The method of general heat treatment of waste water from metal manufacture based on photocatalysis

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Abstract: Photocatalytic treatment of emulsified waste liquid after pre-treatment is carried out, using TiO_2 as catalyst. The influence of crystal structure, particle size, amount of the catalyst and initial pH value on the removal ratio of the chemical oxygen demand (COD) is studied in this essay. The results show that in the conditions that 0.5% quality point, P25-1 photocatalyst, 6.5 pH value and 90 min processing, the treatment effect is most ideal.

Keywords: heat treatment cleaning; emulsion; photocatalysis; post-treatment.

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1 Introduction

For their superior performances of lubricating and cleaning, emulsions have been used widely in modern industry. Meanwhile, with in-depth study of emulsions, the performance and stability have been getting higher and higher. At present, large quantities of effluents are discharged directly in the heat treatment industry. As a result, draining of these effluents not only pollutes the environment but also threatens people's lives.

The chemical oxygen demand (COD) value of the waste liquid is still high after the pre-treatment of heat treatment of emulsified oily waste liquid using the method of coagulation and electrolysis (Qiu et al., 2006). COD is one of the most important indexes to measure degree of the relative pollution of water by organic matter. In order to reduce the COD value, organic pollutants should be degraded as much as possible. Therefore, it is necessary to do follow-up treatment. Commonly used follow-up treatment methods are biochemical, adsorption and advanced oxidation method. Because of its strong oxidation and easily-controlled operating conditions, photocatalytic oxidation is one of the most studied advanced oxidation technologies (Qiu et al., 2005). Under the irradiation of

ultraviolet light, the special electronic structure of TiO_2 can decompose organic pollutants into CO_2 and H_2O and also reduce and oxidise inorganic matter into harmless products (Threrujirapapong et al., 2017; He et al., 2016; Talwar et al., 2018). In view of the high COD value of effluent in pre-treated wastewater, this paper discusses the feasibility of photocatalytic treatment for subsequent treatment and explores the influence of the photocatalytic method.

2 Materials and methods

2.1 Water quality of pre-treated waste water

The test water was obtained from several representative domestic heat treatment enterprises and pre-treated by coagulation and electrolysis. The COD values of waste liquid after treatment are listed in Table 1.

Table 1 COD value of waste liquid after pre-treatment

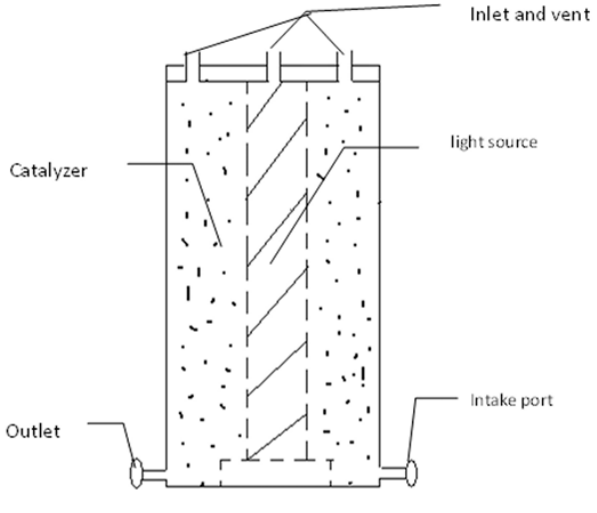
Specific scheme	*COD value / mg·L^{-1}*
Coagulation method	4,535.33
Electrolytic method	854.34

As can be seen from Table 1, after the pre-treatment of the waste liquid by coagulation and electrolysis, the COD value cannot meet the required emission requirements (200 mg L^{-1} according to GB8978-1996).

2.2 Apparatus and method for photocatalytic process

The photocatalytic reaction unit used in the test is shown in Figure 1.

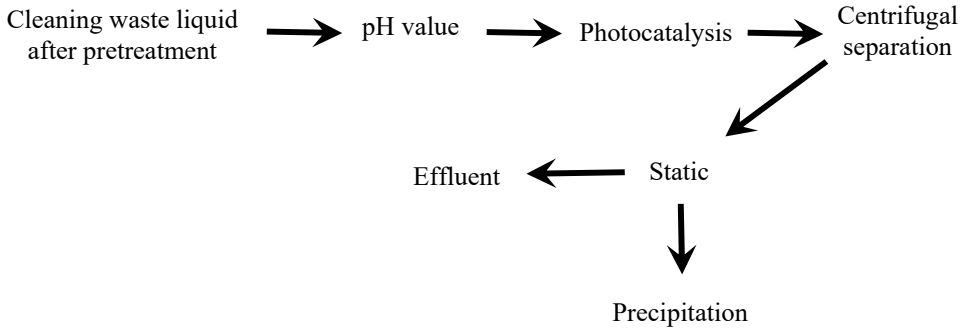
Figure 1 Photocatalytic reaction unit



The device is mainly composed of two parts, the reactor and the breather. The optical reactor is glassware, with a quartz tube and a 300 W tube type ultraviolet high pressure mercury lamp (Ya Ming bulb factory). The aeration device ensures that the TiO_2 powder is uniformly dispersed in the waste liquid, which is beneficial to reduce the recombination of electrons and holes and increase the concentration of OH.

Firstly, taking 10 L pre-treatment of the representative heat treatment of washing wastewater, adjusting pH value after the photocatalytic experiment, the catalyst with mass fraction of 0.75%, centrifugal separation after the reaction is finished, then put it aside for a period of time, and then remove the bottom sediment, the final analysis by the middle water stage. The design of the test flow is shown in Figure 2.

Figure 2 Flow chart of photocatalytic test



2.3 Test method

Potassium dichromate method was used to measure COD; the suspended matter in water was measured by weight method; colorimetric method was used to measure the pH value of platinum and cobalt; the pH value was measured by glass electrode method.

3 Results and discussions

3.1 Discussion of photocatalytic methods

Among various available semiconductor catalysts, TiO_2 is considered to be the most effective (Parent, 1996). Figure 3 shows the mechanism of photocatalytic reaction with TiO_2 as catalyst.

The circle in the diagram represents a TiO_2 molecule. TiO_2 has a deeper outer valence band, and because of the special electronic structure, when TiO_2 is greater than that of its energy band gap energy and is less than or equal to the width of band gap (Eg) light irradiation, the valence band (VB) on the electronic absorption of light energy, will jump and move to the conduction band gap (CB), the formation of electronic high activity (e–). At the same time, a positively charged hole (h+) is generated on the valence band. This hole h+ can interact with the adsorbed water on the surface of TiO_2 particles to capture its electrons and produce hydroxyl radicals (OH) with very high oxidation activity. OH can react with many organic compounds and oxidise them to degrade. The highly active

electrons in the conduction band can react with the dissolved oxygen in water to produce O_2^- OH (Xu, 2002) and further react with H+ in water. The reaction mechanism is expressed by formulas as follows:

$$TiO_2 + h\gamma \rightarrow h^+ + e^-$$

$$h^+ + H_2O \rightarrow OH + H^+$$

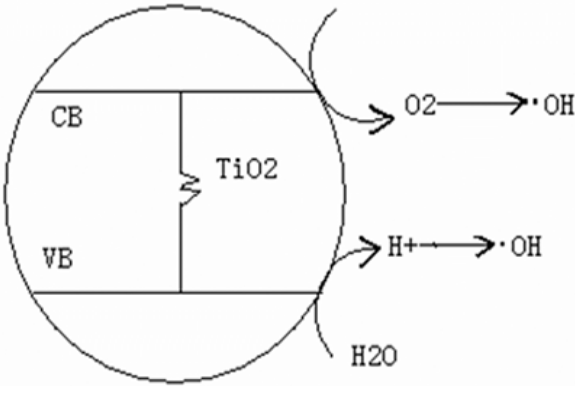
$$e^- + O_2 \rightarrow O_2^-$$

$$O_2^- + H^+ \rightarrow HO_2$$

$$2HO_2 \rightarrow O_2 + H_2O_2$$

$$H_2O_2 + O_2^- \rightarrow OH + OH^- + O_2.$$

Figure 3 Schematic diagram of photocatalytic reaction mechanism



As the band gap of TiO_2 is 3.0~3.2 eV, equal to the energy of 388 nm photons, the electrons on the valence band will be induced to the conduction band by the light of photon irradiation whose wavelength is less than or equal to 388 nm. The result is a photocatalytic oxidation (Ji, 2002).

The waste water mainly include organic oils, surfactants, emulsion stabilisers, extreme pressure additives, anti-mildew additives, rust preventive oils and defoamers, etc. Photocatalytic degradation of organic matter is essentially a free radical reaction. The reaction mechanism mainly includes addition reactions on unsaturated double bonds and triple bonds, hydrogen substitution and electron transfer. The purpose of degradation is achieved by reacting the generated oxygen free radicals with the contaminants in the water to generate water, carbon dioxide, nitrogen, etc.

Because of the difference in hydrolysis degree, calcination temperature and time control, the crystal structure and particle size of nanometre TiO_2 photocatalyst also differ from each other. The specific conditions are listed in Table 2. The nanometre TiO_2 powders used in the study were all supplied by Shanghai fine chemical materials research institute.

Table 2 Physical data of some nanoscale TiO_2 photocatalysts

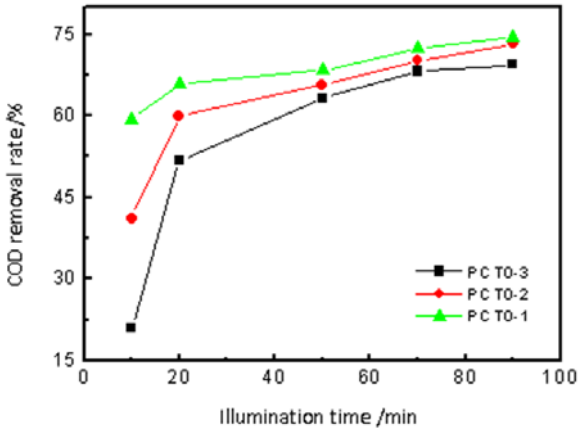
Catalyst number	*Crystal structure*	*Average particle size/nm*
PCT0-1	Anatase (> 90%) rutile	180
PCT0-2	Anatase (60%) rutile (40%)	180
PCT0-3	Anatase (20%) rutile (80%)	180
P25-1	Anatase	25
P25-2	Anatase	6.8

As can be seen from Table 2, PCT0-1, PCT0-2 and PCT0-3 belong to three kinds of catalysts with the same particle size but different crystal structure. PCT0-1, P25-1 and P25-2 belong to three kinds of catalysts with the same crystal structure and different particle sizes. Taking the nanometre TiO_2 photocatalyst listed in the table as the object, the influence of the crystal structure, particle size, dosage and initial pH value of the catalyst on the removal ratio of COD was explored and optimised, and the optimum parameters of the test room were obtained.

3.2 Effect of crystal structure of catalyst on removal ratio of COD

Adjusting the pH value of water sample to 7, adding the catalyst with mass fraction of 0.5% respectively, and testing the removal activity of PCT0-1, PCT0-2 and PCT0-3 catalyst in the photocatalytic reaction of COD, the test results are shown in Figure 4.

Figure 4 Effect of crystal structure of catalyst on COD removal ratio (see online version for colours)



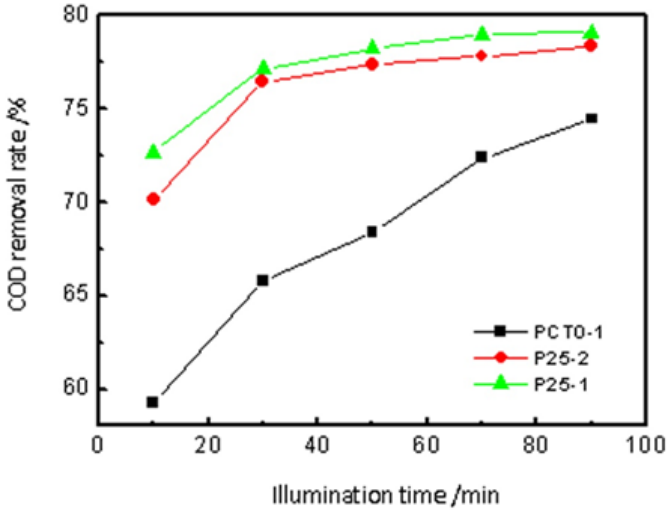
As can be seen from Figure 4, three catalysts with the same particle size but different crystal structure are active for the removal of COD. In the same reaction time, the PCT0-1 catalyst has the best reaction, followed by PCT0-2 and PCT0-3 minimum. This is because, under the same particle size, the larger the proportion of anatase crystalline structure in the photocatalyst, the higher the removal activity of COD. In essence, the photocatalytic activity of a single anatase phase and rutile phase is poor, and the mixed crystal catalytic activity is higher than that (Bickley et al., 1991). This is mainly due to the coexistence of anatase TiO_2 and rutile TiO_2 in a certain proportion, which can

effectively separate the photogenerated hole and electron and reduce the probability of recombination. The photocatalytic activity of anatase TiO_2 is higher than rutile TiO_2 (Tanaka et al., 1991). Therefore, when the two crystal types coexist in a certain proportion, the anatase TiO_2 has better activity.

3.3 Effect of particle size of catalyst on COD removal ratio

Nanoscale catalyst has strong dispersion ability and high photocatalytic efficiency. But with the size difference, the catalytic activity also has some differences. The pH value of the water sample was adjusted to 7, and the catalyst with the mass fraction of 0.5% was added to test the removal of COD in water samples by photocatalysis of PCT0-1, P25-1 and P25-2 catalysts. Figure 5 illustrates the results of experiments using three catalysts with the same crystal size and different particle sizes.

Figure 5 Effect of catalyst particle size on COD removal ratio (see online version for colours)

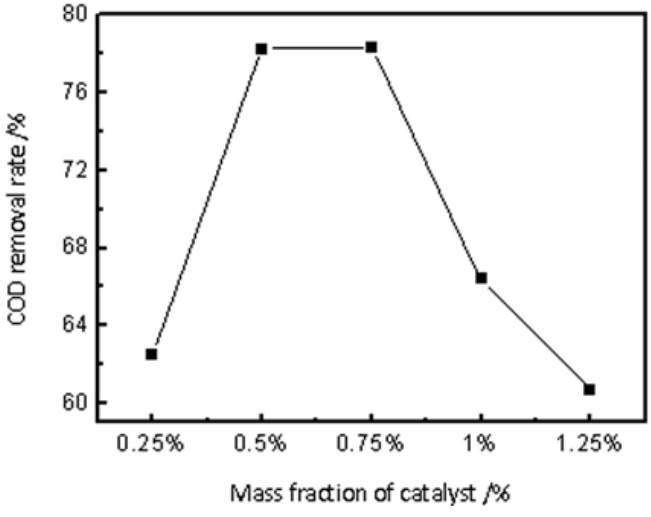


As can be seen from Figure 5, the smaller the particle size is, the better the removal efficiency of COD in the range of a certain catalyst particle size. In the same reaction time, the P25-1 catalyst has the best reaction, followed by P25-2 and PCT0-1 minimum. This is because the photogenerated charge carriers through simple diffusion from particle internal migration to the particle surface and the electron donor or acceptor reduction or oxidation reaction, therefore, in a certain range, the smaller the particle size, electron and hole recombination probability is small, the better effect of separation of charge, thus the activity of the catalyst is higher. However, if the particle size is too small, there are too many particles in the unit volume solution, which will affect the transmission of light, reduce the photocatalytic efficiency, and lead to poor removal effect. Therefore, the P25-1 photocatalyst is selected.

3.4 Effect of catalyst dosage on removal ratio of COD

In the process of photocatalytic treatment, the catalyst particles are dispersed evenly in water samples by ventilation. Therefore, the number of catalyst particles in unit volume will also affect the removal ratio of COD. The pH value of the water sample was adjusted to 7. The P25-1 catalyst with mass fraction of 0.25%, 0.5%, 0.75%, 1% and 1.25%, respectively, was sampled at the time of 50 min illumination, and the results are shown in Figure 6.

Figure 6 Effect of catalyst dosage on COD removal ratio

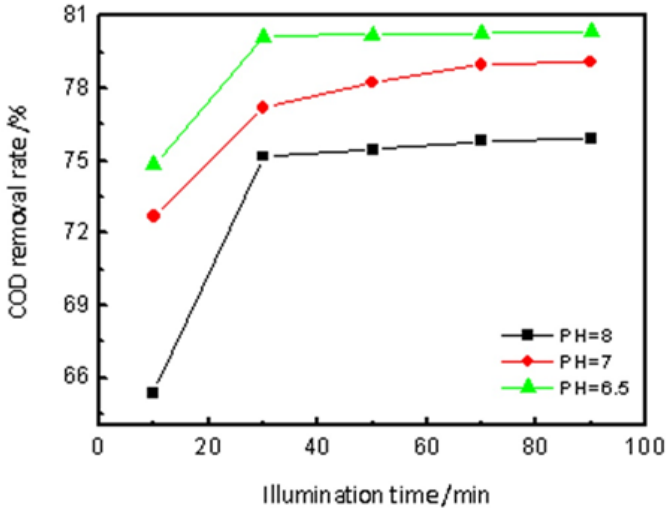


As can be seen from Figure 6, when the amount of catalyst is too small or too great, the removal ratio of COD is low. When the mass fraction is 0.25%, 1% and 1.25%, the removal ratio is not high, while when the mass fraction is 0.5% and 0.75%, the treatment effect is almost the same. This is because the lower the unit volume of the catalyst particles in solution, the less water contact between the organic compounds and the catalyst, which results in worse reaction effect. On the contrary, when the catalyst particles increase, the light transmittance in the solution is affected and the light effect is weakened which also results in worse degradation effect. Therefore, the amount of catalyst is selected with a mass fraction of 0.5%.

3.5 Effect of initial pH of wastewater on removal ratio of COD

Experiments were carried out with a 0.5% (mass fraction) P25-1 catalyst added to a certain amount of typical heat treatment cleaning solution, respectively, with a pH of 6.5, 7, and 8, and the results are shown in Figure 7.

Figure 7 Effect of initial pH of wastewater on COD removal ratio (see online version for colours)



As can be seen from Figure 7, under light conditions, the smaller the pH value, the higher the removal ratio of COD, i.e., when the pH is 6.5, the removal ratio is higher than at the pH values of 7 and 8. Under strong acid conditions, photocatalytic reactions are particularly rapid. According to the literature, the isoelectric point (PZC) of TiO_2 in water is about pH = 6 (Wei et al., 1998; Wang and Hu, 1995). When the pH > PZC in solution, the surface of organic substances in aqueous solution has a negative charge, and when pH < PZC, the surface of organic substances has a positive charge. With the decrease of pH in the solution, the positive charge of the organic surface is enhanced. The adsorption of organic compounds on the photocatalyst surface is a prerequisite for their efficient degradation. Therefore, with the decrease of pH value, the positive surface of organic surface increases, while oil, water and emulsification layer are negatively charged, which results in more TiO_2 becoming adsorbed on oil-water emulsion film, which makes the ratio of photocatalytic degradation increase. Therefore, we selected a pH value of 6.5.

The above optimisation can be achieved by photocatalytic method, and the optimum process for the typical heat treatment cleaning of waste liquid is P25-1 photocatalyst with a mass fraction of 0.5%, with a pH value of 6.5. The process of photocatalytic treatment of water samples within 90 min was carried out by using this process, and the removal ratio of COD was 80.33%. The optimum process after electrolysis and photocatalysis is used to treat the waste liquid, and the relative indexes are listed in Table 3.

Table 3 relative indexes of waste liquid after optimised treatment

Test method	*COD value/mg·L^{-1}*	*Suspended solids/mg·L^{-1}*	*Chroma/times*	*pH value*
Electrolytic method	854.34	2	5	8.1
Photocatalytic method	168.05	2	3	7.3
GB8978-1996	200	250	100	6-9

As can be seen from Table 3, under laboratory conditions, after electrolysis pre-treatment and post-treatment photocatalytic representative heat treatment of washing wastewater, the effluent quality can meet the GB8978-1996 'integrated wastewater discharge standard' two level emission standards. This shows that photocatalytic treatment of such waste liquids has achieved good results.

4 Conclusions

Using TiO_2 as the catalyst of photocatalytic oxidation processing, the results show that with the same catalyst particle size, the higher the anatase crystal structure in the catalyst, the more obvious the degree of decrease of COD. Under the same crystal type, in a certain range of catalyst particle size, the smaller the catalyst particle size, the better the photocatalytic treatment effect. That will lead to worse processing results if the size is too small. Therefore, appropriate dosage of catalyst should be used and either excessive or insufficient dosage could weaken the effect of the initial pH value of wastewater.

When the initial pH > the isoelectric point of TiO_2 in water, the smaller the pH, the higher the removal ratio of COD. With P25-1 photocatalyst with a mass fraction of 0.5%, with a pH value of 6.5, after 90 min processing time, the removal ratio of COD was 80.33%.

By using the ideal processing method explored in this essay, the relevant indicators of COD, suspended solids, chroma and pH value all could meet the second discharge standard in the GB8978-1996 'integrated wastewater discharge standard' after photocatalytic treatment of emulsified waste liquid after pre-treatment.

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