Combination of ozone with nano TiO$_2$ supported by zeolite for the decontamination of raw water from Songhua River

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Abstract. In the present paper, nanosized TiO$_2$ supported by zeolite was used in the ozonation of Songhua River as catalyst. The catalytic activity of TiO$_2$/Zeolite for ozonation was testified by nitrobenzene removal, which is one kind of representatively resistant organic contaminant. And the removal of some organic and inorganic compounds existing in the Songhua River by TiO$_2$/Zeolite catalyzed ozonation was investigated. GC-MS analysis showed that the Songhua River was obviously polluted by organic contaminants. Catalytic ozonation can remove about 30 kinds of organic matters from water and reduce the total organic peak area of feed water by 62.5%.

1. Introduction

Rapid population growth and economic development and the lack of effective environmental protection in China often lead to serious deterioration in the quality of water resources such as the Songhua River. Surface water contamination presents great difficulties and challenges to the capability and performance of conventional water treatment processes.

Ozone is widely used in drinking water treatment for many different purposes such as disinfection and algae control, taste, odour and colour control, oxidation of inorganic pollutants (iron, manganese), oxidation of organic micro- and macropollutants as well as for the improvement of coagulation [1]. It is now widely assumed that ozone reacts in aqueous solution on various organic and inorganic compounds, either by a direct reaction of molecular ozone or through a radical type reaction involving the hydroxyl radical induced by the ozone decomposition in water [2-4]. Since the oxidation potential of hydroxyl radical is much higher than that of the ozone molecule, radical oxidation is faster than that direct oxidation. Ozone decomposition is catalyzed by hydroxide ions and appropriate solid catalyst, which eventually produces free radicals, especially hydroxyl radicals [5-9].

In previous works, nanosized TiO$_2$ was chosen as a catalyst in the ozonation process and showed efficient activity for the degradation of nitrobenzene (NB), which is usually refractory to conventional chemical oxidation or toxic to micro-organisms of conventional biological oxidation [10]. In this work

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the results of the investigation to the removal of some inorganic and organic compounds existing in water from the Songhua River by nano-TiO$_2$/Zeolite catalyzed ozonation processes are presented. These data provide a comprehensive evaluation of the efficacy of the nano-TiO$_2$/Zeolite catalyzed ozonation processes to improve the water quality for potable uses.

2. Materials and methods

2.1. Chemicals
The chemical reagents such as tetrabutylorthotitanate, absolute ethanol, sodium hydroxide and hydrochloric acid etc., purchased from Tianjin reagent Co. (China), were of analytical grade and used without further purification. Artificial zeolite pellets in a diameter of 1-2 mm were used as the supporting material and obtained from Shanghai reagent Co. (China).

2.2. Preparation and characterization of catalyst
Tetrabutylorthotitanate was used as a precursor of titania. Conforming to the sol-gel method, tetrabutylorthotitanate was added into the premixed solution of absolute ethanol, deionized water and hydrochloric acid at room temperature. The solution was mixed for 2 h to obtain titania sol. After the hydrolysis, the artificial zeolite pellets were slowly added into the titania sol and mixed for 24 h to obtain zeolite which carrying titania xerogel on the surface pores. Then the supported catalyst was calcined between 400 to 700 °C to control the TiO$_2$ crystallinity.

XRD studies of catalyst were performed by means of a D/max-r B diffractometer, at 40 kV, 30 mA (1200 W) and using nickel-filtered Cu kα radiation to determine crystal phase and estimate crystallite size. X-ray energy spectrum analysis was performed to test the TiO$_2$ content in S-570 electron microscope (Japan).

2.3. Experimental system

Bench scale tests were performed using a two-stage flow-through system to facilitate the operation of all ozone-based oxidation processes, which consists of two series-wound cylindrical reactors made of pyrex glass with the dimensions of 80 mm in diameter and 500 mm in height (figure.1). 1.5 L test water was used for each experiment. Ozone was continuously introduced through a porous fritted diffuser that can produce fairly fine bubbles at a constant rate of 0.9 mg O$_3$ per minute. Ozone was produced from extra dry oxygen using the “corona discharge” method with a XFZ-581 Laboratory Ozonator. The system was operated by gravity feeding the water into the gas-liquid-contactor and then pumping the ozonated water through the catalyst bed. Surplus ozone in off-gas was trapped by two
bubblers, containing 250 mL of a 2% KI solution. Unless otherwise stated, the catalyst dose was 10 g L⁻¹. Sample waters for nitrobenzene analysis were taken from the sampling port at an appropriate time interval. Na₂S₂O₃ was added to the sample immediately to quench possible further reaction by residual ozone. The temperature was maintained at 20±3 °C. Ozone decomposition experiments were performed using similar apparatus to that described above.

2.4. Feed water and analytical methods
Water samples used for this study were obtained from the Songhua River (Harbin, China), which is a water supply source for many northeastern cities of China. Since the traditional techniques such as coagulation and sedimentation are strictly connected with the transference of ozone from gas to solution phase, so water was pumped into the feed water tank for ozonation after the pretreatment of coagulation and sedimentation.

Water samples were analyzed for key water-quality parameters such as TOC, UV absorbance at 254 nm, NH₄⁺ and NO₃⁻. All analyses were performed following the Standard Methods. A TOC analyzer (Shimadzu TOC-VP, Japan) and a UV/VIS spectrophotometer (Shimadzu UV2550, Japan) were used in the analysis, respectively.

GC/MS apparatus (Agilent GC7890/MS5975) was used for qualitative analysis of organic matter. GC conditions are as follows: HP-5MS chromatographic column (30 m×250 μm×0.25 μm); column temperature is programming heated-up from 45 to 270 °C; detector temperature: 250 °C; injector temperature: 250 °C; carrier gas: N₂; split ratio: 20:1; shunt volume: 23.943 mL min⁻¹. MS conditions are as follows: ionization mode: electron bombardment; ion source temperature: 230 °C; scanning area: 45-450 m z⁻¹.

3. Results and discussion

3.1. Activity of nano TiO₂ supported by zeolite
The crystal structure and crystallite size of nano TiO₂ are important factors that determine catalytic activity, which is strongly influenced by heat treatment temperature. Table 1 showed the catalytic ozonation efficiency by the supported TiO₂/Zeolite catalyst calcined at different temperatures with nitrobenzene as indicator compound.

The supported TiO₂/Zeolite catalyst did increase the removal rate of nitrobenzene compared with single ozonation. And the heat treatment process enhanced the activity of catalyst by increasing the crystallinity of TiO₂ and the connection between TiO₂ and support. It is shown from table 1 that 600 °C is the best temperature for calcination. XRD analysis shows that TiO₂/Zeolite calcined at 600 °C were synthesized by a majority of rutile and the approximate crystallite size is 20-30 nm. X-ray energy spectrum analysis shows that the weight percentage of TiO₂ is about 8% as compared with the Zeolite support. Because of the best activity of the supported catalyst calcined at 600 °C, it was adopted for the latter research.

Table 1. Catalytic activity of TiO₂/Zeolite for nitrobenzene removal.

| Process | O₃ | O₃+C₁ | O₃+C₂ | O₃+C₃ | O₃+C₄ | O₃+C₅ |
|---------|----|-------|-------|-------|-------|-------|
| NB removal, % | 13.1 | 19.8 | 20.3 | 28.1 | 33.8 | 31.9 |

C₁: TiO₂/Zeolite calcined at 0 °C; C₂: TiO₂/Zeolite calcined at 400 °C; C₃: TiO₂/Zeolite calcined at 500 °C; C₄: TiO₂/Zeolite calcined at 600 °C; C₅: TiO₂/Zeolite calcined at 700 °C; O₃: 0.9 mg·min⁻¹; Catalyst: 10 g L⁻¹; Reaction time: 10 min; Temp: 20±3 °C; pH: 5.4–5.8

3.2. Catalytic ozonation of Songhua River for TOC and UV₂₅⁴ removal
The TOC and UV\textsubscript{254} value of feed water approximately ranges from 7–13 mg L\textsuperscript{-1} and 0.08–0.13 cm\textsuperscript{-1}, which indicated that the Songhua River was obviously polluted by organic contaminants. The results are presented in table 2 and the data from the table clearly indicate a high catalytic activity of TiO\textsubscript{2}/Zeolite in the process of TOC and UV\textsubscript{254} due to ozonation.

Using ozonation alone with high ozone dosage, resulted in approximately 40\% efficiency of TOC removal after 30 min ozonation time. About 15\% TOC removal was achieved by adsorption of organic matter on catalyst surface. Ozonation in the presence of TiO\textsubscript{2}/Zeolite gave as a result approximately 65\% of TOC removal efficiency. This shows that catalytic ozonation increased 25\% efficiency of TOC removal from water when compared with ozonation alone.

Despite the relatively low efficiency of dissolved organic carbon removal from water, ozonation alone resulted in the high efficiency of UV\textsubscript{254} absorbance reduction of solution, 58\% of UV\textsubscript{254} absorbance reduction after 30 min contact time. Catalytic ozonation gave slightly better results: 73\% of UV\textsubscript{254} absorbance reduction after 30 min contact time. The high ability of ozone to lower UV\textsubscript{254} absorbance of solution and its relatively low ability to degrade TOC can be explained by the fact that only a partial oxidation of organic matter, without organic matter conversion to carbon dioxide, takes place. This can be explained by the nature of natural organic matter, which is known to consist of aromatic and aliphatic unsaturated constituents. Because of the direct reaction of ozone molecules with natural organic matter, these components, which are responsible for the absorption of UV\textsubscript{254} light, change into saturated, non-adsorbing UV\textsubscript{254} light intermediates. In summary, the results showed that catalytic ozonation on TiO\textsubscript{2}/Zeolite might be a successful tool for the removal of natural organic matter from water of high TOC value.

### Table 2. Degradation of TOC and UV\textsubscript{254} by TiO\textsubscript{2}/Zeolite catalyzed ozonation.

| Processes          | O\textsubscript{3}  | C\textsubscript{4} adsorption | O\textsubscript{3}+C\textsubscript{4} |
|--------------------|----------------------|-------------------------------|-------------------------------------|
| TOC removal, %     | 39.8                 | 15.0                          | 65.2                                |
| UV\textsubscript{254} removal, % | 57.9                 | 9.0                           | 72.5                                |

C\textsubscript{4}: TiO\textsubscript{2}/Zeolite calcined at 600 °C; O\textsubscript{3}: 19.8 mg min\textsuperscript{-1}; Catalyst: 100 g L\textsuperscript{-1}; Reaction time: 30 min; Temp: 20±3 °C; pH: 7.3–8.0.

3.3. Catalytic ozonation of Songhua River for ammonia and nitrate removal

![Figure 2. Variation of ammonia nitrogen concentration during catalytic ozonation.](image1)

![Figure 3. Variation of nitrate nitrogen concentration during catalytic ozonation.](image2)

Catalyst: TiO\textsubscript{2}/Zeolite calcined at 600 °C; O\textsubscript{3}: 19.8 mg min\textsuperscript{-1}; Catalyst: 100 g L\textsuperscript{-1}; Reaction time: 30 min; Temp: 20±3 °C; pH: 7.3–8.0
The concentration of ammonia nitrogen and nitrate nitrogen need to be controlled because of the possible eutrophication that may be caused by nitrogen. The results about the variation of ammonia nitrogen and nitrate nitrogen concentration during catalytic ozonation are shown in figure 2 and figure 3, respectively.

It is noticeable that single ozonation of the feed water caused the increase of ammonia nitrogen concentration at the first 5 min and then followed a decrease trend with reaction time. It is assumed that parts of organic nitrogen in the raw water were converted to inorganic nitrogen which is in the formation of ammonia by oxidizing action of ozone. That is the reason about the increase of ammonia concentration in the first stage of single ozonation process. And then ammonia was sequentially oxidized to nitrate or other form of inorganic nitrogen, thus lead to the following decrease of ammonia concentration as shown in figure 2.

Since zeolite has well adsorption ability and can do ion exchange with ammonia in the solution, the ammonia nitrogen concentration decreased from 2.59 mg L\(^{-1}\) to 0.57 mg L\(^{-1}\) within 30 min of contacting time to TiO\(_2\)/Zeolite catalyst.

With the combination of ozone and TiO\(_2\)/Zeolite catalyst, ammonia was transferred from solution to the surface of zeolite support by adsorption effect and ion-exchange reaction on the one hand, on the other hand, organic nitrogen in the solution was oxidized by catalytic ozonation so caused the increase of ammonia concentration. As a result, the ammonia nitrogen concentration follows a slower decrease curve during catalytic ozonation process with comparison to adsorption process and then approach to the final value at about 30 min.

It can be seen from figure 3 that the nitrate concentration of the solution keeps unchanged during the adsorption process, but nitrate concentration increased from 2.3 to 2.6 mg L\(^{-1}\) in ozonation process and from 2.5 to 2.2 mg L\(^{-1}\) in catalytic ozonation process, respectively. That is to say, some other forms of nitrogen were converted into nitrate nitrogen, which indirectly testified the imagination above-mentioned.

3.4. GC-MS chromatographic analysis results about catalytic ozonation

Organic impurities in surface water supplies have always been one of major concerns in drinking water treatment. Sewage discharge without sufficient treatment has become the main source of organic impurities in surface water. The Songhua River was obviously polluted by sewage and industrial waste. GC-MS analysis showed that even the raw water from Songhua River was treated by coagulation and sedimentation, there still remained about 50 kinds of organic matters in the solution. It can be seen from figure 4 that the organic mainly are acid, ester, phthalate ester, heterocyclic hydrocarbon, and aliphatic hydrocarbon.

**Figure 4.** GC-MS chromatographic analysis results.

Catalyst: TiO\(_2\)/Zeolite calcined at 600 °C; O\(_3\): 19.8 mg min\(^{-1}\); Catalyst: 100 g L\(^{-1}\); Reaction time: 30 min; Temp: 20±3 °C; pH: 7.3–8.0.
Both single ozonation and catalytic ozonation can decrease the organic content of the water. There were about 36 kinds of organic matters after the single ozonation process and the total organic peak area reduced by 23.5%. It is evident that catalytic ozonation process degraded the organic matter from water more efficiently. When the catalytic ozonation reaction carried 30 min, there still remained 20 kinds of organic matters which can be detected and the total organic peak area reduced by 62.5%.

4. Conclusions
Nanosized TiO₂ supported by zeolite was used in the ozonation process as catalyst. Nitrobenzene removal showed that TiO₂/Zeolite catalyst did increase the ozonation efficiency and 600 °C is the appropriate heat treatment temperature. Investigation about the TiO₂/Zeolite catalyzed ozonation of Songhua River was carried for TOC, UV₂₅₄, ammonia nitrogen and nitrate nitrogen removal. Catalytic ozonation gave as a result approximately 65% of TOC removal efficiency and 73% of UV₂₅₄ removal efficiency. This shows that catalytic ozonation increased 25% efficiency of TOC removal and 15% of UV₂₅₄ removal when compared with ozonation alone. The zeolite support shows good ability to remove ammonia nitrogen from water. It is assumed that some forms of organic nitrogen in the solution were oxidized into ammonia and then transferred into nitrate in catalytic ozonation process. GC-MS analysis results showed that about 30 kinds of organic matters were removed from water by catalytic ozonation and the total organic peak area was reduced by 62.5%. As a conclusion, TiO₂/Zeolite catalyzed ozonation is a promising deep treatment technique which can be used to control organic contaminant for drinking water.

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