Bibliometric Analysis on Decontamination of Chemical Warfare Agents in Last Thirty Years

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Abstract. Occurrence of large-scale biochemical wars is of little possibility today, but the international chemical security situation is still not optimistic. Effective decontamination of chemical warfare agents has received close attention, becoming a global necessity. In this paper, data in the Web of Science Core Collection database were selected to systematically investigate the relevant literature about the research progress on decontamination of chemical warfare agents from 1990 to 2020. Origin Pro 2019b and CiteSpace were conducted for multi-dimensional bibliometric analysis on literature type distribution, number of annual publications, countries, institutions, journals, authors, literature co-citation and citation bursts. By August 1, 2020, there are 2,602 papers related have been published and the number of annual publications shows a linear growth tendency. Amongst all 71 countries, United States is the country with the most publications as well as the largest centrality value. US ARMY ranks fourth in the number of publications while with the highest institution-based cooperation. “Nerve agents and blister agents”, “metal-organic frameworks” and “applications of metal-organic frameworks” are prevailing in recent years, which highlights the latest development direction and research frontiers. This article promotes scientific predictions and impact assessments of decontamination of chemical warfare agents.

1. Introduction
Chemical weapons are weapons of mass destruction, they cause physical damage to people, bringing enormous and profound fear of humans and society. Since the World War I, the German army used chlorine as a weapon to kill the enemy in actual combat for the first time, various chemical warfare agents (CWAs) emerged one after another. Although the Chemical Weapons Convention restricts the use of chemical weapons, the threat of traditional chemical weapons still exists, especially in local wars and terrorist activities [1]. Terrorist activities such as the Tokyo subway Sarin attack and the Novichok incident have shocked the world [2]. In the meanwhile, the emergence of new chemical weapons and the diversification of threat sources make it impossible for us to relax our vigilance. From the perspective of national defense and civilian life, chemical warfare agents (CWAs) have always been an urgent issue of concern around the globe [3]. As a result, it is of great significance to investigate the decontamination of CWAs.

In this research, bibliometrics and visualization tools were used to systematically sort out the research process on the decontamination of CWAs. An objective and comprehensive summary of the research status and hotspots was provided to help scholars conduct further research. Up to our best knowledge,
this study is the first to apply CiteSpace for visualizing and better understanding the global research trends and hotspots from big data in this field.

2. Methods
Using a comprehensive search strategy, the literatures on the decontamination of CWAs were screened from the core collection of Science Web (WoSCC), including SCI-EXPANDED, A&HCI, SSCI, CCR-EXPANDED, IC, etc. The Boolean operation run in the "Advanced Search" column of the WoSCC platform was comprised by two kinds of subject terms “decontamination” and “chemical warfare agents”. 2602 results were extracted, including citations, as samples of the analysis data. All the retrieval results of the 2,602 papers were exported to both Origin Pro 2019b and CiteSpace V for analyzing. The Origin Pro 2019b was utilized to analyze the characteristics of annual publications. The CiteSpace V was used to conduct multi-dimensional bibliometric analysis on countries, institutions, journals, authors, document clusters, literature co-citation and citation bursts in this field.

3. Results and Discussion

3.1 General data
In the past 30 years, the number of annual publications on the degradation of CWAs has shown a linear growth trend ($R^2=0.9527$), indicating that this field has obtained continuous attention (Figure 1). There were 1,438 documents issued from 2010 to 2019, accounting for a proportion of 55.26%, which was 1.83 times and 5.06 times that of 2000-2009 and 1990-1999, respectively. The tendency of published papers is sustainably upward, revealing that this field has developed rapidly in recent years.

The global cooperation relationship map between countries/regions from 1990 to 2020 was shown in Figure 2, which consisted of 47 nodes and 244 links in the network of collaborating countries. The size of the network node indicates the contribution of the country/region and the connecting line indicates that there is a cooperative relationship between the countries. The warmer the color in the map, the closer the published article is to the current time. Cooperation among countries around the world is relatively close. The USA has a tremendous advantage over other countries in the degree of cross-country cooperation and its number of published papers is 4.37 times more than the second-ranked China. Meanwhile, the centrality value of the USA is the highest, at 4.26 times that of India, which ranks second.
Figure 2. A visualization of the country collaboration network

2,602 papers were published by 1,806 institutes with 338 nodes and 381 links in the network of collaborating institutes from 1990 to 2020 (Figure 3). Different from the global cooperation relationship, cooperation among global institutions is relatively loose. An institution with an output of 31 papers is in the top 10, indicating that no institution has conducted abundant research in this domain or there is a good deal of their achievement has not been disclosed. Nonetheless, combining the number of publications and the centrality value for analysis, it can be seen that the quantity of papers issued by US ARMY (44 papers) ranks fourth, and the degree of institution-based cooperation is the highest. Relevant data suggested that the outcome of this institution in this field is worthy of attention by scholars.

Figure 3. A visualization of the institution collaboration network

3.2 Citation data
The network of author co-citation was comprised by 1,155 nodes and 8,031 links from 1990 to 2020 (Figure 4). JOURNAL OF CHROMATOGRAPHY A ranks first concerning the number of published papers. JOURNAL OF HAZARDOUS MATERIALS appears in both the top ten most productive journals and the top ten co-cited journals, which is one of the world's preeminent journals in the areas of Environmental Science and Engineering, manifesting its far-reaching impact in this field.

As shown in Figure 5, the network of author co-citation was comprised by 1,155 nodes and 8,031 links from 1990 to 2020. Authors, whose publications exceed 30, enter the top 10 and they are classified as "prolific authors". Three of these most productive authors (WOREK F, PRASAD GK, WAGNER GW) are also listed in the top 10 co-cited authors, indicating that these three authors have papers of high quality in addition to plenty of outputs.
3.3 Research hotspots
Burst citations are responsible for making reasonable predictions about the frontiers of a field, which contributing to accurately grasp the development dynamics and hotspots. There are 36 documents still prominent until 2020 among all 124 burst citations, which highlighted the latest development direction and research frontiers in this field. Through the analysis of the 36 burst citations, the following three hotspots were found.

3.3.1 The most popular CWAs
Almost all the papers that have sharply emerged are about decontamination of nerve agents or blister agents. Guo, W. et al. [4] claimed that among all the chemical weapons, nerve agents and sulfur mustard, known as “the king of chemical agents”, are the most common. Organophosphate nerve agents, designed to inhibit the activity of acetylcholinesterase, destroy the normal function of the nervous system and ultimately result in death by asphyxiation [5]. The nerve agents VX is of primary concern due to the fatal reactivity [6], and one of its detoxification products, EA-2192, is highly toxic [7].

3.3.2 Metal-organic frameworks
Metal-organic frameworks (MOFs) are made through network synthesis, which form strong bonds between the inorganic and organic units. Organic units are polytypes of organic carboxylates and other similar negatively charged molecules. When connected with metal-containing units, they produce a strong crystalline MOF structure [8]. Compared with activated carbon, its performance, capable of both acidic and basic chemistries, is more prominent [9]. Owing to extraordinarily high surface area, ultrahigh porosity, adjustable internal surface properties and water stability, MOFs attracted widespread attention [10,11].

Zr-MOFs emerge as state-of-the-art catalysts and cause extensive research [12] due to the combination of the strong Lewis-acidity and bridging hydroxide anions, which lead to ultrafast decontamination of nerve agents [13]. Compared to microcrystalline material, nanocrystals of Zr-based MOFs significantly enhance the decontamination of a nerve agent simulant which may be attributed to the larger external surface areas and faster diffusion [14]. Pyrene-based [15] and Zr-based30 [16] MOFs generate singlet oxygen under ultraviolet radiation, effectively and selectively oxidizing sulfur mustard to non-toxic products. On the basis, Atilgan, A. et al. [17] improved the photo oxidation method by synthesizing a BODIPY-functionalized Zr-MOF and using a simple incorporation method (SALI) which can screen various tunable BODIPY molecules as detoxifying photosensitizers for sulfur mustard. Scholars try their best to optimize the decontamination performance of materials. Related research showed that the presence of an amine is one of the most crucial factors controlling the rate of hydrolysis in water [18]. Peterson, G. W. et al. [19] tailored the functionality of UiO-type MOFs by changing the linker size and property to
perfect destroy CWAs. Dual function MOF catalysts that can detoxify both nerve agents and sulfur mustard, which are research hotspots, simultaneously are also discussed [20,21]. Due to the special structure of MOF materials, its decontamination performance to CWAs deserves our attention.

3.3.3 The applications of metal-organic frameworks

The present protective equipment perform only as the physical barrier, but CWAs may cause secondary contamination due to desorption [3]. Hence the development of self-detoxifying materials is an effective measure against attacks using CWAs. Due to the special properties of the MOF materials, it can be integrated into fiber, film or fabric through multifarious advanced technologies to degrade CWAs [22], such as electrospinning, dipping, coating, spraying and crystal growth on fiber surface.

Giannakoudakis, D. A. et al. [23] synthesized smart textiles composed of Cu-BTC MOF, cotton and g-C$_3$N$_4$-ox, which can effectively detoxify a nerve gas surrogate. The decontamination process along with visible gradual discoloration is used to selectively detect CWAs and monitor their penetration in a protective layer. Similarly, the nanofiber textiles and MOF materials were compounded to prepare materials to decontaminate CWAs, which may be used in the preparation of protective clothing in the future [24,25]. Silica nanoparticles impregnated with reactive chemicals such as trichloroisocyanuric acid showed good physisorption and degradation performance of CWAs [26]. Lithium alkoxide was loaded on Zr-MOFs to improve phosphotriesterase catalytic activity. These materials were integrated into textiles to combine the air permeability of textiles with the self-sterilizing properties of MOF materials. These MOFs have excellent degradation ability, but they mainly exist in the form of dispersed powders. As a skin protection material, they need to be combined with polymer matrix materials to increase the flexibility of MOFs and make them into clothing materials. Although there are many challenges remaining for combining MOFs with protective garments [27,28], it provides some references for further research with the advancement of science and technology.

MOFs have good thermal and chemical stability, which has greatly improved the gas storage capacity and led to their extensive research in selective adsorption and separation, molecular and optical/thermal sensing, organic reaction catalysis, biomedical imaging and so on. Currently, methods for manufacturing and incorporating MOF nanocrystals into devices are being developed [29,30]. Similarly, powdered MOFs are difficult to employ and need to be granulated to better achieve the above functions.

4. Conclusions

This bibliometric analysis on decontamination of chemical warfare agents may be helpful for researchers to realize the research frontiers and hotspots of this field. Investigation indicated that the number of annual publications increased linearly from 1990 to 2020. The USA has a tremendous advantage over other countries in the number of publications as well as the highest centrality value. What is different from close country-based cooperation is looser inter-institute cooperation. DEF RES DEV ESTAB was the largest productive institute, while US ARMY had extensive collaborations with other institutes, whose papers deserve our attention. The leading edge was detected as follows: “nerve agents and blister agents”, “metal-organic frameworks” and “applications of metal-organic frameworks”, which deserve much attention in further study. It is significant for maintaining world peace and sustainable development.

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