Patent Analysis of Sulfur Autotrophic Denitrification Technology in China

Yihai Chen 1,2,*, Donghe Yang 1,2, Guangsheng Li 1,2, Qing Liu 3, Tao Huang 2,4

1. Shanghai Investigation, Design & Research Institute Co. Ltd., Shanghai 200335, China
2. China Three Gorges Corporation, Beijing 100038, China
3. School of Environment, Tsinghua University, Beijing 100084, China
4. Yangtze Ecology and Environment Co. Ltd., Wuhan 430062, China

* chenyh06@foxmail.com

Abstract. In order to grasp the overall status of sulfur autotrophic denitrification related patents, and better carry out sulfur autotrophic denitrification related research and intellectual property protection, based on the SooPAT Chinese patent search engine and Baiteng.com platform, from the first patent application year to the search deadline was to analyze the number, legal status, technical field distribution, and patent value of the sulfur autotrophic denitrification patents filed in China. The results showed that the number of patents filed each year had increased rapidly since 2012. The number of patents filed in 2019 was 10 times the number of patent applications from 2001 to 2011, and the patents granted were mainly concentrated in the field of sewage (waste) water treatment, accounting for 83.64% of the total number of patents. The overall patent value was in the middle and lower level, and there were no high-value patents.

Keywords: Sulfur Autotrophic Denitrification; Patent Value; Analysis.

1. Introduction

The removal methods of nitrate mainly included physical chemistry, chemistry and biology. The latter was generally considered as the most economical and effective method to remove nitrate pollutants in water [1]. According to the different carbon sources used by bacteria, biological denitrification could be divided into heterotrophic denitrification and autotrophic denitrification. The latter had the characteristics of low cost (no need to add organic matter), low energy, low sludge yield and high efficiency[2], especially in the field of low C/N ratio wastewater treatment[3], which had obvious economic advantages and broad application prospects. According to the different types of electronic donors, autotrophic denitrification technology mainly included hydrogen autotrophic denitrification, sulfur autotrophic denitrification, iron autotrophic denitrification and anaerobic ammonia oxidation[3-4]. The main research direction of autotrophic denitrification was sulfur autotrophic denitrification. The reduction sulfur (S2-, S0, SO32-, S4O62-, S2O32- etc.) was used as the electronic donor for sulfur autotrophic denitrification, and the dissolved oxygen was required to be less than 1mg/L. But denitrification process consumed alkalinity and produces high concentration of sulfate[5-6].

In this paper, the SooPAT patent search engine is used to search the patent status of sulfur autotrophic denitrification from the first relevant patent application year to the search deadline, and the patent value is inquired in Baiteng network. On this basis, the number, legal status, application year, process coupling, sulfate purification and patent value degree of the patents are analyzed, so as to provide reference for the research and intellectual property protection of sulfur autotrophic denitrification.
2. Overall Patent Situation

This paper was based on the patent data of SooPAT Chinese patent search engine (www.soopat.com). SooPAT is a free patent retrieval tool commonly used by users[7]. The search engine was founded in 2007, which could carry out domestic and worldwide patent search. Among them, the link of Chinese patent data come from the patent database of the State Intellectual Property Office. Taking "sulfur autotrophic denitrification" as the key word, the bibliographic information of sulfur autotrophic denitrification patents from the first related patent application year (2001) to the search deadline (January 13, 2021) was analyzed, so as to grasp the overall situation of sulfur autotrophic denitrification related patents in China.

From the first related patent application year (2001) to the search deadline (January 13, 2021), there were 154 patents on sulfur autotrophic denitrification, including two directions, namely denitrification and perchlorate removal. Among them, there were 148 denitrification patents and 6 perchlorate patents. Although sulfur autotrophic removal of perchlorate had been studied[8-10], this paper only analyzed the patents of sulfur autotrophic denitrification. Among 148 patents of sulfur autotrophic denitrification, 55 were entitled, 76 pending, and 17 not entitled.

During the 11 years from 2001 to 2011, the number of patent applications per year was small, with a total of only 4 patent applications. The number of patents applied in 2012 was 4, and the number of patents applied each year had increased rapidly since then. The number of patent applications in 2019 was 40, which was 10 times of the number of patent applications from 2001 to 2011. Among the 57 patents, 20 were utility model patents and 35 were invention patents. The latter held 63.64% of the total number of patents, and the proportion of invention patents was relatively high.

There were 32 applicants (the first applicant) for 55 patents. Except Nanjing University, Hangzhou Normal University and Zhihe Environmental Protection Technology Co., Ltd., which had the top 3 patents, 8 applicants, including Dalian University of technology, Jiangnan University and Zhongshan University, had 2 patents respectively, and one for 21 other applicants. The average number of patents was less than 2, and the applicants were scattered on the whole. However, the applicants with the top 3 patents held more patents, 18 patents in total, 32.73% of the total number of patents in possession, of which 11 were Nanjing University and 20.00% of the total number of patents.
Fig 1. Patent analysis of sulfur autotrophic denitrification
3. Application

3.1 Technical Field Analysis

There were 46 patents in the field of sewage or waste treatment technology, accounting for 83.64% of the total patents; There were 5 natural water treatment projects, accounting for 9.09% of the total patents; 3 gas purification patents, accounting for 5.45% of the total number of patents; One in-situ oxidation of sediment accounts for 1.82% of the total patents. Among the three patents for gas purification, one was the use of denitrifying tank to purify sulfide in biogas, one was a treatment system for simultaneous removal of hydrogen sulfide in waste gas and nitrogen removal in waste water, and the other was the use of selected strains to realize simultaneous denitrification or sulfur autotrophic denitrification.

Overall, sulfur autotrophic denitrification of patent protection mainly concentrated in the field of sewage or wastewater treatment technology, while in the natural water treatment, gas purification and sediment in situ oxidation of layout was less, and in chromium[11], bromate[12] and hexavalent uranium[13] have not yet had the right to the achievement of research, such as patents. There would be more space for research and intellectual property protection in the future.

![Fig 2. Distribution of patent technology fields of sulfur autotrophic denitrification](image)

3.2 Process Coupling

Among the 55 sulfur autotrophic denitrification patents, 32 only adopted sulfur autotrophic denitrification patents, occupying 58.18% of the number of patents, and the other 23 were coupling technologies of sulfur autotrophic denitrification and other denitrification technologies. Including 10 heterotrophic sulfur autotrophic denitrification - coupling technology, 7 pieces of anaerobic ammonia oxidation coupled - sulfur autotrophic denitrification technology, three pieces of autotrophic - hydrogen sulfide autotrophic denitrification coupling technology, 1 piece of iron autotrophic - sulfur autotrophic denitrification technology, 1 piece of iron autotrophic and heterotrophic sulfur autotrophic denitrification technology, and 1 piece of anaerobic ammonia oxidation - heterotrophic - sulfur autotrophic denitrification technology. The coupling processes of iron autotrophic and sulfur autotrophic denitrification [14], heterotrophic and sulfur autotrophic denitrification [15-16], anammox and sulfur autotrophic [17-19], and hydrogen autotrophic and sulfur autotrophic denitrification [20] could improve the denitrification efficiency and reduce the generation of sulfate and the consumption of alkalinity.
3.3 Sulfate Purification

In addition to 6 patents for which the sulfur source for autotrophic denitrification was not specified, the sulfur source in the remaining 49 patents was elemental sulfur (19 cases), sulfur ion (14 cases), pyrite (4 cases), pericarp (2 cases), and 2 combinations of the first 3 sulfur sources (6 cases) or 1 combination with other low-price sulfides (4 cases). Sulphur elemental substance was cheap, non-toxic, stable and easy to obtain[3], and was widely used. Among the 16 patents that used sulfur ions or sulfur ions and other sulfur sources, 5 patents were for added sulfur ions, 1 patent was for the treatment of wastewater containing sulfur, and the rest 10 patents were for the treatment of wastewater containing sulfur and nitrogen, realizing "waste treatment with waste". Pyrite mainly exists in the form of waste from mineral processing plants [3], and could be used as sulfur source for sulfur autotrophic denitrification to realize resource utilization. Sulphur autotrophic denitrification using sulfide [21]and pyrite[22] as sulfur sources could reduce the production of sulfate compared with that using sulfur as sulfur source. From the perspective of wastewater resource utilization, the anaerobic ammonium oxidation-sulfur autotrophic denitrification (ANAMMOX) and heterotrophic sulfur autotrophic denitrification (HUTD) based on sulfur compounds could not only synchronously remove nitrogen and sulfur but also recover resources, and would become the mainstream technology of sulfur autotrophic denitrification [21].

As for the sulfur products after sulfur autotrophic denitrification, except for the specific products which were not specified in the 13 patents, 8 were elemental sulfur, occupying 14.55% of the number of patents, which could realize resource utilization. 34 were sulfates, accounting for 61.82% of the patents. It could be seen that there were more patents in which the product of sulfur autotrophic denitrification was sulfate. Studies had shown that the actual sulfate produced was very close to the theoretical value[23-24]. When the influent NO$_3^-$-N mass concentration is 30mg/L, the sulfate concentration was 274.7mg/L, and when the influent NO$_3^-$-N mass concentration was 80mg/L, the sulfate concentration was 698.4mg/L, which proved that the actual sulfate produced was very close to the theoretical value[24]. According to China's Drinking Water Sanitary Standards (GB5749-2006), sulphate concentrations in water above 250mg/L were considered a pollutant, and excessive intake of sulphate could cause gastrointestinal disorders. Therefore, the sulfate concentration in the effluent of sulfur autotrophic denitrification needed to be controlled.

Among 34 sulfur autotrophic denitrifying products with sulfate, 18 patents were sulfate-free purification measures. Although there were no sulfate purification measures in the 10 patents, the coupling technologies (such as iron autotrophic - sulfur autotrophic denitrification, heterotrophic - sulfur autotrophic denitrification, Anammox - sulfur autotrophic anaerobic ammonium oxidation, hydrogen autotrophic - sulfur autotrophic denitrification, etc.) could reduce the generation of sulfate root; Only six patents had specific sulfate purification measures, including electrodialysis, adsorption of modified hydrotalcite, fixation of calcium ions in solid carriers, reduction to divalent sulfur as a further sulfur source, or conversion to elemental sulfur, etc. In addition, there were few patents on how to remove sulfur ions as by-products [25], and even the related research is very limited [23].

Due to technological reasons, the process of sulfur autotrophic denitrification was accompanied by the consumption of alkalinity[3]. As the main denitrification process, external addition of alkalinity was required. 21 patents included no or no mention of alkalinity adjustment, 27 patents included process adjustment to reduce alkalinity consumption by directly adding acid or alkali or using alkaline fillers to balance pH, and 7 patents included process adjustment to reduce alkalinity consumption.

4. Analysis of Patent Value

4.1 Patent Value

The patent value analysis adopted the index system of patent value analysis jointly developed by the State Intellectual Property Office of China and China Technology Exchange in 2010, and the
research was carried out on the platform of Baiteng (https://www.baiten.cn). The patent value degree of Baiteng.com constructed the patent value evaluation from three aspects: technical, economic and legal value. The technical value was mainly mined from the description information and legal events of the patent application, the economic value mainly indicated the expected benefits that the patented technology might bring in the process of commercialization, industrialization and marketization, and the legal value was mainly evaluated from the perspective of the stability of patent right. The total score of patent value was 100 points, including 55 points for technical value, 20 points for economic value and 25 points for legal value. The patent value of each patent was available free of charge.

4.2 Analysis of Overall Patent Value

Among the 55 patents, the maximum value of patent value was 66, the minimum value 46, the mean value and the median value both 53.0, and the dispersion degree is 0.09, indicating that the overall patent value of sulfur autotrophic denitrification was below the medium level, and there were no high-value patents, and the patent value is relatively concentrated.

The value degree of utility model patents mainly concentrated between 52 and 54, with 12 patents, accounting for 60% of the number of utility model patents, while there were 16 utility model patents with medium value, accounting for 80% of the number of utility model patents. The value of invention patents mainly concentrated in the range of 46~50 and 54~57, with 16 and 12 patents, respectively, accounting for 45.71% and 34.29% of the number of patents, while there were 22 patents with medium value, accounting for 62.86% of the number of patents. Although the number of invention patents with medium patent value was more than the number of utility model, the proportion of the number of invention patents occupying was still low. At the same time, in terms of low level patent value, invention patents were superior to utility model patents in both number and proportion of patents. Therefore, compared with utility model patent, invention patent should enhanced its patent value.

![Fig 3. The number distribution of patents with different patent values](image)

Through the comparative analysis of technical value, economic value, legal value and the total score of their respective values, it was found that the ratio of the average value of technical value and the average value of legal value to the total score of technical value and legal value was 0.57 and 0.54, which was similar to the ratio of the median value of patent value (53/100=0.53). The ratio of average economic value to total economic value was 0.37, which was far from the median value of patent value. It showed that both utility model patents and invention patents had lower overall economic
value, and that the patented technology might bring lower expected benefits in the process of commercialization, industrialization and marketization.

Table 1. Contribution of patent value

<table>
<thead>
<tr>
<th>Type</th>
<th>Average score of technical value/total score of technical value</th>
<th>Average score of economic value/total score of economic value</th>
<th>Average score of legal value/total score of legal value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utility model patent</td>
<td>0.59</td>
<td>0.36</td>
<td>0.52</td>
</tr>
<tr>
<td>Invention patent</td>
<td>0.55</td>
<td>0.39</td>
<td>0.57</td>
</tr>
<tr>
<td>Total</td>
<td>0.57</td>
<td>0.37</td>
<td>0.54</td>
</tr>
</tbody>
</table>

SPSS22.0 version was used to analyze the relationship between patent value degree and patent type, technical value, economic value, legal value and remaining protection years, and it was found that patent value degree was significantly correlated with legal value and remaining protection years at 0.01 level (bilateral). At the same time, there was a significant correlation between legal value and patent remaining protection years at the level of 0.01 (bilateral). The results showed that the patent value of sulfur autotrophic denitrification was significantly related to the legal value and duration of the patent. Improving the legal protection and extending the duration of patent maintenance could help to improve the patent value.

5. Conclusion and Prospect

5.1 Conclusion

Based on SooPAT Chinese patent search engine and Baiteng.com platform, the patents in sulfur autotrophic denitrification filed for publication from the first patent application year (2001) to the search deadline (January 13, 2021) in China were analyzed. There were 148 patents for sulfur autotrophic denitrification, among which 55 patents were entitled, 76 patents were under review and 17 patents were not authorized. In the 11-year period from 2001 to 2011, there were only four patent applications. The number of patents filed each year had increased rapidly since the beginning of 2012, and the number filed in 2019 was 10 times the number filed in the 11-year period from 2001 to 2011.

The patents were mainly concentrated in the field of sewage (or wastewater) treatment technology, occupying 83.64% of the total number of patents, the layout of groundwater treatment, sulfur-containing gas purification, in-situ oxidation of sediment and surface water treatment was less, there was more room for research and intellectual property protection in the future. Sulphur sources were mainly elemental sulfur and sulfur ions, and the products after the utilization of sulfur sources were mainly sulfate, but there were also a small number of patents devoted to the recovery of sulfur elementals, so as to realize the utilization of waste resources. However, only a small number of patents with sulphate as the product of the autotrophic denitrification considered sulphate purification measures.

Among the 55 patents, the average value and median value of patent value were both 53.0, and the dispersion was 0.09. The overall patent value was below the medium level, and there were no high-value patents. In terms of low level patent value, both the number of patents and the proportion of invention patents were higher than that of utility model patents. At the same time, the analysis also found that the overall economic value of both utility model patents and invention patents was low, and the expected benefits of patented technology in the process of commercialization, industrialization and marketization were low. Patent value degree was significantly related to the legal value of relevant patents and the duration of patent maintenance. Improving the legal protection and extending the duration of protection in the application of intellectual property protection would help to enhance patent value degree.
5.2 Prospect

With the deepening of ecological civilization construction and the continuous increase of wastewater resource utilization, the sulfur autotrophic denitrification technology with the characteristics of low cost (no need to add organic matter), low sludge yield and high efficiency will get more research. Accordingly, the relevant research results will receive more intellectual property rights protection, and the patent of sulfur autotrophic denitrification will further increase in the future. Its patents will not only focus on the field of sewage (or wastewater) treatment technology, in natural water treatment, gas purification, sediment in situ oxidation and other aspects of the layout will also have a considerable scale.

In the patent of sulfuric autotrophic denitrification product is sulfate, on the basis of realizing denitrification function, sulfate purification measures and alkalinity adjustment will be two important perspectives to consider, which will be more intuitionistic reflected in more patent texts.

As China pays more and more attention to the protection of intellectual property rights, the examination of invention patents will be stricter, the number and proportion of low-value invention patents will decrease, and the economic value of patents will increase. When applying for intellectual property protection, more attention will be paid to improving legal protection and extending protection time to enhance value.

Acknowledgments

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References


