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Water-soluble TiO_2 Nanoparticles for Removal of Cr(VI) from Water

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Abstract

In this work, we prepared water-soluble TiO2 Nan particles, and applied to removal of Cr(VI) from Water. Research Findings, preparation of the water-soluble TiO_2 Nan particles under different lactic acid concentration, there was a big difference between dispersion and catalytic activity. In addition, the pH of system on Cr (VI) photo catalytic removal has a crucial impact. Under the condition of pH = 3, it can make the 40 mg/L of Cr (VI) removal efficiency reached 100%.

Keywords

Water-soluble TiO_2, pH, Cr(VI), photo catalysis.

1. Introduction

The heavy metal chromium (Cr) is widely applied in the fields of electroplating, alloy, leather, dyeing and light and textile industries[1,2]. There is a large amount of untreated chrome-contained wastewater discharged directly into the waterways which pollutes the environment, even threats the health of biology. The main existence forms of Cr are Cr (VI) and Cr (III) in nature, and the Cr (VI) in the water mainly exists in the form of anion, such as CrO_4^{2-},$Cr_2O_7^{2-}$,$HCrO_4^-$ and so on. Chromium salt has high solubility and strong liquidity[3]. In addition, Cr (VI)'s toxicity does harm to the human liver, kidneys and lungs. Meanwhile, It is generally recognized as one of the prime culprits that contribute to malformation and cancer [4,5]. Moreover, chromium compounds are hazardous to crops and aquatic lives. Cr(III) is a vital nutrient for humans that helps the body utilize sugar, protein and fat[6] The World Health Organization recommends that Cr (VI) content in drinking water should be controlled in 0.05 mg L^{-1} [7]. Therefore, finding the treatment of Cr (VI)-contained wastewater is one of the urgent tasks to solve the pollution problems.

Recently, there are mainly three ways to remove the Cr (VI) in the water, including co precipitation, ion exchange, membrane separation, adsorption, biological adsorption and electrochemical reduction. Whereas, using these methods to deal with Cr (VI) wastewater, not only expensive, but also the effect is poor[8-10]. Moreover, it's easy to cause secondary pollution as well. Therefore, the methods are applied only in certain cases, and are restricted by the technology and economy[11].

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Using photo catalysis to restore Cr (VI) into Cr (III) which has less toxicity is a new method. Photo catalytic reduction has some advantages of high efficiency, low energy consumption, clean and no secondary pollution. It's considered to be a promising technology[12]. In the 1979s, Yoneyama et. al [13] did a research that without other electron donors, Cr (VI) can be reduced from the surface of TiO_2 to Cr (III) by the light stimuli. Afterwards, The researchers were studied of the reaction mechanism that photo catalytic reduction of Cr (VI) from water on the surface of TiO_2[14,15], They found that Cr (VI) can get electronic from light excitation of the surface of the TiO_2, and reduction of Cr (VI) to Cr (III) in the water. However, From a practical point of view, the photo catalytic activity of TiO_2 is not up to par. To this end, the posterity continuously improves TiO_2-based catalysts in order to get the photo catalyst which conforms to the practical standard. For instance, Fan et. al [16] synthesized TiO_2 Nan particle adopts the method of sol-gel, and deposition Pt on the surface of the TiO_2. In addition, Luo et. al[17] adopted deposition method to manufacture Au/TiO2 heterojunction nanotubes; Chen et. al[18] has found that using chemical deposition method can generate Pd/ TNT (TiO_2 nanotubes). These modification TiO_2 showed a high photo catalytic activity in the photo catalytic reduction of Cr (VI) from water. Nonetheless, these TiO_2-based catalyst dispersions is limited in water. Thus, the photo catalytic reaction is conducted in the catalyst slurry. Therefore, light penetration effect is not effective in the suspension, and it leads to the improvement of the TiO_2-based catalysts' light that it absorbed. If it can use water-soluble TiO_2 Nan particles as photo catalyst to build a similar homogeneous system of photo catalytic system, it will improved the light absorption efficiency of TiO_2-based catalysts in some extent. After that, the efficiency of photo catalytic reduction of Cr (VI) will be improved further.

In this research, we have synthesized water soluble TiO_2 by hydrothermal method, and potassium dichromate is considered as simulated pollutants. On this basis, we have explored its applications in the UV catalysis to reduce Cr (VI). At last, we had a preliminary study of catalytic interpretation's mechanism.

2. Experiments

All solvents and chemicals were of analytical grades, obtained from commercial suppliers, and used without purification unless otherwise stated.

Preparation of water-soluble TiO_2 nanoparticles has been reported[19], we refer to this method is the preparation of water-soluble TiO_2 nanoparticles.

Photo catalytic reaction was carried out in a quartz reactor (150 ml) at room temperature. A 500 W mercury lamp equipped with an optical filter (λ<420) was used as a light source. The distance between the lamp and the reactor is 8 cm. At first, Pour a certain amount of water-soluble TiO_2 and a certain concentration of potassium dichromate solution into the quartz reactor. After stirring constantly for 30 min in the dark, the photo catalytic degradation experiment begins. Fetch a quantitative reaction liquid regularly, Change the reaction liquid pH value to make TiO_2 precipitation down. and then, using the membrane filter to remove the titanium dioxide precipitation. At last, adopt the method of 1, 5-diphenylcarbazide spectrophotometer[20] to determine the concentration of Cr (VI) in the filter liquor: Cr (VI) and diphenylcarbazide Complexing into purplish red complex under the acid condition, and the maximum absorption happen with 542.5 nm. Its standard working curve is

$$Y=28.0026X - 0.227 \quad R=0.9995 \tag{1-1}$$

In this formula: Y refers to the concentration of Cr (VI) (mg/L);

X refers to the corresponding absorbance of Cr (VI);

R refers to the linear correlation coefficient.

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3. Conclusion and Discussion

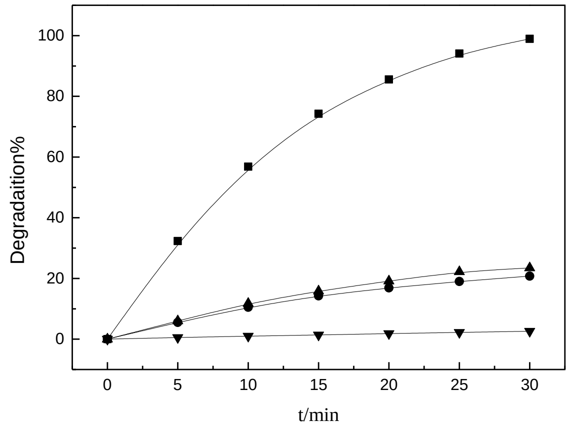

Fig. 1 – Under ultraviolet light, Cr (VI) photocatalytic reduction reaction kinetics curves (Catalyst dosage 2 g/L, Cr(VI) concentration 40 mg/L, pH = 3)(■) Water soluble TiO_2, (○) P25. (△) blank (▲)solvent hot preparation of TiO_2

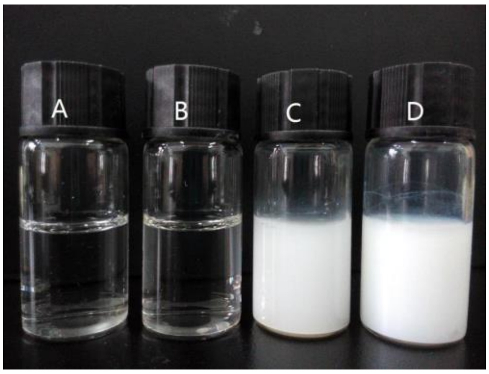

Fig. 2 – pictures of TiO2 in water dispersion Water (A), water-soluble TiO2 (B), solvent hot preparation of TiO2 (C) and P25 (D) dosage were 5 g/L

In order to investigating the potential application of water-soluble TiO_2 in Cr(VI) pollution treatment, we have studied its photo catalytic reduction of Cr (VI) activity. Figure 1 shows that the curve of potassium dichromate photo catalytic reduction reaction kinetics on the water-soluble TiO_2 nanoparticles should be under uv irradiation. Among them, Cr (VI) content is 40 mg/L. It can be seen from the figure 1 that although the Cr (VI) has a strong ultraviolet absorption, it is almost no reduction reaction in the absence of catalyst. Conversely, water soluble TiO_2 nanoparticles for Cr (VI) reduction illustrates a very high photocatalytic activity. Under the Water soluble TiO_2 catalytic role, Cr (VI) photocatalytic reduction of 30 minutes aims to achieve the balance. During these time, the degradation rate of Cr (VI) reaches at 99.89%. Besides, the water soluble TiO_2 nanoparticle photo catalytic activity is much higher than normal TiO_2 nanoparticles. When using the P25 and hydrothermal preparation of TiO_2 nanoparticles as photo catalyst, Cr (VI) degradation rates are only 20.7% and 23.7% under the same conditions to illumination 30 min respectively. The phenomenon may be resulted from multiple factors. Firstly, the size of the water-soluble TiO_2 nanoparticles are smaller. Therefore, water soluble TiO_2 nanoparticles has relatively large specific surface area and more surface atoms. It is advantageous for photo catalytic process. Secondly, as can be seen from the figure 2, water soluble TiO_2 can be highly dispersed in water and form a transparent solution dispersion system. It leads to the light penetration distance that increases in catalytic systems. In addition, because of the water-soluble TiO_2 nanoparticles are highly dispersed in water in the form of individual particles, we can enhance the effective absorption of light for TiO_2 nanoparticles. As a result, the area of effective contact between TiO_2 and water is quite large. It is also a favorable factor

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for photo catalytic reaction. Briefly speaking, preparation of water-soluble titanium dioxide nanoparticles for Cr (VI) removal has a very high photo catalytic activity.

3.1 Effect of Catalyst dosage

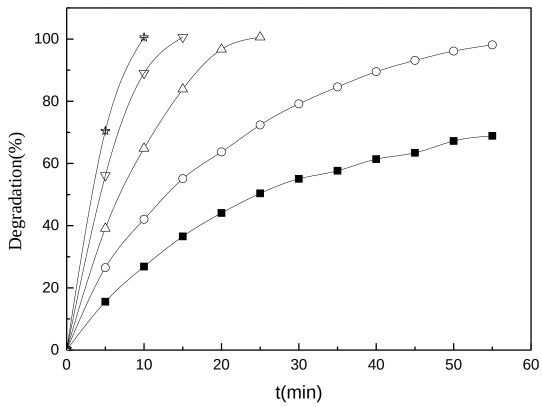

Fig. 3 – Catalyst dosage on the influence of Cr (VI) reduction reaction Catalyst dosage were 0.5 g/L (■), 1 g/L (○), 2 g/L (△) , 3 g/L (▽), 4g/L (☆)

Figure 3 shows the catalyst dosage on the influence of Cr (VI) reduction reaction. As shown in figure 3, Cr (VI) photo catalytic reduction efficiency increases with the increase of the TiO_2 dosage. One possible reason it that the active site increase with the increase is as the TiO_2 dosage. Meanwhile, its light absorption rate has been increased. By the Figure 3 we can also find that when the catalyst dosage is 2 g/L,its, Cr (VI) can be quickly removed in a short time, and the removal rate is of nearly 100%. Hence, based on the principle of saving, we believe that the 2 g/L be suitable catalyst dosage.

3.2 Effect of Cr (VI) concentration

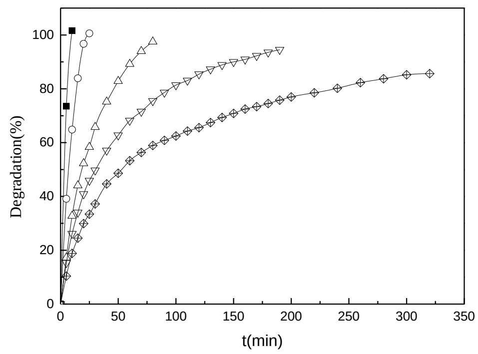

Fig. 4 – Different initial concentration of Cr (VI), Water soluble TiO2 nanoparticle photocatalytic reduction of Cr (VI) reaction kinetics curves Cr (VI) concentration were 10 mg/L(■), 20 mg/L(○), 40 mg/L(△), 60 mg/L(▽), 80 mg/L(◇)

The Cr(VI) initial concentration is an important factor that the efficiency of photo catalytic reduction. Figure 4 shows the curve that when the initial concentration of Cr (VI) was different, water-soluble TiO_2 nanoparticle photo catalytic reduction of Cr (VI) reaction. Water soluble TiO_2 nanoparticles is suitable for low concentration of Cr(VI) solution to photo catalytic treatment. The main reasons are that: On the one hand, with the non-ferrous potassium dichromate solution concentration increase, the solution colors was deepened, light penetrating will be declined in the solution. In addition, Cr(VI) has strong ultraviolet absorption, which helps to reach the surface of the catalyst of the photon number decreases. Thus, the results of the degradation of Cr(VI) rate was declined. On the other hand, Catalyst photo production generated by the electron is not enough for rapidly restore the Cr(VI) when the Cr(VI) solution concentration is higher. Therefore, the photo catalytic reaction rate were decreased

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in a high concentration of Cr (VI) solution. Apart from that, it will happen to dimerization with the increase of initial concentration of Cr (VI)[21]. It leads to the presence of Cr (VI) state and it has changed on the surface of TiO_2. It will also impacts its degradation effect.

Although Cr (VI) in the solution of the photo catalytic degradation efficiency is inversely proportional to its initial concentration, high concentrations of Cr (VI) absolute removal amount is quite large. Therefore, comprehensive consideration, we think that the initial concentration of Cr (VI) is about 40 mg/L is which is much more suitable.

3.3 Effects of pH

PH of the reaction system affects the existing way of Cr (VI) ions and the oxidation reduction potential of Cr (VI). At the same time, it also influences the adsorption behavior on the surface of the catalyst and the ability to capture of electronic for Cr(VI). Therefore, it is an important factor of the photo catalytic efficiency.

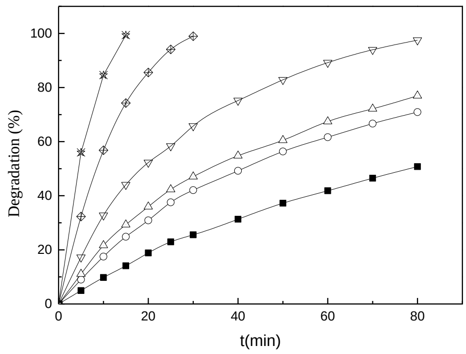

Fig. 5 – Different pH values, the preparation of TiO2 nanoparticle photocatalytic reduction of Cr (VI) reaction kinetics curves (■)pH=11,(○) pH=9,(△) pH=7,(▽) pH=5,(◇) pH=3,(☆) pH=2

Figure 5 shows the curve that when the solution's pH is different, the situation of the preparation of the water-solubility TiO_2 nanoparticle photo catalytic reduction of Cr (VI). It can be seen from figure 5 that photo catalytic removal of Cr (VI) will be better and faster when pH is becoming smaller of the solution. It is because the Cr (VI) in photo catalyst may occur under the action of the following reaction under acid condition [22,23]

$$TiO_2 + hv \rightarrow TiO_2(e^-+h^+) \quad (1\text{-}2)$$

$$2Cr_2O_7^{2-}+28H^++12\ e^- \rightarrow 4Cr^{3+}+14H_2O \quad (1\text{-}3)$$

$$6H_2O + 12h^+ \rightarrow 3O_2 + 12H^+ \quad (1\text{-}4)$$

It illustrates that Cr (VI) reduction needs to consume H^+, so lessen the pH value is advantageous to the reduction reaction. Besides, according to the nernst equation, Cr^{6+}/Cr^{3+} redox potential will be reduced with the rise of pH. Owing to the resulting in a decline in the oxidation capacity of the Cr (VI), the efficiency of photo catalytic reduction of Cr (VI) decreases with the increase of pH value[24]

In the other hand, under the alkaline environment, it is the possible reaction [22,23]

$$Cr_2O_7^{2-} + 14H_2O+3e^- \rightarrow Cr(OH)_3+5OH^- \quad (1\text{-}5)$$

It indicates that the reduzate of Cr(III) could be transformed into precipitation of $Cr(OH)_3$ under the condition of alkaline. $Cr(OH)_3$ will deposit on the surface of TiO_2 and the active site will be obscured. This may be another reason that the Cr(VI) reduction rate becomes slow under the condition of alkaline

Besides, solution pH can affect the position of the valence band and the conduction band for TiO_2. According to a report in the literature, when pH increases 1 unit, valence band and conduction band positions will move to the cathode 59 mV [25,26]. The degrees of match between the location of the TiO_2 conduction band and Cr^{6+}/Cr^{3+} redox potential are gradually becoming poor. This is a disadvantage for photo catalytic reaction.

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Although the lower the pH value, the higher the efficiency of photo catalytic reduction of Cr (VI), the water-soluble TiO_2 nanoparticles surface coated with a layer of organic material will be no longer existed in the "water soluble" in acid environment. Moreover, the experimental results is proved our speculation. It can be observed that a part of TiO_2 is precipitated from the solution when the pH = 2. Thus, we believe that the pH = 3 is the best reaction conditions.

4. Conclusion

To sum up, water soluble TiO_2 nanoparticles is an excellent photo catalyst for Cr (VI) photo catalytic reduction. It can be used to quickly remove Cr (VI) from water. Due to its mild preparation condition, the method is simple and cheap material. Therefore, it is expected that it will be widely used in the next Cr (VI) processing.

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