

Determination of chemical oxygen demand values by a photocatalytic oxidation method using nano-TiO₂ film on quartz

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Abstract

A COD measurement by a photocatalytic oxidation method using nano-TiO₂ film was investigated. K₂Cr₂O₇ was added into the solution to enhance the efficiency of photocatalytic degradation, and simultaneously K₂Cr₂O₇ was reduced to Cr(III) by photogenerated electrons, which were adsorbed on the surface of TiO₂. The measuring principle was based on direct determination of Cr(III) concentration which was proportional to the COD value. Under the optimized experiment condition, the application range was 20–500 mg l⁻¹, and the detection limit was 20 mg l⁻¹. The immobilization of photocatalyst on the supports could not only solve the problem of low recovery of the catalyst and hard separation from the solution, but also overcome its shortcoming of poor stability. Applied this method to the determination of real samples, it was found to be rapid and environmentally friendly. Additionally, the method proposed above for determination of COD was in excellent correspondence with values obtained by using the conventional method.

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Keywords: Nano-TiO₂ film; Photocatalytic oxidation; Chemical oxygen demand

1. Introduction

Analytical determination of the quantity of organic matter in waters and wastewaters was crucial for water quality assessment and pollution control [1]. This quantity could only be presented by aggregative means. The biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were commonly used to express this aggregative quantity. The conventional method for BOD determination had a tedious procedure, and its results were specific to the body of water in question. Thus, COD was preferred for estimating organic pollution [2–7], but conventional COD evaluation methods had several disadvantages [8–12], such as long analysis time (2–4 h), high probability of errors due to complex procedures dependent upon the operators skill, and consumption of expensive (Ag₂SO₄) and toxic chemicals (Cr and Hg).

Recently, the photocatalytic decomposition of organic pollutants in water has received much attention because of its

complete and efficient manner [13–16]. This photocatalytic method was based on the reactive properties of electron–hole pairs generated in the semiconductor particles under illumination by light whose energy was greater than the semiconductor bandgap. These electrons and holes could recombine or reach the particles' surface and react with species in solution with suitable redox potentials [17,18]. When inorganic compounds as electron scavengers and organic substances were both in the solution, redox reactions could take place simultaneously, avoiding the possibility of recombination of the electron–hole pairs. Hence, these two processes must be influenced synergically. It has been reported that many inorganic compounds, such as O₂, Cr(VI), and S₂O₈²⁻ were used as electron scavengers, which could inhibit the recombination of electrons and holes and enhance the rate of photocatalytic degradation of organic compounds [19–22].

TiO₂ nanoparticle remained one of the most promising materials in the field of photocatalysis due to its high photosensitivity, non-toxic nature and large bandgap. The studies of titanic oxide as a catalyst in powder form have been reported [23,24]. However, the powder of TiO₂ nanoparticle was so

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tiny that aggregation could easily happen in solution, which increased the difficulty of the catalyst recovery greatly and led to the loss of active component largely. The major drawback of the suspension system was the requirement for a filtration that was an expensive process. Recently, different studies were carried out to avoid this step by coating TiO₂ on many supports, such as stainless steel [25], quartz [26], pyrex [27] and fiberglass [28]. Martyanov and Klabunde compared TiO₂ particles in powder form and as a thin nanostructured film on quartz [29]. As a result, the photocatalytic activity of TiO₂ on quartz was better than that in the powder form because of higher quantum yields.

In this paper, a COD measurement by a photocatalytic oxidation method using nano-TiO₂ film was studied. TiO₂ was deposited on a quartz support, which could avoid the filtration and provide higher quantum yields than TiO₂ in powder form. In addition, K₂Cr₂O₇ was used as electron scavenger, which could inhibit the recombination of electrons and holes and enhance the oxidation of organic compounds. The change in Cr(III) concentration produced by the photocatalytic reduction was measured by a colorimetric method. It was considered that the value obtained by the proposed method could be reliably correlated with the COD obtained by using the conventional methods.

2. Experimental

2.1. Reagents

Titanium tetraisopropoxide, ethanol, diethanolamine, polyglycol and K₂Cr₂O₇ were analytical grade and purchased from Shanghai Chemical Reagent Company. A standard solution of D-glucose, corresponding to 1000 mg l⁻¹ COD, was prepared by dissolving 0.9753 g D-glucose in 1 l of distilled water. Appropriate dilutions gave solutions of different COD values, and were checked by using the conventional standard method (dichromate method). KOH and H₂SO₄ were used to adjust pH of the reaction solution.

2.2. Device

A bath reactor system in which there was a quartz tube coated with TiO₂ film was used to perform the photocatalytic reaction. A UV irradiator with an 11 W lamp (Shanghai Jinguang Lamps Factory), in the center of the reactor, was used as the UV source and the reactor was equipped with a water jacket to maintain constant temperature.

X-ray data were collected using an X-ray power diffractometer (Rikagu, Japan) based on Cu K α radiation ($\lambda = 0.15418$ nm). The 2θ (two-theta) angle of the diffractometer was stepped from 20° to 60° by 0.03° increments. The scanning tunneling microscopes (STM) were obtained by an AJ-I (Shanghai AJ Nanoscience Development Co. Ltd).

2.3. TiO₂ film preparation

Titanium tetraisopropoxide (12 ml) and ethanol (48 ml) were mixed under an inert atmosphere. Subsequently, a solution of diethanolamine (4 ml) and water (0.5 ml) were added to the mixture under agitation for 1 h at ambient temperature, which led to the formation of a sol–gel. Then, polyglycol was added to the sol–gel solution before dip-coating the quartz tubes. The TiO₂-coated quartz tube was then dried at 100 °C for 5 min, and then heated at 500 °C for 3 h. The operation of coating and drying was repeated four times.

2.4. Experimental procedure

The sample and Cr(VI) solution were added to the reactor which was water-jacketed to maintain constant temperature and magnetic stirrer was used through the experiment. The pH value of the solution was maintained at a desired level with KOH or H₂SO₄. The total volume of reaction solution was maintained at 40 ml for each experiment. Once the UV lamp was turned on ($\lambda_{\text{max}} = 253.7$ nm), photocatalytic oxidation of the organic compounds began to occur, accompanying an increase in Cr(III) concentration by the photocatalytic reduction of Cr(VI). After 40 min irradiation reaction, the absorbance of Cr(III) was determined colorimetrically at 590 nm with a UNICOTM 2100 spectrophotometer, and the COD values of samples were obtained.

For preparing a COD calibration, the standard solutions of different concentrations were added to the reactor respectively and the corresponding absorbance of Cr(III) was determined. The COD calibration graph was generated showing the absorbance of Cr(III) against the standard COD value.

2.5. Analysis of wastewater samples

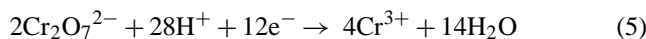
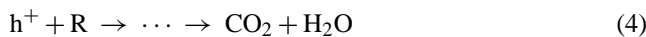
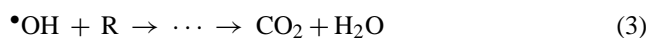
Real wastewater samples were collected from different companies in Shanghai. Collection conditions varied slightly, but all samples were taken at a depth of 50 cm and were kept below 4 °C until use. Experiments were performed within a day or two after collection. COD values of wastewater samples were compared with those determined using the conventional method (dichromate method).

3. Results and discussion

3.1. Measurement principle

When TiO₂ particles were irradiated by UV (<390 nm), they generated h⁺/e⁻ pairs and these species migrated to the solid surface. The valance band holes as powerful oxidants could degrade the organic compounds of aqueous solution. If K₂Cr₂O₇ simultaneously existed in the solution, it acted as an acceptor of photogenerated electrons and was reduced.

The whole reaction was shown from Eqs. (1) to (6):



or



where h was a hole and R was an organic compound.

Theoretically, with these holes and electrons, organic compounds were degraded. When $\text{K}_2\text{Cr}_2\text{O}_7$ was stoichiometrically added, the degradation was enhanced. This indicated that the COD value was proportional to the amount of Cr(III) produced by the photocatalytic reduction of $\text{K}_2\text{Cr}_2\text{O}_7$.

3.2. The characteristics of nano-TiO₂ film

The prepared nano-TiO₂ film was observed with STM. As presented in Fig. 1(a), it was seen clearly that the diameter of the particles was about 30 nm.

The crystal structure of the nano-TiO₂ film was examined with XRD. Fig. 1(b) gives an X-ray diffraction pattern for

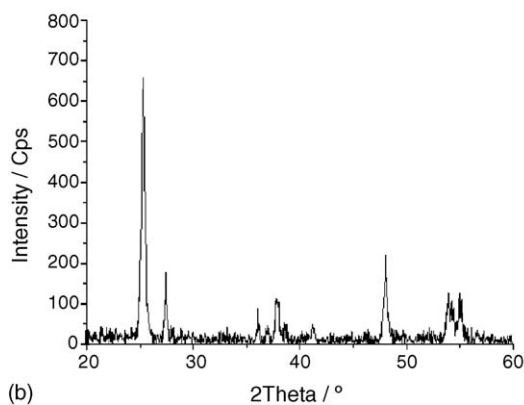
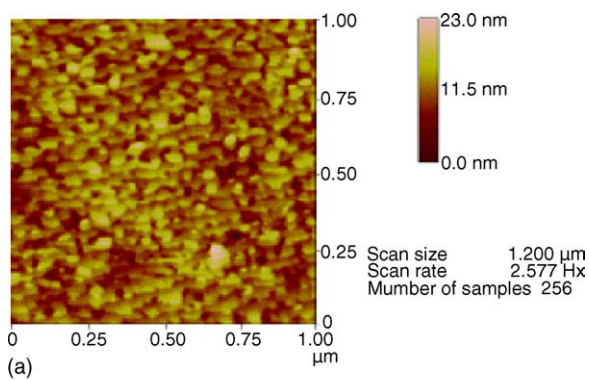


Fig. 1. Characterization of the nano-TiO₂ film: (a) STM image of nano-TiO₂ film and (b) XRD pattern of nano-TiO₂ film.

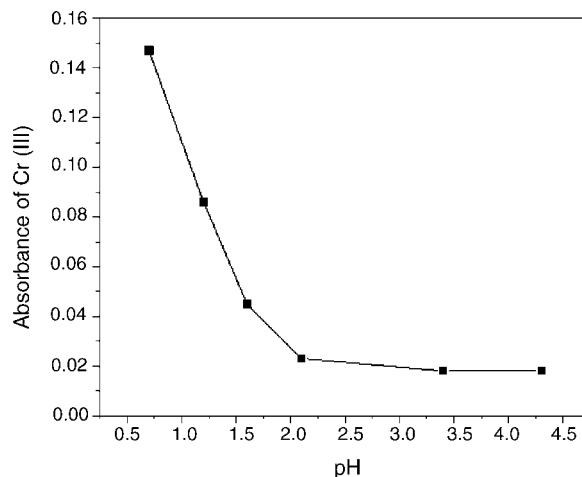


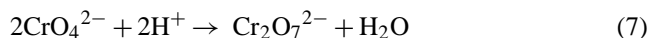
Fig. 2. Effect of pH on the absorbance of Cr(III) . Conditions: $C_{\text{Cr(VI)}}$ 0.03 mg l^{-1} ; $t = 40 \text{ min}$; $\text{C}_6\text{H}_{12}\text{O}_6$ 400 mg l^{-1} and $T = 60^\circ\text{C}$.

2θ diffraction angles between 20° and 60° . The presence of an intense peak at 24.74° indicated a predominant anatase crystalline structure. However, a small signal corresponding to the rutile phase (26.76°) was also observed. These results showed that the prepared nano-TiO₂ film consisted of anatase mainly.

3.3. Optimization of operation conditions

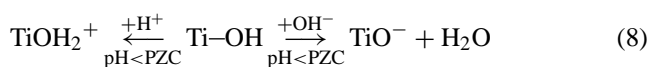
3.3.1. Selection of pH value

Since $\text{C}_6\text{H}_{12}\text{O}_6$ can be degraded at different pH values, controlled experiments were performed to choose the best condition (as presented in Fig. 2). It was noted that the absorbance of Cr(III) decreased with the increment of pH at a fixed COD value of 100 mg l^{-1} , which showed that the photocatalytic oxidation ability for organic compounds was enhanced when the pH decreased. This was mostly due to the effect of pH on the distribution of Cr(VI) species in aqueous solution based on the reaction showed in Eq. (7).



With the increment of H^+ concentration, the distribution of $\text{Cr}_2\text{O}_7^{2-}$ increased. The oxidizing ability of $\text{Cr}_2\text{O}_7^{2-}$ was greater than that of CrO_4^{2-} .

On the other hand, it was reported that the point of zero charge (PZC) of TiO₂ was about 6.25 [30]. When pH value was higher than 6.25, the surface of the TiO₂ became negatively charged and it was opposite for $\text{pH} < \text{PZC}$, according to the equilibrium (8):



Therefore, at $\text{pH} < 6.25$, the surface was electropositive, which favored the adsorption of $\text{Cr}_2\text{O}_7^{2-}$ anions. Hence, the oxidation rate of organic compounds rose with decreasing pH. But if the pH value decreased, the homogeneous catalysis reaction in which substrates were directly oxidized by

$K_2Cr_2O_7$ may affect the COD determination [31,32]. Fig. 4 showed that when $pH=0.7$, the photocatalytic degradation of organic compounds was more efficient than the degradation without photocatalyst (The homogeneous catalysis reaction was dominated without photocatalyst). This indicated that heterogeneous photocatalysis reaction was dominating in the reaction system when $pH=0.7$. Consequently, $pH 0.7$ was selected for further experiments.

3.3.2. Selection of temperature

The effect of temperature on the absorbance of Cr(III) was studied. The results showed that the absorbance of Cr(III) increased with increment of temperature. When the temperature was too high, the solution somewhat vaped so that the reproducibility decreased. Therefore, $60\text{ }^\circ\text{C}$ was selected for further experiments.

3.3.3. Initial concentration of Cr(VI)

Photocatalytic reaction mainly took place on the surface of photocatalyst, so the adsorption of reactants on the surface of photocatalyst was important for Photocatalytic reaction. Fig. 3(a) indicated the adsorption/desorption of Cr(VI) on the surface of TiO_2 after the reactions were in progress for 40 min at $pH 0.7$ but under different other experiment conditions. It illustrated that the adsorption/desorption of Cr(VI) reached equilibrium when Cr(VI) concentration was up to 0.015 mol/L in dark reaction. When UV irradiated without glucose, Cr(VI) adsorbed on the surface of photocatalyst could react to photogenerated electrons (as shown in Eqs. (5) and (6)), which facilitated the adsorption of Cr(VI). With the concentration of Cr(VI) increasing to 0.02 mol/L , the wastage of Cr(VI) was almost increased to a limiting value. This indicated that adsorption/desorption of Cr(VI) was in equilibrium. In photocatalytic degradation of glucose, photocatalytic reduction of Cr(VI) was influenced synergically by photocatalytic oxidation of glucose, which accelerated the consumption and favored the adsorption of Cr(VI). When $C_{Cr(VI)}$ came to 0.03 mol/L , the adsorption/desorption of Cr(VI) was also in equilibrium.

The effect of the initial concentration of Cr(VI) for the photocatalytic determination of COD was studied. The results were shown in Fig. 3(b) (conditions: $pH 0.7$; $t=40\text{ min}$; $C_6H_{12}O_6\ 400\text{ mg l}^{-1}$ and $T=60\text{ }^\circ\text{C}$). The absorbance of Cr(III) increased with increasing Cr(VI) concentration up to 0.03 mol/L , and the increase seemed to change more slowly for higher Cr(VI) concentration. This may be due to the adsorption of Cr(VI) on TiO_2 . At lower $C_{Cr(VI)}$, the photocatalytic oxidation of organic compounds was mainly governed by the adsorption of Cr(VI) on TiO_2 . An increase in initial concentration of Cr(VI) led to an increase in the amount of adsorptive Cr(VI). This was why larger signals were observed for increased Cr(VI) concentration. At very high concentration, however, slight increment was detected owing to reaching adsorption/desorption equilibrium. Thus $C_{Cr(VI)}\ 0.03\text{ mol/L}$ was chosen for further experiments.

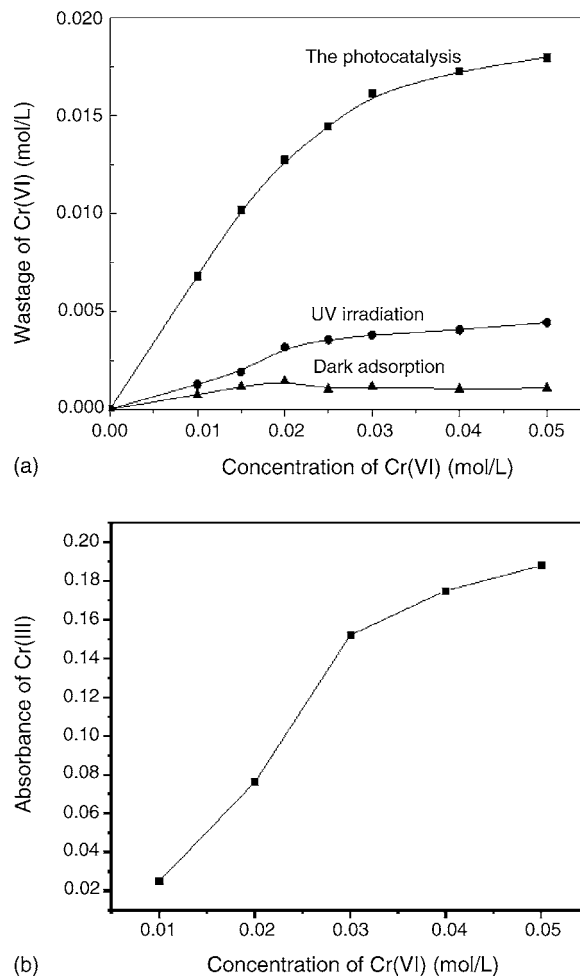


Fig. 3. Selection of initial Cr(VI) concentration: (a) the adsorption/desorption of Cr(VI) on TiO_2 under different experiment conditions and (b) effect of initial Cr(VI) concentration on the absorbance of Cr(III).

3.4. Oxidizing ability of nano- TiO_2 - $K_2Cr_2O_7$ co-existed system

The photocatalytic degradation of glucose using nano- TiO_2 film exposed to ultraviolet radiation was compared to the UV irradiation (without TiO_2) and to the dark reaction (with TiO_2) as shown in Fig. 4. No significant direct photolysis of glucose occurred in the absence of TiO_2 . As for the dark reaction with TiO_2 present, the concentration of glucose dropped slowly by about 36% of the initial concentration and remained constant after reaching adsorption/desorption equilibrium owing to the remarkable adsorption of glucose on TiO_2 . The temporal concentration of glucose decreased rapidly in the photocatalysis (with TiO_2 under ultraviolet irradiance). The efficiency of photocatalytic degradation of organic compounds reached above 80% when UV irradiated for 40 min. The degradation process followed apparent first-order kinetics (inset of Fig. 4, least-square linear correlation coefficient $R=0.9940$, apparent rate constant $k_{app}=0.0538\text{ min}^{-1}$).

Table 1
Comparison of COD values (mg/L) obtained by the proposed method with those from the conventional COD method (dichromate)

Sample	COD values (mg l ⁻¹)				
	The proposed method	R.S.D. (%) (n=7)	COD _{Cr}	R.S.D. (%) (n=7)	Relative error (%)
Chemical manufacture					
Sample 1	421.7	1.0	434.9	1.9	-3.0
Sample 2	356.4	3.3	372.1	1.3	-4.2
Civic sewage					
Sample 1	186.4	1.8	178.4	2.1	4.5
Sample 2	239.6	2.9	235.7	1.8	1.7
Sample 3	143.9	2.7	141.2	1.1	1.9

The controlled experiments showed that the proposed photocatalytic system possessed high catalytic ability for organic pollutant degradation. At the same time, the process was carried on under moderate conditions, so it was prominent to be used in polluted water treatment.

3.5. Calibration graph, detection limit, stability and analysis of real samples

Calibration graph of COD was produced by using standard solutions of glucose. Glucose was used because it reacted quantitatively in the classical COD measurement method. The relationship between the absorbance of Cr(III) and the concentration of the standard solution was shown in Fig. 5. A series of standard solutions of different COD values ranging from 50 to 500 mg l⁻¹ were tested (repeated seven times at each COD value). The linear equation was $y = 0.0003x + 0.0046$, $R^2 = 0.9967$.

The average value of blank samples was 16.8 mg l⁻¹ which was tested for seven times, and the standard deviation was 1.6 mg l⁻¹. Defining the detection limit as the mean value of blank analyses plus two standard deviations [33], the detection limit of proposed method was 20.0 mg l⁻¹.

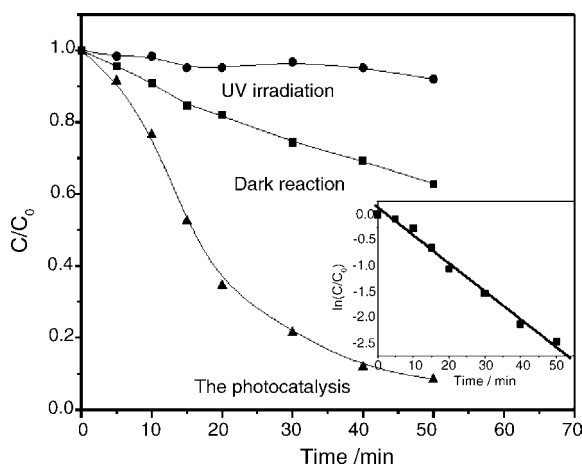


Fig. 4. Oxidation ability of quartz/nanoTiO₂ - K₂Cr₂O₇ co-existed system. Conditions: C_{Cr(VI)} 0.03 mg l⁻¹; t = 40 min; T = 60 °C; C₆H₁₂O₆ 400 mg l⁻¹ and pH 0.7.

The long-term stability of quartz tube coated with TiO₂ film was tested over a 15-day period. On each day, 10–15 samples were determined, i.e., a total of about 180 samples were detected. During this period, the slope changes of calibration graph were less than ±5%.

Various types of wastewater samples obtained from chemical manufacture, civic sewage and food factories, were analyzed by the present method. The results were given in Table 1, which showed that COD values obtained by using the proposed method were within ±5% of those given by the conventional COD method.

Incorporating known amounts of a standard substance in the wastewater samples (five samples) and determining the COD values checked the results. Good recoveries (92–103%) of the standard substance added were obtained. Each sample was tested for seven times and the R.S.D. was less than 5%.

Fig. 6 showed the relationship between the results obtained by the proposed method and conventional method (dichromate) for 30 wastewater samples, and the correlation was satisfactory. The linear regression equation was $y = 1.0044x - 0.202$, where x and y were the data obtained by using conventional methods and the proposed method, respectively. Correlation coefficient were $R^2 = 0.9936$ ($n = 7$).

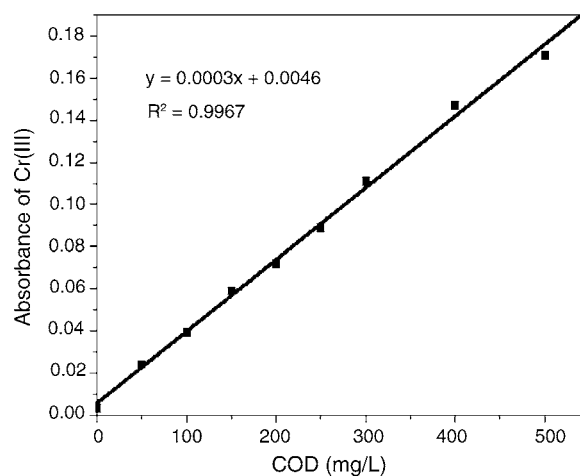


Fig. 5. Calibration graph for COD. Conditions: C_{Cr(VI)} 0.03 mg l⁻¹; T = 60 °C; t = 40 min and pH 0.7.

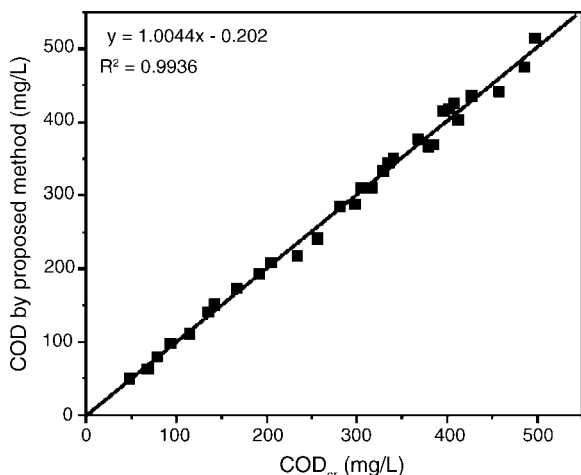


Fig. 6. Relationship between COD obtained by the proposed method and the conventional COD method (dichromate). Conditions: $C_{Cr(VI)}$ 0.03 mg l^{-1} ; $T = 60^\circ\text{C}$; $t = 40 \text{ min}$ and $\text{pH } 0.7$. Substrates are real wastewater samples.

4. Conclusion

The purpose of this work was to develop a new method using a $\text{TiO}_2\text{-Cr(VI)}$ system in which TiO_2 was deposited on a quartz support as oxidizing photocatalyst for monitoring COD, where $\text{K}_2\text{Cr}_2\text{O}_7$ was stoichiometrically involved and could easily accept photo-excited conduction band electrons and enhanced the ability of photocatalytic degradation of organic compounds. Therefore, the COD of a given sample could be assessed by tracing the change of the concentration of $\text{K}_2\text{Cr}_2\text{O}_7$. The optimized operation conditions were studied by using glucose as standard substance. The application range was $20\text{--}500 \text{ mg l}^{-1}$, and the detection limit was 20 mg l^{-1} . The proposed COD measurement method had many advantages, such as mild operation conditions, short analysis time, no requirement of expensive and toxic reagents. The results were satisfactory as regards to sensitivity and correlation according to the detection of 30 real samples. Additionally, the method for determination of COD was in excellent correspondence with values obtained by using conventional method.

Acknowledgements

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