constant for cyanide in both stages decreased from 2.84 \times 10^{-2} and 1.28 \times 10^{-2} to 1.363 \times 10^{-2} and 7.41×10^{-3} min⁻¹. This phenomenon proved that formic acid could restrain the removal of cyanide. From observed above, we may conclude that formic acid has accelerating effect on the photocatalytic reduction of copper and inhibitory effect on the photocatalytic oxidation of cyanide in the presence of TiO₂@yeast. Similar results have been reported by Zheng et al. [35] and they found that significantly enhanced by the addition of formic acid, which can act as a holes scavenger and enhance the reduction processes initiated by the conduction band electron.

3.4 Effect of electron acceptor on cyanide and copper removal

AgNO₃, as electron acceptor, was added into the solution in order to enhance the hydroxyl radicals and also to inhibit the electron/hole (e^{-}/h^{+}) pair recombination. As shown in Fig. 6a, the addition of AgNO₃ dramatically restrained the Cu(II) reduction from about 75.0 to 30.0 %. This



Fig. 6 Effect of Ag(I) on **a** the photocatalytic removal of cyanide and copper and **b** linear plot of $-\ln(C/C_0)$ versus time

Table 3 First-order kinetic constant k' and Adj. R-Square R^2 for removing copper and cyanide (formic acid or not)

Constants	Copper (blank)	Copper	Cyanide (blank)	Cyanide
$k_1' (\min^{-1})$	3.44×10^{-2}	7.09×10^{-2}	2.84×10^{-2}	1.36×10^{-2}
R^2	0.9563	0.9968	0.9100	0.9862
$k_{2}' (\min^{-1})$	7.65×10^{-3}	1.49×10^{-2}	1.28×10^{-2}	7.41×10^{-3}
R^2	0.9538	0.9822	0.995	0.9800

phenomenon can be explained by the redox potential (versus NHE) of the Ag(I)/Ag(0) couple (0.799 V), which can compete more favorably with copper ions for electrons. The inhibitory effect of Ag(I) on Cu(II) reduction by the UV/TiO₂@yeast process may also be attributed to catalyst deactivation. Considering that although Ag(I) has been converted to Ag(0) after 90 min of irradiation (in Fig. 6), the rate of Cu(II) reduction was still slow at this stage. To verify this hypothesis, we have filtered the suspension after 180 min of irradiation in order to remove the used catalyst and to replace it with fresh TiO2@yeast hybrid microspheres at 0.75 g/L of the remaining solution. As shown in Fig. 7, after 90 additional minutes of irradiation, the reduction of Cu(II) is almost the same as the one without any additive. It can be concluded that Ag(0) species depositing on the surface of TiO₂@yeast hybrid microspheres after Ag(I) photo-reduction results in the loss of TiO_2 photocatalytic activity. The detrimental effect of silver ions on the photo reduction of copper ions can also be confirmed by the kinetic analysis presented in Fig. 6b and Table 4. As shown in Fig. 6b, the rate of copper reduction decreases dramatically. With the presence of silver ions, the rate constant for copper reduction dropped rapidly at the first regime from 3.44×10^{-2} to 9.30×10^{-3} min⁻¹ and the second regime from 7.65 \times 10⁻³ to 1.50 \times 10⁻³ min⁻¹.

From Fig. 6a, we can also observe that after the pouring of AgNO₃, the amount of cyanide removed by the catalyst was only increased slightly, yet the rate of cyanide oxidation increases significantly (Table 4). The



Fig. 7 Effect of Ag(I) on the photocatalytic reduction of Cu(II)

enhancement of photodegradation rate by the addition of AgNO₃ is attributed to that silver ions act as electron acceptor to reduce the recombination rate of the photogenerated hole-electron pairs. Gupta et al. [27] arrived at similar conclusions to explain the dramatic effect of hydrogen peroxide addition on the initial rate of the photocatalytic decomposition of toxic dye amaranthin on TiO₂/ UV in aqueous suspensions.

3.5 Effect of NaCl on cyanide and copper removal

It is well known that the solubilities of gases in water change with the composition of the aqueous solution, being dependent on the ionic strength of the solution and the chemical nature of the anions and cations involved [8]. This effect is sometimes referred to as the "salting out" effect [36, 37]. In the presence of strong electrolytes, such as NaCl, the solubility of oxygen is lower than in pure water, then affecting the composition of groups in solution. Thus, the photocatalytic process investigated the effect of the addition of chloride ions on the photocatalytic removal of cyanide and copper was conducted.

Figure 8a gives the effect of NaCl on the photocatalytic removal of copper and cyanide in the presence of TiO₂@yeast. The results showed that NaCl inhibited the removal of copper and cyanide at the same time. The degradation rate of cyanide without additives is 79 % after irradiation for 90 min, while 71.5 % after the addition of chloride. The inhibition of photocatalytic activity can be explained by the scavenging of hydrogen radicals by chloride ions as well as the competitive adsorption. Specifically, choride ions consume ·OH to form ·Cl and the existence of Cl⁻ in solution may result in the blocking of active surface sites on TiO₂@yeast catalyst. Pertinent literatures also reported a detrimental effect of chloride ions on the photodegradation rate of organic molecules. Augugliaro et al. [8] found that the detrimental effect of chloride ions on cyanide photooxidation rate is not only determined by a competition mechanism of chloride ions with cyanide ions or oxygen molecules for adsorption on active sites, but also affect the photoreaction rate by lowering the concentration of dissolved oxygen to values for which oxygen may become a rate limiting reactant. Boonstra and Mutsaers [38] also reported that the presence of chloride ions in the solution decreases the oxygen photo adsorption as chloride ions decrease the hydroxyl group content of TiO₂

Table 4 First-order kinetic constant k' and Adi, R-Square	Additive	Copper				Cyanide	
R^2 for removing copper and even ide (A cNO, or pot)		$k_1' (\min^{-1})$	R^2	$k_{2}' (\min^{-1})$	R^2	k' (min ⁻¹)	R^2
cyanide (AgnO ₃ of not)	No additive AgNO ₃	3.44×10^{-2} 9.30×10^{-3}	0.9563 0.9727	7.65×10^{-3} 1.50×10^{-3}	0.9538 0.9710	1.53×10^{-2} 7.08×10^{-2}	0.9466 0.9660

powders. We can conclude from above that the addition of chloride ions decrease the concentration of oxidizing agent which can oxidize the cyanide into small units like carbon dioxide and water, thereby restrained the phtocatalytic removal of cyanide.

It can also be noticed from the data reported in Fig. 8a that, with the addition of chloride, the photo-reduction rate of copper was retarded from 69.5 to 31.5 %. The detrimental effect of chloride on photocatalytic reduction of copper may also be due to the less active sites of TiO₂@yeast catalyst available. The existence of Cl⁻ in solution may result in the blocking of active surface sites



Fig. 8 Effect of NaCl on **a** the photocatalytic removal of cyanide and copper and **b** linear plot of— $\ln(C/C_0)$ versus time

Table 5 First-order kinetic constant k' and Adj. R-Square R^2 for removing copper and cyanide (NaCl or not)

on TiO₂@yeast, since the positively charged TiO₂ surface at pH 2.0 contributes to Cl⁻ adsorption [20]. On the other hand, the lowered dissolved oxygen resulted by the chloride ions lead to a less-trapping for electrons, thus promote the recombination of holes and electrons.

For the experiments performed with the aim of investigating the influence of chloride ions on the cyanide and copper photodegradation, Fig. 8b exhibited the kinetic fit of the experimental data by first-order kinetic model. Table 5 tabulated the main parameters of constant rate and coefficients. As seen, first-order kinetics fit data reasonably well; for instance, the regression coefficient of the linear fitting, R^2 , is over 0.9 for all the runs. For the runs for photocatalytic reduction of copper by TiO₂@yeast (with or without addition of NaCl), two regimes appear to exist with different kinetic constants: a faster one at the beginning of the reaction followed by a slower one. For the run without the addition of NaCl, k_1' is $3.435 \times 10^{-2} \text{ min}^{-1}$ over the first 20 min and decreases to $7.65 \times 10^{-3} \text{ min}^{-1}$ by an order of magnitude thereafter. As the reaction proceeds, fewer copper ions become available to react with TiO₂@yeast (concentration gradients become smaller), while the active sites on the catalyst are also consumed to reactions with refractory degradation intermediates; both would justify slower kinetics at prolonged times [31]. Figure 8b also shows representative data for photo-reduction of cooper in the presence of NaCl. The existence of two kinetic regimes is, in this case, less pronounced due to the adverse (i.e. decrease of dissolved oxygen in the photocatalytic reaction system) role of NaCl. As shown in Table 5, the rate constant for photo-reduction of copper in the presence of NaCl showed a decline of approximately 4.0 times compared with that of copper reduction at the absence of NaCl. The detrimental effect of NaCl on the photocatalytic reduction of copper by TiO₂@yeast can also be affirmed by this change. It can also be observed from Fig. 8(b) that the data for cyanide photo oxidation by TiO₂@yeast can be well represented over the entire time region considering first order kinetics. NaCl had a relatively slight negative effect on the photo oxidation of cyanide compared with the photo reduction of copper in the presence of TiO₂@yeast. From the observations above, we may conclude that chloride ions affect the photoaction rate of copper and cyanide by lowering the concentration of dissolved oxygen to values for which oxygen may become a rate limiting reactant.

Additive	Copper				Cyanide		
	$k_{1}' (\min^{-1})$	R^2	$k_{2}' (\min^{-1})$	R^2	k' (min ⁻¹)	R^2	
No additive	3.44×10^{-2}	0.9563	7.65×10^{-3}	0.9538	1.53×10^{-2}	0.9466	
NaCl	9.01×10^{-3}	0.9024	3.81×10^{-3}	0.9460	1.25×10^{-2}	0.9474	

3.6 Mechanism

The removal of copper and cyanide by the raspberry-like $TiO_2@$ yeast could be attributed to the combined bio-adsorption processes of yeast and the photo-catalysis processes of TiO_2 nanoparticles, including the photo-oxidation and photo-reduction processes. A model for these processes can be assumed in an integrated bioadsorptionphotocatalysis process, as shown in Fig. 9.

In Fig. 9, pollutant molecules, including copper and cyanide, are firstly absorbed at the surface of TiO₂@yeast hybrid composite and then be oxidized and reduced into non-toxic molecules. During the period of bio-adsorption, it is obvious that the surface charges of TiO₂@yeast adsorbent and pollution molecules make a great difference on intermolecular forces. Moreover, the photocatalytic processes would contribute to the removal of copper ion and CN⁻ to a higher degree since the TiO₂ nanoparticles attached on the surface of yeast acted as both a reductant and oxidizing agent. Specifically, the irradiation of TiO₂ particles on the yeast with photons of energy (hv) equal to or higher than those of band gap results in the excitation of electrons from the valence band (vb) to the conduction band (cb) of the particle, which can produce the electrons (e^{-}) in the conduction band and the holes (h^{+}) at the valence band edge of the TiO_2 (Eq 14) [39]. Without any



Fig. 9 Schematic of the photocatalytic processes that influence cyanide and copper photocatalytic reaction: A without additive, B HCOOH, C AgNO₃ and D NaCl

additive electron acceptor or hole scavengers, photooxidation of H₂O to \cdot OH (Eq 15) and H⁺ (reaction A) is the major hole-scavenging reaction in the system, and electron scavenging by the incipient O₂ is the corresponding reaction that provides O₂.⁻ (Eq 16):

$$\operatorname{TiO}_2 + hv \to \operatorname{TiO}_2(e^-) + \operatorname{TiO}_2(h^+)$$
(14)

$$H_2O + h^+ \to \cdot OH + H^+ \tag{15}$$

$$O_2 + e^- \to O_2^{--} \tag{16}$$

The photo-generated electrons (e⁻) and superoxide species $(O_2 \cdot \overline{})$ will reduce the Cu(II) to Cu(I), and probably eventually to Cu(0) [40]:

$$\mathrm{Cu}^{2+} + \mathrm{e}^{-} \to \mathrm{Cu}^{+} \tag{17}$$

$$Cu^+ + e^- \to Cu^0 \tag{18}$$

$$Cu^{2+} + O_2 \cdot^- \to Cu^+ + O_2$$
 (19)

$$Cu^{+} + O_2 \cdot - +2H^{+} \to Cu^{0} + O_2$$
 (20)

At the same time, the photo-generated holes (h^+) will oxidize the CN⁻ to CNO⁻, and finally to free CO₃⁻ and NO₃⁻. The photo-catalysis course was described as the following reaction formula [41, 42]:

$$CN^{-} + 2h^{+} + 2OH^{-} \rightarrow CNO^{-} + H_2O$$

$$\tag{21}$$

$$CNO^{-} + 4O_2 + 2OH^{-} + 3H_2O \rightarrow CO_3^{2-} + NO_3^{-} + 4H_2O_2$$
(22)

In such a way, the photo-oxidation processes of CN^- in conjunction with the photo-reduction processes of Cu(II) have been regulated to occur at the same time through using bi-functional TiO₂@yeast hybrid microspheres.

The addition of formic acid can act as an efficient electron donor during the reaction B in Fig. 9. Formic acid accelerated the photocatalytic reduction efficiency of copper by filing the valence band holes with its own electrons (Eq. 23), i.e. prolonging the recombination lifetime of electrons and holes as follows [35]:

$$2\text{HCOO}^- + 2h^+ \rightarrow 2\text{CO}_2 + 2\text{H}^+ \tag{23}$$

Our experiments also confirmed that using an electron acceptor such as $AgNO_3$ is an essential condition to initiate the photocatalytic oxidation reaction of cyanide (reaction C). After pouring $AgNO_3$ into the reaction system, electrons were consumed by silver ions rather than the holes, causing an important reduction of the recombination and thus promoting the photo oxidation of cyanide [43]:

$$Ag^+ + e^- \rightarrow Ag^0$$
 (24)

As is known, the holes can either recombine, releasing heat, or move to the surface of the semiconductor where they can react with adsorbed hydroxyl groups or water molecules to form reactive hydroxyl radicals [27]. It is worth note that the acceptor, typically dissolved oxygen, plays a key role in the reaction by removing the excited electrons from the system (Eq. 16). However, the presence of NaCl lowered the concentration of dissolved oxygen to values which oxygen may become a rate limiting reactant because of the "salting out" effect (Eq. 16). And on the other, the inhibition of Cl^- for photocatalytic removal of cyanide and copper can also be explained by the scavenging of hydrogen radicals and holes by chloride ions and thereby decrease the photocatalytic efficiency (reaction D) [44]:

$$\mathrm{Cl}^- + \mathrm{h}^+ \to \mathrm{Cl}$$
 (25)

$$\cdot OH + Cl^- \to Cl + OH^- \tag{26}$$

In brief, the removal for copper and cyanide via the synthesized $TiO_2@$ yeast hybrid composites should be owed to the synergic functions from the bio-adsorption of yeast and photo-catalysis of TiO_2 nanoparticles. And the addition of various addictives offers a high potential as a new technology processes for copper/cyanide wastewater remediation.

4 Conclusions

Based on the results obtained in this study, the following conclusions can be shown. The adsorption and photocatalytic behavior of TiO₂@yeast hybrid particles for cyanide and copper ions depends to a considerable extent on the pH of the system. Specifically, the optimal pH for photo oxidation of cyanide was 2.0, at which the photocatalytic removal efficiency was more than 90 %. As for copper, the maximum photocatalytic removal efficiency (70 %) occurred at pH = 5.0. The addition of formic acid as an organic holes scavenger increases the photo-reduction rate of copper and inhibited the photo-oxidation of cyanide. AgNO₃, as electron acceptor, restrained the Cu(II) reduction from 75.0 to 30.5 %, whereas accelerate the photo-oxidation of cyanide. Besides, the presence of chloride ions retarded the removal efficiency of both cyanide and copper. The firstorder kinetic model describes the photo-reactivity results. A model for such process can be assumed in two-step reaction as follows: adsorption of copper/cyanide complexes at TiO₂ surface, followed by oxidation of CN⁻ and the reduction of copper from the solution. One possible mechanism of the effects of additives on copper and cyanide degradation were discussed. This paper may be useful for further research and practical applications of the novel TiO₂@yeast composite in cyanide/copper wastewater treatment.

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