

Study on The Application of Composed TiO_2 -diatomite in The Removal of Phenol in Water

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Abstract. As an environmentally friendly pollution control technology, TiO_2 photocatalytic technology has a broad prospect in the field of environmental protection. In this paper, composed nano- TiO_2 -diatomite were prepared by depositing TiO_2 nanoparticles on the surface of diatomite microparticles. The nano- TiO_2 /diatomite composed photocatalyst is used to remove phenol in water in a specific designed reaction box under 4 different operation factors such as different reaction time, different pollutant concentration, different UV light powers and different amount of catalytic powder. The experimental results indicate that the phenol removal percentages are influenced by the reaction time most significantly, the second is the phenol concentration, the next one is the photocatalyst amount and the UV light powers' effect is quite limited. The degradation of phenol typically slows down at the reaction time about 30 or 60 minutes. Besides that, the phenol removal kinetic removal rates were also investigated.

1. Introduction

Global drinking water pollution has brought serious challenges to human health. WHO survey showed that 80% of the world's disease and 50% of children's deaths are related to poor drinking water quality [1]. With the aggravation of water pollution, the conventional water treatment process has exposed a lot of limitations. For example, this cannot effectively remove trace organic contaminants, inorganic contaminants, pipe network and water storage tanks attached microorganisms. At present, domestic and foreign has developed TiO_2 adsorption technology, photocatalysis technology, advanced treatment technology of membrane and enhanced coagulation and filtration of traditional processing technology to improve and ensure the quality of drinking water [2].

Since the early development of this technology in the 1970s, TiO_2 constitutes the archetypical photocatalyst due to its relatively high efficiency, low cost and availability [3]. Photocatalytic technology has the advantages of no twice pollution, low energy consumption, fast response, simple operation and high efficiency, so it has gradually become a research hotspot in the advanced treatment of drinking water. Thiruvengkatachari et al. (2008)[4] and Fan et al.(2001)[5] found out that TiO_2 photocatalytic oxidation can effectively remove the humic substances in drinking water. Humus is the main precursor to produce toxic by-products (DBPs) in drinking water disinfection, and it is also the main factor leading to the increase of the mutagenic activity of drinking water. TiO_2 photocatalytic technology can remove organic pollutants such as dyes, pesticides, phenols, hydrocarbons and surfactants in water, and can make the halogen atoms (X), sulfur atoms, phosphorus Atoms and



nitrogen atoms into X-, SO₄²⁻, PO₄³⁻ and NO₃⁻ and other inorganic salts, to reduce or even completely eliminate its original harm [6]. Liu et al. (2009) [7] used the nano-TiO₂/Diatomite compound photocatalyst to degrade rhodamine B dye wastewater in photochemical reactor. The best technical conditions are concentration of rhodamine B solution 10mg/L, ultraviolet light 300W, the compound photocatalyst amount used 1g/L, the pH 5.8, reaction time 20min. Under these conditions the rate of photodegradation of rhodamine B may reach as high as 97.80%. TiO₂ photocatalytic technology in the pharmaceutical wastewater, pesticide wastewater, oil-containing wastewater, paper waste water and other fields have been applied [8]. Cheng Cangcang et al. [9] fixed TiO₂ photocatalyst film on the inner wall of stainless steel reactor, and the introduction of Fenton reagent in Wuhan, a pharmaceutical factory for pharmaceutical wastewater treatment. The results showed that the removal percentage of COD_{Cr} was 92.3% and the content of nitrobenzene compounds decreased from 8.05 mg / L to 0.41 mg / L. Zhang Haiyan et al. [10] prepared nano-TiO₂ semiconductor photocatalyst, investigated the catalyst crystal structure, particle size, dosage, pH and the photocatalytic degradation of Fe³⁺ or H₂O₂ coexisting wastewater containing oil. The results show that TiO₂ has a high photocatalytic activity of oil degradation. When it is coexisted with Fe³⁺ + or H₂O₂, the removal percentage of oil can be increased by 5% ~ 16% under the same illumination time. Degradation properties of phenol using nano-TiO₂ as photocatalyst in aqueous solution were investigated. In Wang et al.'s work as well [11], the effect of annealing temperature and ionic modification on the degradation was studied. The results showed that photocatalyst nano-TiO₂ material doped with Fe³⁺ was prepared quickly by sol-gel process and was used as photocatalyst to degrade phenol solution of 100mg/L under UV irradiation for 3 hours. The phenol degradation percentage was 94.18%. SP Kunjalukkal et al. [12] in 2014 found that the photocatalytic reaction follow a pseudo-first-order rate law and the composite catalyst crystallized at 500°C shows the highest catalytic activity toward RhB degradation. It was observed that diatomite substrate significantly enhanced the photodegradation efficiency of TiO₂ due to higher surface area, mesoporous structure and uniform deposition of the small sized TiO₂ particles.

From the above summary, we can see that the investigation of composed nano-TiO₂-diatomite material in the application of phenol degradation in water is still quite limited. The different influence reaction factors and kinetic removal rate were not yet explored in depth. With this in mind, we did some preliminary experimental work.

2. Experiments

2.1. The preparation of the composed nano-TiO₂ and diatomite

In this paper, according to the method proposed by Akpan in 2009 [13] and Shi enbin in 2014 [14], we used the modified bought P25 nano-TiO₂ (40% by weight) loaded onto the porous diatomite (60% by weight) and dried. Then the composed powder particles were sieved to the size larger than 45 μm (figure 1).

Moreover, the reasons why we preferred to use the composed nano-TiO₂ and diatomite material instead of only nano-TiO₂ is the composed material should have higher effective efficiency than the pure nano-TiO₂ material in removing pollutants because it has diatomite which has porous structure. The diatomite was responsible for the porous matrix so that this kind of materials can have relatively huge surface area covered by P25 nano-TiO₂.

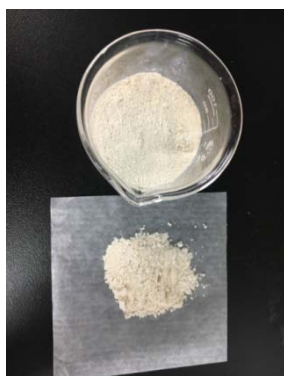


Figure 1. The composed P25 Nano-TiO₂ and diatomite material after sieving

2.2. Design of the UVC reaction box

Different from other researcher's work, most of them applied the method by directly inserting the high power UV lights into the liquid to make reaction happen more efficiently. But this method can be limited to use in lab and the UV lights、catalytic materials have relatively shorter life time. In this paper, we used the designed reaction box to carry out the experiments to avoid the UV lights contact with liquid. In this box, there are maximum 4 UV lights (power 55W) can be stalled at the top ceiling which can be shown in figure 2. From above description, the UV light tube power in this paper can be changed to 55W (1 light tube installed), 110W (2 light tubes installed), 165W (3 light tubes installed) and 220W (4 light tubes installed). In figure2, we also can see that during the experimental process, the glass ware can be settled on the platform in the UVC reaction box and the top of water level in glass wares is about 5 cm from the UV tubes. During the experiments, when the UV lights should be on we could close the UVC box and press the ON/OFF button as figure 3 showed. In this way, the UV lights can make reaction happen as expected even not contact with the liquid, and the harm caused by the UV lights could be reduced to minimum.

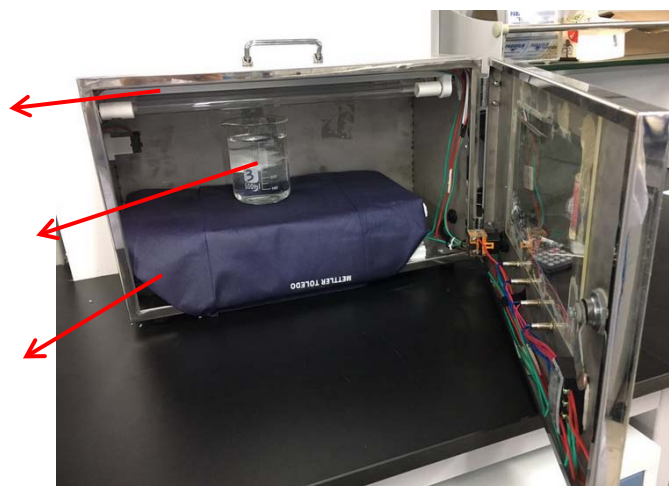


Figure 2. The inside of the Reaction box(UVC)

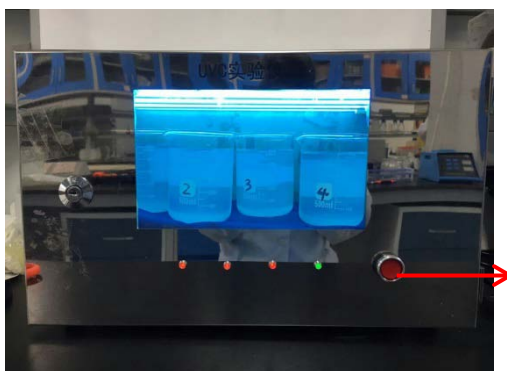


Figure 3.UVC box with UV lights on

2.3. The preparation of water sample

The water samples we used in the experiments are the purified water polluted by phenol ($\text{C}_6\text{H}_5\text{OH}$, Sigma-Aldrich, 99%, Shanghai, China) and were prepared by 0.005mg/L, 0.01mg/L, 0.02mg/L (phenol concentration limit in drinking water in the New National Standard is 0.002mg/L). The catalytic powder amount in water samples were chosen to 0.05g/L or 0.2g/L.

2.4. Experimental Process

Based on the 4 different main influence factors to effect phenol removal efficiency, we got amount of samples. The 4 different factors are:

- (1) Water samples with different initial phenol concentration, Co, 0.005mg/L, 0.01mg/L, 0.02mg/L;
- (2) Different catalytic powder amount, 0.05g/L or 0.2g/L;
- (3) Different UV lights tube powers, 110 W and 220W;
- (4) Reaction time, 15 mins, 30 mins, 45 mins, 60 mins, 90 mins, 120 mins.

The water samples obtained from experiments under the above different factors were collected out the UVC box and then filtrated by the 22 μm membrane as figure 4. As described before in this paper, the catalytic powder chosen in this paper were sieved to $> 45 \mu\text{m}$ so the catalytic powder can be removed all. The residue phenol concentration in water samples after filtrated from catalytic powders were measured by the UV Visible spectrophotometer UV 1700 in the following figure 5.



Figure 4.Filtration membrane (22 μm)



Figure 5.UV Visible Spectrophotometer UV1700

The standard calibration line of the UV Visible spectrophotometer UV 1700 were obtained as well in figure 6 so from figure 6, we can see that the analysis results of the UV visible Spectrophotometer 1700 in this paper were reliable.

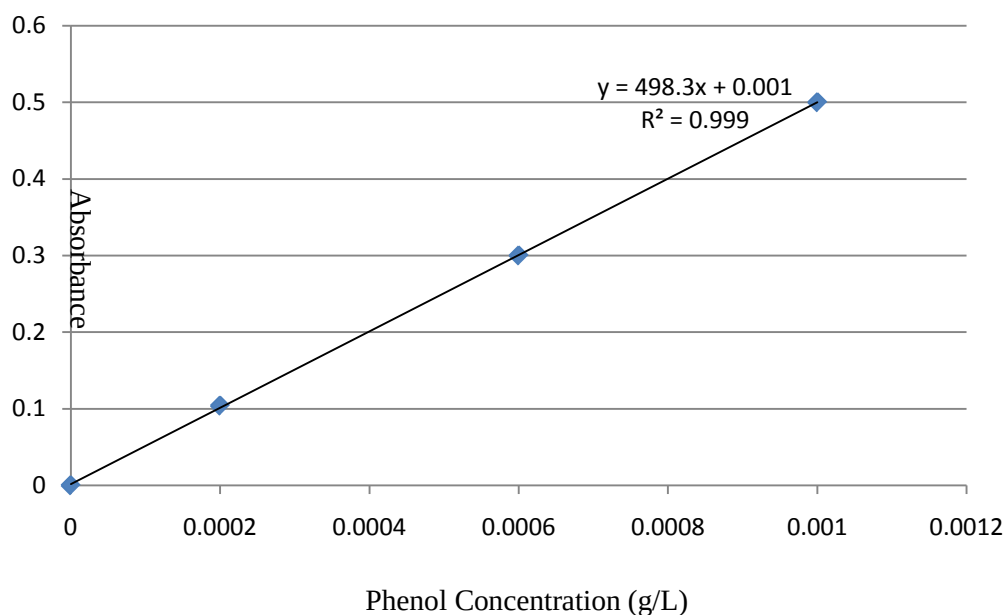


Figure 6.The standard calibration line of the UV Visible spectrophotometer UV 1700

3. Results and Discussion

3.1. The effect of reaction time on removal percentage and kinetic rates

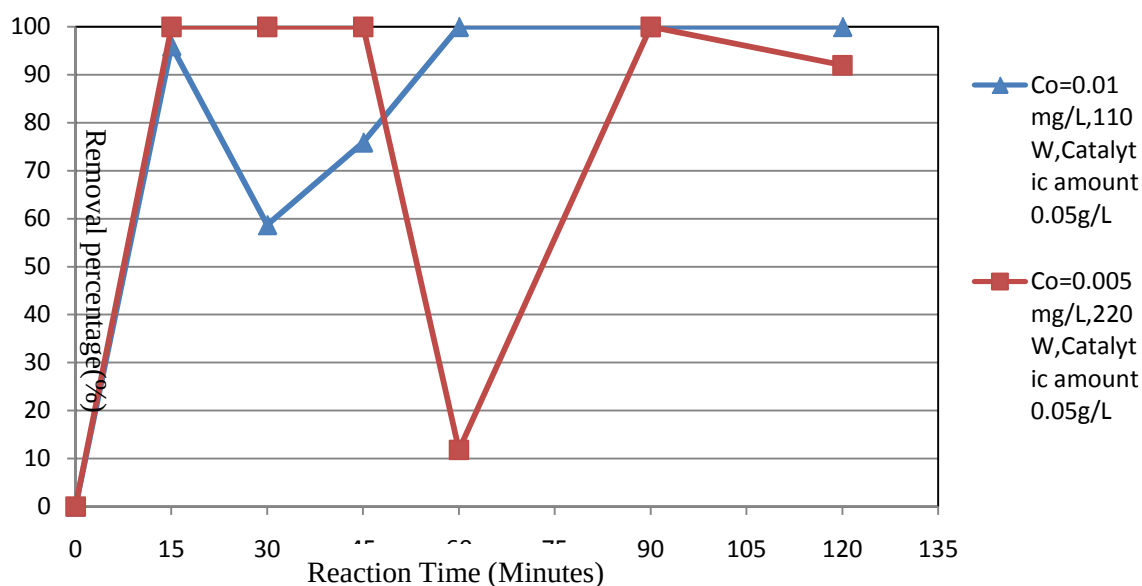


Figure 7. The removal percentage at different time (minutes)

In figure 7, the x-axis is the reaction time (unit: minutes) and y-axis is the phenol or other pollutants removal percentage which can be calculated as: $(C_t - C_0)/C_0$ (unit: %).

From above figure 7, we can see that for different operation conditions such as different UV light powers or water samples with different initial phenol concentrations, the phenol removal percentages all appeared a declined trend at the reaction time about 30-60 minutes. The reason why the degradation removal percentages have declined is because that as reaction going on, the composed nano-TiO₂ and diatomite materials absorption ability achieved quite relatively high and the desorption of phenol happened. Then the TiO₂ photocatalytic reaction happened again and the phenol removal percentage became stable.

The phenol degradation typical declined is one of the most innovative findings in this paper. Based on this result, it gives us a hint that when we use composed nano-TiO₂ and diatomite catalytic powder to remove phenol or some other organic pollutants in water or air, we should consider about the removal percentage slowed down.

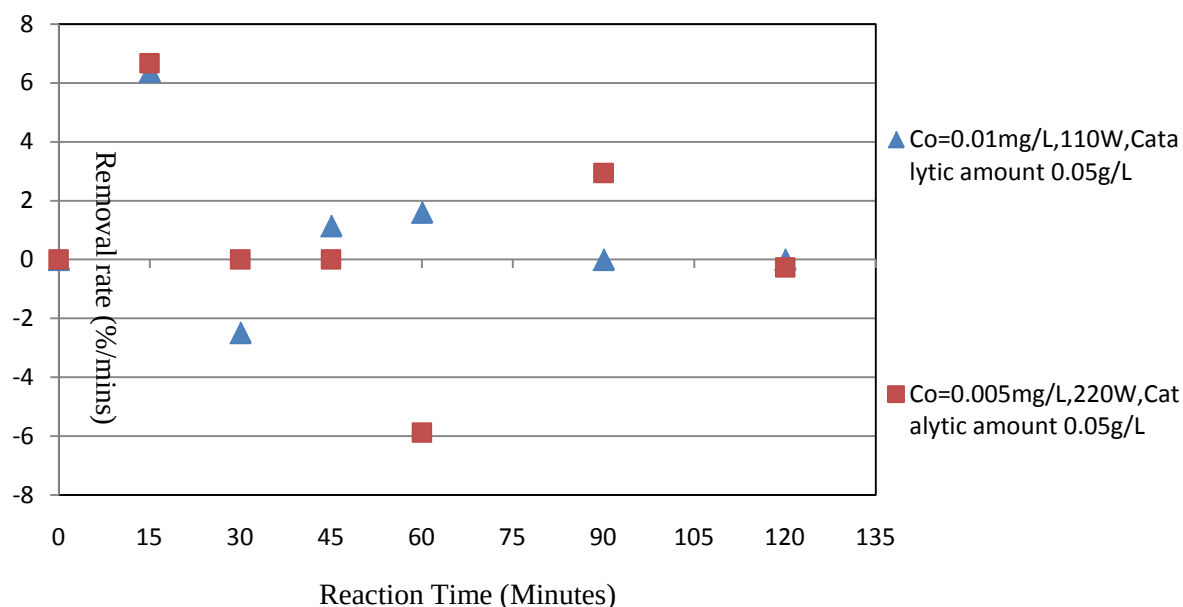


Figure 8. The effect of reaction time on removal kinetic rate

To investigate the reaction kinetic removal rate, we got figure 8. The x-axis is reaction time which has the unit as minutes. Y-axis is the removal kinetic rate which can be calculated as removal percentage/time lapse and the unit can be expressed as %/minutes. From figure 8, it can be seen that the kinetic removal rate appeared wave shape. At reaction time about 30 minutes, the kinetic removal rate decreased and then the removal rate appeared increased. We tried to find the relationship between reaction time (minutes) and removal rate (%/minutes), but from figure 9, it can be seen that even the 2 first order lines describing the relationship between reaction time (minutes) and removal rate (%/minutes) appeared quite close but both the correlation coefficients R square appeared quite low, so the 2 lines are not reliable.

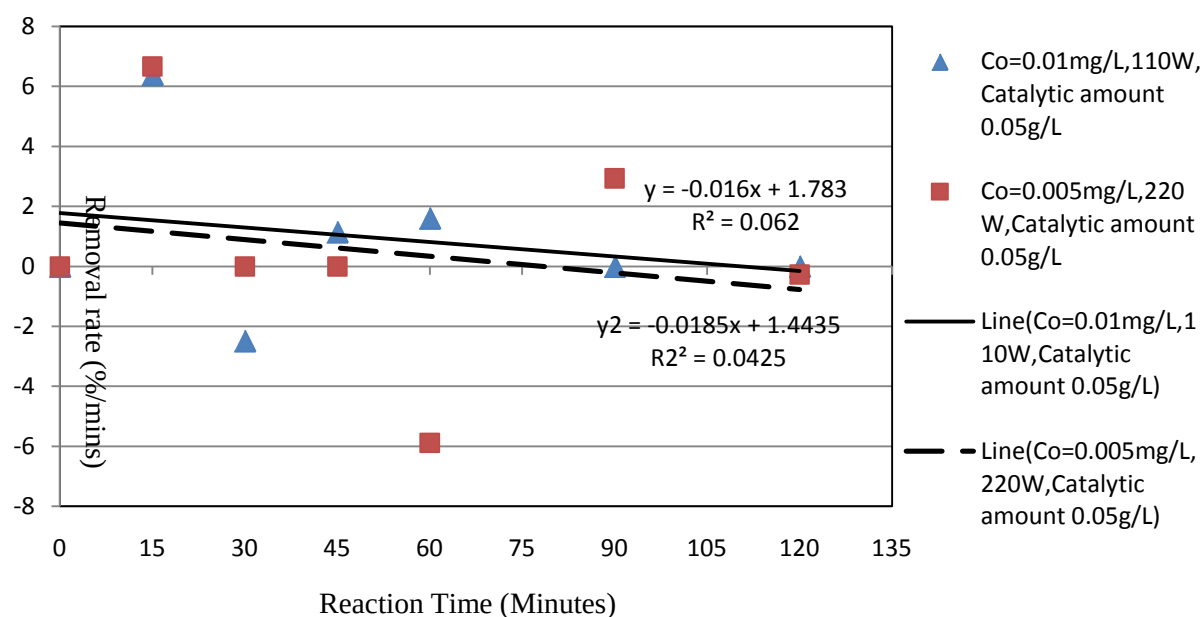


Figure 9. The effect of reaction time on removal kinetic rate with the correlation coefficients R square

3.2 The effect of water samples with different initial phenol concentrations on removal percentages and kinetic rates

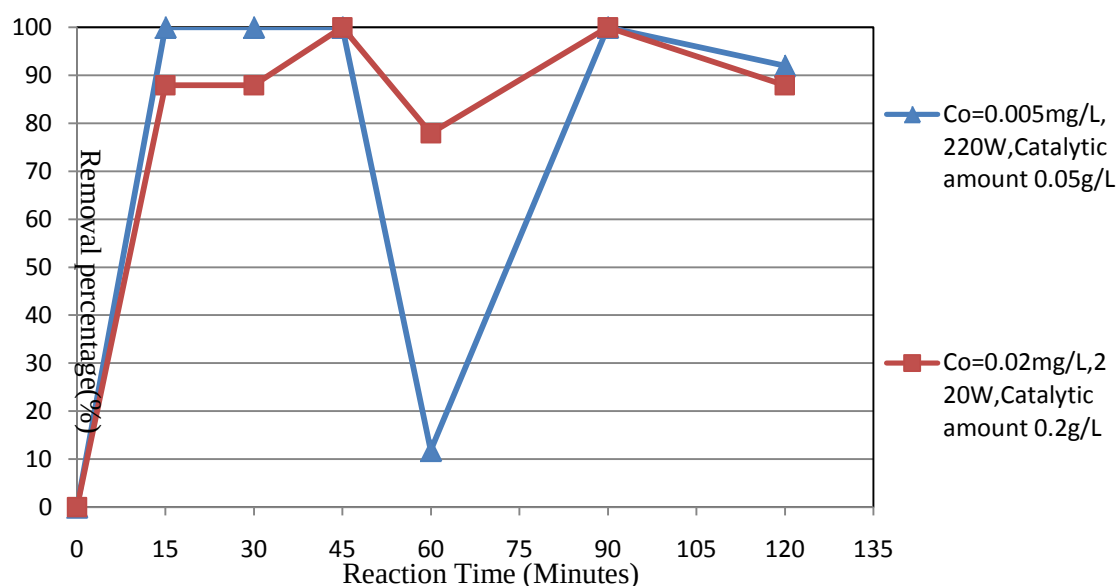


Figure 10. The effect of water samples with different initial phenol concentrations on removal percentages

From figure 10, we can see that for different water samples (different C_0), the phenol remove percentage decreased as the C_0 increased under the same experimental condition. It means that the photocatalytic technology in our paper was effective in the removal of trace concentration of phenol in water.

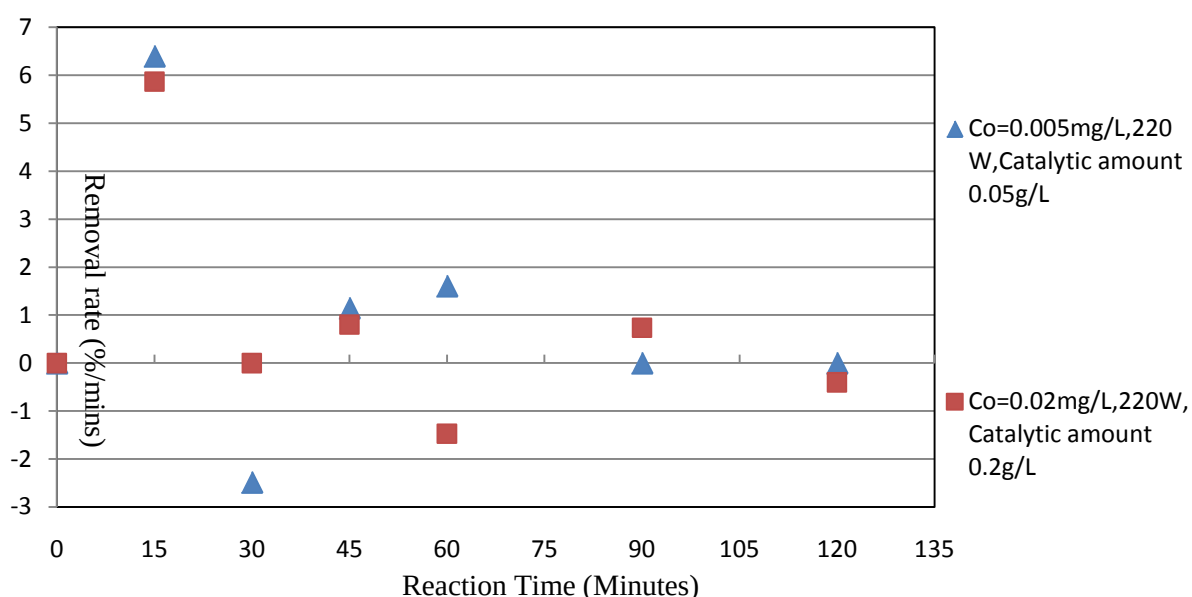


Figure 11. The effect of water samples with different initial phenol concentrations on removal kinetic rate

Similar with figure 8, from figure 11 it can be seen that the kinetic removal rate still appeared wave shape as reaction time passed. For water samples with different initial phenol concentrations, the lower initial phenol concentration, the change rate higher.

3.3 The effect of UV light powers on removal percentages and kinetic rates

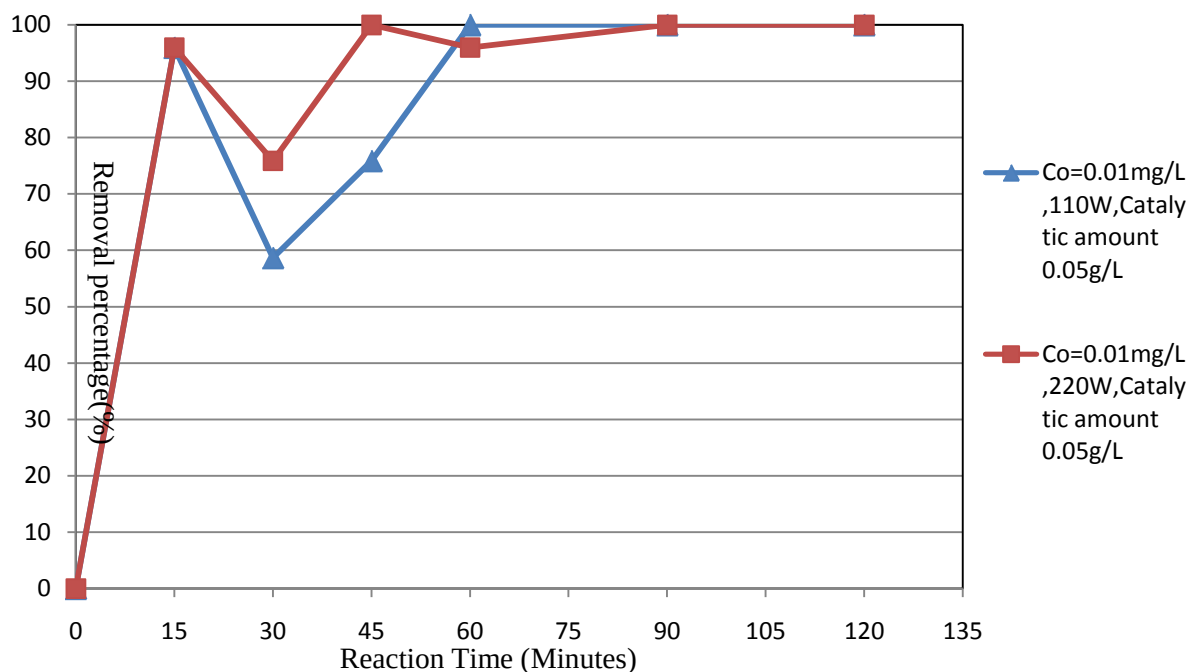


Figure 12. The effect of UV light powers on removal percentage

From figure 12, we can see that the effect of UV light powers on removal percentages appeared more effective at the reaction time before 60 minutes. The higher UV light power, the higher phenol remove efficiency we got.

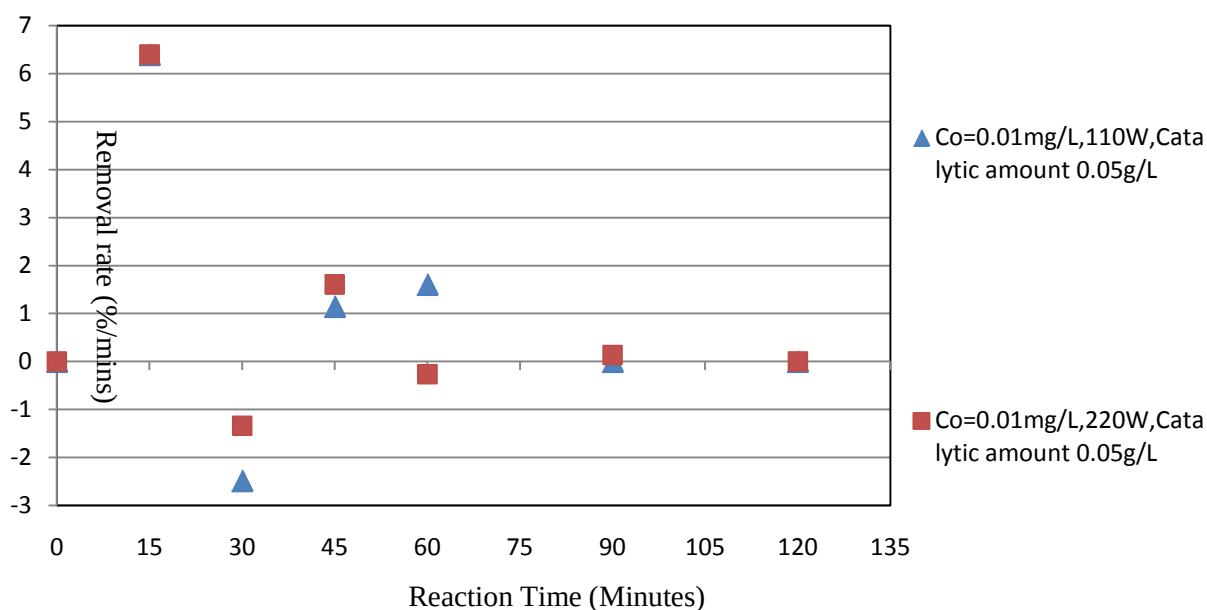


Figure 13. The effect of UV light power on removal kinetic rate

Again, the removal kinetic rate appeared wave shape and the UV light power has quite limited effect on the removal kinetic rate in figure 13.

3.4 The effect of different catalytic powder amounts on removal percentages and kinetic rates

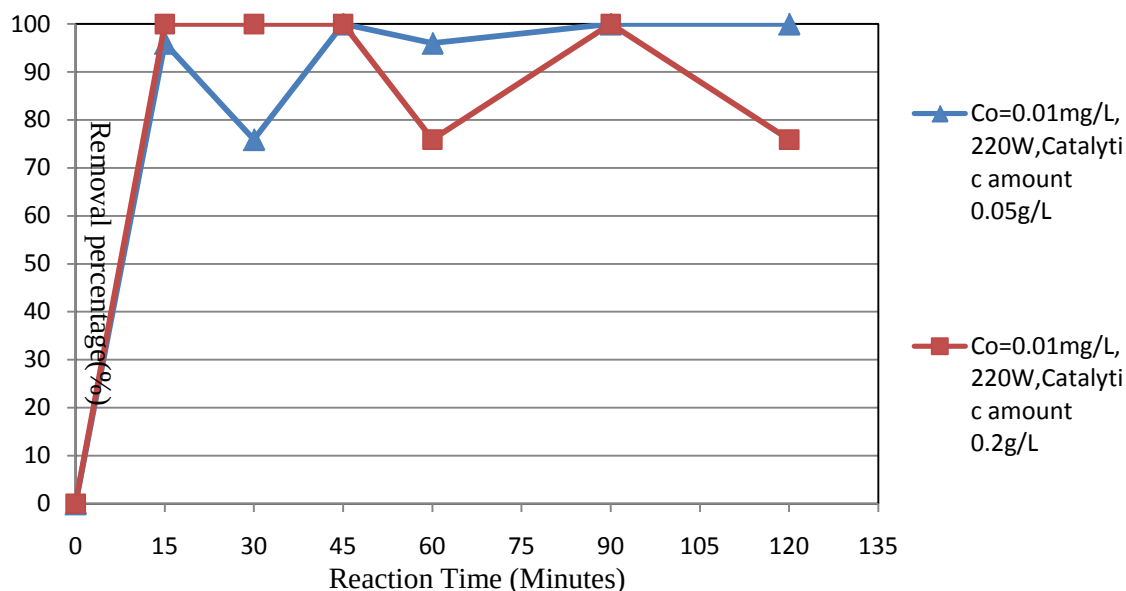


Figure 14. The phenol removal percentage at different amounts of catalytic powder

In figure 14, we get 2 different lines about removal percentages under the same UV tube powers and same C_0 0.01mg/L but different catalytic powder amounts 0.05g/L, 0.2g/L. It can be seen from figure 14 that at the beginning stage of reaction, the more catalytic powder amount, the higher removal percentage. But the removal percentage increased not so much compared with the increase of catalytic amount from 0.05g/L to 0.2g/L. And as reaction going on, the removal percentage decreased a little bit for the operation condition 220W, C_0 =0.01mg/L, catalytic amount 0.2g/L. So the effect of the catalytic powder amount can be summarized not significant. Very little amount of catalytic powder can achieve quite good removal results.

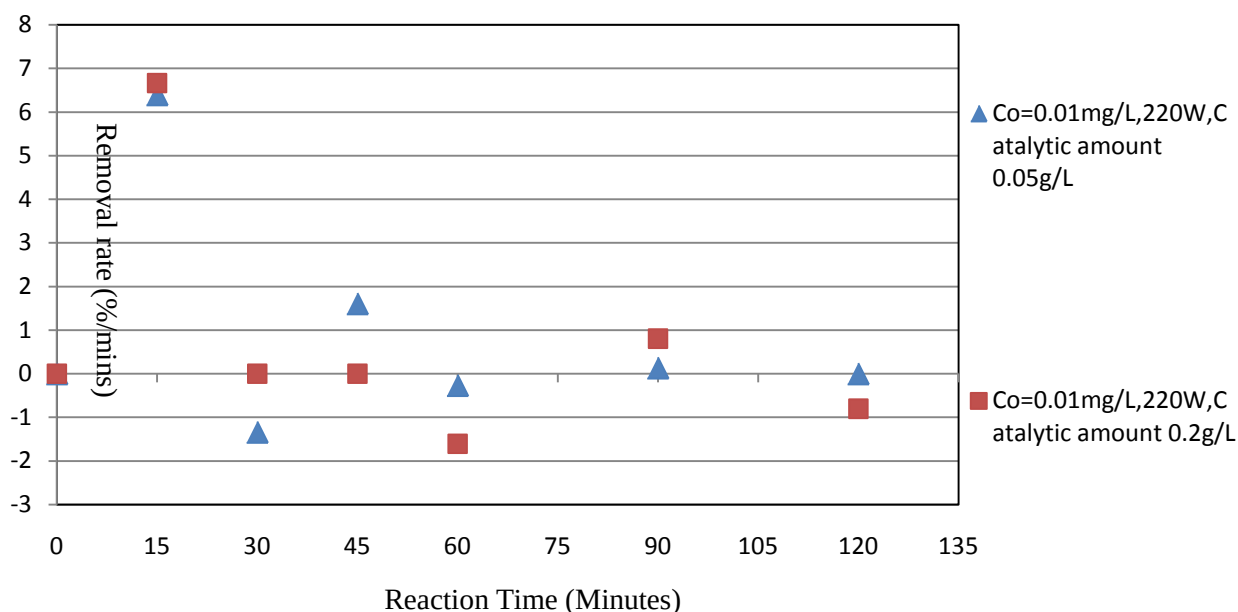


Figure 15. The phenol removal kinetic rate at different amounts of catalytic powder

From figure 15, we can see that the phenol removal kinetic rate still appeared wave shape but the effect of different catalytic amount on removal kinetic rate can not be ignored. The lower catalytic powder amount, the kinetic removal rate change more significantly.

Besides the above experimental data, blank experiments were done as well. The phenol concentration in water samples under UV without catalytic powder, or with catalytic powder without UV both appeared not effected and proved that the actual efficiency of composed nano-TiO₂ diatomite as catalytic materials.

In this study, we firstly investigated the research background and research status of the topic; then on the basis of theoretical knowledge, we constructed composed nano-TiO₂ and diatomite material as catalytic powder in the water treatment; through the analysis of specific experiments and experimental results of the system, we verify the feasibility and effectiveness of the treatment system. It proves that the research is fruitful and meaningful.

4. Conclusions

The conclusions can be summarized as: (1) The phenol removal percentages are influenced by the reaction time most significantly, the second is the phenol concentration, the next one is the photocatalyst amount and the UV light powers' effect is quite limited. (2) The degradation of phenol typically slows down at the reaction time about 30 or 60 minutes. Because the type of reaction kinetics which depends on pollutant concentration. (3) The higher UV light power, the higher phenol removal percentage at the beginning of the reaction stage. But after time passed, lower UV tube power can achieve the 100% removal percentage. But for kinetic removal rate, the UV light power has limited effect. (4) The more catalytic powder amount, the higher removal percentage at the beginning of the reaction time. But the removal percentage increased not so much compared with the increase of catalytic amount. But also it appeared that the removal percentage can achieve very high at about 1 hour and later. So the effect of the catalytic powder amount can be summarized not significant. Very little amount of catalytic powder can achieve quite good removal results. But the effect of different catalytic amount on removal kinetic rate can not be ignored. The lower catalytic powder amount, the kinetic removal rate change more significantly.

Acknowledgments

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5. References

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