Research on the Development Status of biochar for Cr (VI) remediation Technology Based on Patent Analysis

Miao Liu*
Department of Applied Chemistry, Liaoning Petrochemical Vocational Technology College, Jinzhou, Liaoning, China

*Corresponding author e-mail: amelia_lau820@hotmail.com

Abstract. More and more chromium (Cr) is being discharged into the environment, which is posing ecological risks to animals, plants and microorganisms, and endangering human health. Hexavalent Cr (VI) was more toxic than trivalent Cr (III), and the mobility of Cr (VI) in the water environment was higher than that of Cr (III). Therefore, various effective methods of reducing Cr (VI) were developed. In this research, the "biochar", " chromium remediation", were taken as keywords for patent retrieval. The retrieval time is from 1986 to 2019. A great number of patents about Cr (VI) remediation and biochar are collected and analysed applying big data. Based on the number and the legal status of patent applications, and the trend of patent applications, the research situation of biochar for Cr (VI) remediation in China is studied by S-curve law which is used to describe the technology life cycle theory in TRIZ theory. The results show that the technology of biochar for Cr remediation is still in its initial stage and full of potential.

1. Introduction

Heavy metals are characterized by strong harmlessness, long residence time and difficulty in degradation. Curing/stabilization remediation technology can effectively reduce the solubility, migration and toxicity of heavy metals in water and soil [1]. Chromium is listed as one of the key heavy metal elements for prevention and control in China's comprehensive prevention and control of heavy metal pollution during the 13th five-year plan. It mainly exists in Cr (III) and Cr (VI) valence states and largely comes from industrial wastewater such as electroplating, dyeing, tanning, pigments, and photographic materials. Chromium is an essential trace element in human body, which is closely related to lipid metabolism. It is generally considered that Cr (III) is less harmful as it is easy to form alkaline precipitation in water and reduce the migration in the environment while Cr (VI) has a strong toxicity and strong oxidation, and is highly corrosive to the skin and mucous membrane [2]. As it is easy to dissolve in water, Cr (VI) also has a strong migration in the environment, causing great harm. Therefore, Therefore, the removal of Cr (VI) has become a hot issue in environmental research.

Adsorption method is one of the main methods to remove heavy metal ions from water and soil because of its high efficiency, simplicity, and good selectivity. Due to the low cost, large specific surface area, high porosity, alkalinity and easy adsorption of soluble organic matter, biochar has gradually become a research focus of adsorption methods in recent years, which can be used as an adsorbent to reduce the content of transportable heavy metal ions in water and soil. It is reported that biochar prepared
by peanut shell, rice straw or corn straw haves good adsorption effect on heavy metals in water, and biochar can be modified to improve its adsorption effect [3].

In 1946, Genrich S. Altshuler, from the former Soviet Union, reviewed a large number of patents and found that the success of some products was due to the compliance with a certain objective law, which is the development law of the technical system. He combined the patent analysis method with the invention problem solving theory and summarized the TRIZ theory, which means "invention problem solving theory". The problem-solving tools used by TRIZ theory include the invention principle, the invention problem solving algorithm ARIZ, and the standard solution system. During the development of the technical system, the main parameters of the technical system change, which is the regular and continuous transformation of the system from one specific state to another. These parameters are not linear over time and have a shape like an S-curve [4]. Therefore, S-curve law is one of the important analytical tools of TRIZ theory. In this paper, many patents about Cr (VI) remediation and biochar are analyzed applying big data combined S-curve law in TRIZ theory to investigate development prospect of biochar remediation for Cr (VI).

2. Application of big data analysis

Big data includes structured data, semi-structured data, and unstructured data. With the development of The Times, unstructured data will occupy more proportion. Only through analysis can big data obtain in-depth and valuable information. Prediction based on correlation analysis is the core of big data. When knowing "what", "why" is not so important. Therefore, in the era of big data, the analysis of data no longer pursues the elusive causal relationship but focuses on the correlation of things. The analysis of big data relationship is to directly study the dependency between phenomena, which is both connected and related.

The most important content of big data analysis is data mining, which is a process of extracting hidden, unknown and potentially applicable patterns from a large number of incomplete, noisy, fuzzy and random data by scientific methods in the fields of mathematics, statistics, artificial intelligence and machine learning. The related methods of data mining include clustering method, neural network method, genetic algorithm, decision tree method, fuzzy set method, etc. The foundation of big data is big data computing. Big data computing is a necessary way to discover information, mine knowledge and satisfy the application. It is also the core link of big data from collection, storage, calculation to application. The big data computing mode mainly includes batch computing, stream computing and interactive computing. Currently, the typical application system for bulk computing of big data includes Hadoop, which is composed of name node, data node and client node. The client node realizes file operation by communicating with the name node and data node and accessing HDFS. The data is organized by means of HDFS, all kinds of data are stored on various external storage media, and the calculation logic is allocated to each data node for data calculation and knowledge discovery through MapReduce mode [5].

3. Methods and results

3.1. Data collection and patent analysis for “biochar” in CPFTD

Data have been collected from China Patent Full-Text Database (CNKI Version) which contains three suture database -- invention patent, utility model and appearance design patent in China. Each database from CPFTD is the source of patents' relevant literatures and achievements. In the patent search, the keyword “biochar” was firstly searched in Title OR Abstract OR Claims. A total of 16,842 biochar patents published from 1986 till now were retrieved from 10,6991,078 patents published. Then Remove irrelevant patents to environmental remediation were excluded by the IPC classification. The retrieval time is from 1986 to 2019. There were 3,451 cases left, including 2,142 invention patents and 1309 utility model patents. At present, 1,375 cases are authorized, 1,166 case are under verification and 910 cases are invalidated. The results of patent analysis were shown in Fig.1. The number of patents filed from 1986 to 2001 was in the single digits, and the number of patents grew very slowly, accounting for
1.16% of the total. Since 2002, the biochar for environmental remediation patent began to speed up the growth rate, especially in latest 5 years. From 2015 to 2019, the number of patents in this field in China increased rapidly, accounting for over 70% of the total.

3.2. Data collection and patent analysis for “chromium remediation” in CPFTD

Keyword "chromium remediation" were searched in CPFTD as well. As shown in Fig.2, 926 relative patents were published from 1986 to 2019, including 836 invention patents, 89 utility model patents and 1 design patent, which is much less than keyword “biochar”. Among those patents, 237 cases are authorized, 399 case are under verification and 290 cases are invalidated. The number of patents filed from 1986 to 2004 was in the single digits, and the number of patents grew very slowly, accounting for 4.86% of the total. Since 2005, the Cr remediation patent began to speed up the growth rate. In 2010, the number of patent applications increased over twice compared with 2005. From 2015 to 2019, the number of patents in this field in China increased rapidly, accounting for 63.39% of the total.

Figure 1. Trend in patent application for biochar in China

Figure 2. Trend in patent application for chromium remediation in China
3.3. Data collection and patent analysis for “biochar for chromium remediation” in CPFTD

The keyword "biochar for chromium remediation" were searched in CPFTD as well. As shown in Fig.3, 22 relative patent applications were published from 2013 to 2019, all of which are invention patents. Among those patents, 3 cases are authorized, 14 cases are under verification and 5 cases are invalidated. Among those patents, there are 14 cases from universities and research institutes, accounting for 63.64% of the total, 5 cases from enterprises, 2 cases from individuals and 1 case from enterprise combined university.

Figure 3. Trend in patent application for chromium remediation in China

4. Discussion

The life cycle of a technology is usually composed of four parts, which are initial stage, growth stage, maturity stage and decline stage. In the initial stage, the technology development level is very low, and the number of patent applicants and patent applications is very small as well. With the gradual expansion of relevant industrial markets and the attention of the state, enterprises and scientific research institutions, technological innovation has been rapidly promoted, and technological development has entered the growth stage. When the technology level reaches a certain level, the number of patents increases slowly, the r&d investment decreases, and the technology development enters the mature stage. When the technology development is relatively mature and meets the technical bottleneck, it enters the recession period. Technology life cycle analysis has become an important method for scholars to study the development of technology innovation in a certain industry[6]. Since the S-curve can well reflect the development trend of an industry technology field from the introduction period, growth period, maturity period to the decline period, this paper selects the S-curve method to analyze the technical life cycles of
biochar, Cr remediation and biochar for Cr remediation. According to the result of patent analysis, the annual distribution of patent applications can be directly reflected by drawing a curve for the number of patent applications per year in Fig. 4.

![Figure 4. Trend in patent application for chromium remediation in China](image)

It can be seen from Fig. 4 that the patent application for biochar in environmental remediation field was developed very slowly from 1986 to 2001, which indicates that technology of biochar applied in environmental remediation belongs to the first stage of the S-curve. In this period, the raw materials of biochar were considered as wastes rather than resources which lead to the lock of biochar production and utilization. In addition, the government did not pay high attention to environmental pollution, especially the disposal of heavy metals, which is also the main reason that technology of chromium remediation was in the initial stage of the S-curve at the same time.

Since 2005, biochar is considered as a kind of remediation material developed rapidly in recent years with a good effect on heavy metal pollution remediation and becomes a hot issue in the field of environmental research. The numbers of patents for biochar and Cr remediation have almost been increasing year by year, that means these technologies have entered the second stage of the S-curve, which is the growth stage of the technical system. Based on the research achievements in recent years at home and abroad, it is known that the physical and chemical properties of biochar are mainly affected by raw materials and pyrolysis temperature, which together determine the effect of repairing heavy metal contaminated soil. Biochar was treated by activation, magnetization, oxidation and digestion, which significantly improved the properties of biochar and improved the restoration efficiency. Due to the porous structure, biochar can repair heavy metals in the soil, thus affecting the mobility and bioavailability of heavy metals, including two aspects: fixing heavy metals reduces bioavailability or transferring heavy metals increases bioavailability. The former is the main restoration effect, while the latter can improve the performance of biochar and reduce the mobility and bioavailability of heavy metals through modification. Furthermore, biochar can be applied with other curing materials to improve the strength of the Solidification. In this stage, the main performance parameters of the technology are rapidly improved, the output is rapidly increased, and the cost is reduced. And as the rate of return increases, the amount of investment in the market increases dramatically, and the introduction of specific resources makes the system more efficient. This stage is suitable for the popularization of technology and products.

Although the technology of both Cr remediation and biochar for environmental remediation is becoming more and more mature, the technology of biochar for Cr remediation is still in its infancy. That is mainly because of Cr (VI) is difficult to be absorbed directly by biochar, so Cr (VI) needs to be
reduced to Cr (III) or immobilized by biochar modified or combined other materials. However, on the bright side, due to the development of biochar production technology and remediation technology of Cr contaminated Site, the biochar chromium restoration technology can be widely used as soon as the key point of Cr adsorption or immobilization is solved. Therefore, it is considered that biochar for Cr remediation technology is a huge potential field with sufficient raw materials, the gradually improved market and the technical development pattern.

5. Conclusion
Based on the patent analysis applying big data combined S-curve law in TRIZ theory, technological innovation trend of biochar for Cr (VI) remediation in China is studied, from which we can get the following conclusions. After more than 30 years of scientific and technological development, combined with the rational guidance and strong support of government policies, biochar for environmental remediation technology has entered a growth period, showing a rapid development state, the industrial ecological structure has been gradually improved, the technical development pattern has been preliminarily established while the technology of biochar for Cr remediation is still in its initial stage and full of potential.

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