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PHOTOCATALYTIC ACTIVITY OF MOLYBDATES: A TECHNOLOGICAL PROSPECTING

ATIVIDADE FOTOCATALÍTICA DOS MOLIBDATOS: UMA PROSPECÇÃO TECNOLÓGICA

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Abstract

Among the several applications of molybdates, the photocatalysis is a highly appealing process with multiple applications, mainly in the fields of pollution removal. In view of this, the main objective of this work was to study the potentialities and the evolution of the technological features inherent to patent deposits, and panorama of publications of articles on molybdates, as well as the related photocatalytic a properties, specifically in the range years from 2000 to 2017. The study was performed using information from the Web of Science, SciELO, European Patent Office (EPO), United States Patent and Trademark Office (USPTO), Derwent Innovations Index, and the database of the National Institute of Industrial Property (INPI) of Brazil. The research has shown growth in the number of patents and articles over the years. Brazil is well positioned in the world ranking of publications of articles containing photocatalytic properties of molybdates, but does not display patents filed with INPI. Regarding the world stage, the results indicate a promising area with significant growth in the number of patents and scientific articles. .

Key-words: Molybdate, Patents, Articles, Technological Prospecting.

1. Introduction

Molybdates constitute an important class of materials belonging to the group of transition metal oxides that exhibit various functional properties, which depends on the structure (MACZKA et al., 2012, p. 1337). The molybdates have attracted wide attention due to their physical properties and applications such as photoluminescence (GOUVEIA et al., 2014, p. 5589), photocatalytic properties (MOURA et al., 2017, p. 261), humidity sensor (RAJ et al., 2002, p. 230), magnetic properties (DING et al., 2007, p. 747), anode for lithium-ion batteries (ZHENG et al., 2015, p. 449), pressure induced amorphization (MOURA et al., 2016, p. 88), phase transition (MOURA et al., 2016, p. 98) and antibacterial activity (TANG et al., 2013, p. 124). In addition to diverse applications, these materials have the advantage to be obtained with different synthesis routes, favoring a wide variety of sizes, morphologies, and structures (GOUVEIA et al., 2014, p. 5590; MOURA et al., 2016, p. 89; TANG et al., 2013, p. 124).

With the great rationing of drinking water in the world, leaders have focused on mechanisms of water decontamination, thus promoting the disposal of water in nature in order to reduce environmental pollution. The contamination of water is mainly due the agricultural practice with the use of pesticides and the contamination of water by the use of dyes in the industry. As a consequence, it has become a theme of study by the scientific community around the world, with the intention of reducing the damages caused on the environment. Faced with this series of factors, water pollution has been a subject of extreme interest in all parts of the world in both developed and developing countries. Brazil is a pioneer in the issuance of regulatory standards for the disposal of liquid effluents, as exemplified in the Normative Instruction No 2, of January 3, 2008 (BRASIL, 2008, p. 3). These are new labor standards to be followed by agricultural aviation in accordance with the operational and safety technical standards for this sector (MOURÃO; MENDONÇA, 2009, p. 2181).

In view of this, the search for new technologies applicable to the treatment of domestic and industrial effluents, which are more innovative, less expensive and that prioritize the environmental component, has grown. However, it is not enough to develop technologies to qualify, quantify, control and treat effluents. An issue as important as treating what is already polluted is to develop processes with the minimum generation of waste, thus avoiding the production of more effluent to be treated. Advanced oxidative processes have been widely used as an alternative in the treatment of contaminated effluents, especially photocatalytic processes used in the treatment of water contaminated by organic compounds. Among several applications of molybdates, the photocatalysis is a highly appealing process with multiple uses, mainly in the field of pollution removal (MOURA et al., 2017, p. 262). The molybdates have opened interesting perspectives of use in the photocatalysis area because of the possibility of their production with different morphologies, high

surface area and reduced size (CAVALCANTE et al., 2013, p. 344; FU et al., 2007, p. 696; LI; XUE; LIU, 2015, p. 1911; SONG et al., 2010, p. 1123).

Based on the foregoing, the main objective of this work was to study the potentialities and the evolution of the technological features inherent to patent deposits, and a panorama of publications of articles on molybdates, as well as the related photocatalytic properties, specifically in the years expanding from 2000 to 2017. In order to obtain the data, research was carried out in the patent databases: Derwent Innovations Index (DII), European Patent Office (EPO), United States Patent and Trademark Office (USPTO) and National Institute of Industrial Property of Brazil (INPI) (DII, 1963; EPO, 2018; USPTO, 1994; INPI, 2014). It is important to note that the Derwent Innovations Index is not a patent filing platform, it is a patent search database.For the search for information regarding the publication of articles, the Web of Science and SciELO databases were used (WEB OF SCIENCE, 2015; SCIELO, 2014).

2. Methods

The present work was based on the technological prospection having as source of patents deposited in the following databases: Derwent Innovations Index, European Patent Office (EPO), United States Patent and Trademark Office (USPTO) and National Institute of Industrial Property of Brazil (INPI). The search in the patent databases was carried out using the advanced search options, with keywords present in both title and abstract, also employing the Boolean operator´s features, the truncation characters and the filing date of patents between 2000 and 2017. The terms and combinations used for the research were: “Molybdate (Molibdato)”; and “Molybdate AND Photocataly* (Molibdato AND Fotocatali*)”. The asterisk (*) truncation character was used with the purpose of facilitating the search, the term "Photocataly* (Fotocatali*)”, comprises the words “Photocatalysis (Fotocatálise)”, “Photocatalytic (Fotocatalítica)” and “Photocatalyst (Fotocatalizador)”. For the search of scientific articles, were used the databases Web of Science and SciELO, using the same search procedures and words used to search for patents. The term "molybdate" was chosen because it is the class of materials focus study in this work. In addition, the words "photocatalysis", "photocatalytic" and "photocatalyst" (photocataly*) were used in the search because they refer to the process of application of molybdates in environmental remediation ("photocatalysis"), to photocatalytic properties of this materials ("photocatalytic”), and to the adjective referring to molybdates that have photocatalytic properties ("photocatalyst"), respectively. The research of articles and patents was conducted between March and April 2018.

3. Results and discussion

3.1. Patents

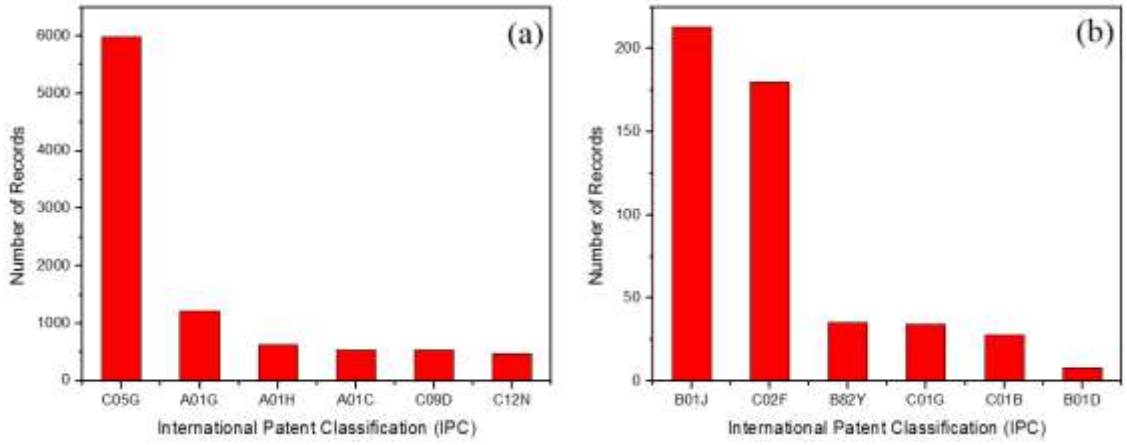
Table 1 shows the number of patent deposits found at INPI, EPO, USPTO and Derwent Innovations Index related to the keywords of the present research, and based on Table 1, we see that the overwhelming majority of deposits are revealed by the search in the Derwent Innovations Index database, both in the search using the word "Molybdate (Molibdato)", and also using the combination "Molybdate AND Photocataly* (Molibdatato AND Fotocatali*)". Unlike the Derwent Innovations Index database, the national patent office INPI presented a small number of search records using the word "Molibdato" (only 38 deposits) and did not present any patent filings on the search with the combination "Molibdato AND Fotocatali*". The very low number of patents shown in the INPI database reveals a worrying situation, since the number of patent registrations shows the Brazilian property on inventions generated, being an obstacle to the technological innovation of the country. Due to the large patent registration number, we used the search results in the Derwent Innovations Index database to perform a detailed analysis of the International Patent Classification (IPC), which is a tool used for classification or retrieval of patent documents. Figure 1 shows the number of patents found in function of the International Patent Classification (IPC).

Table 1 – Patents filed by database.

Search Terms	INPI	EPO	USTO	Derwent
Molybdate (Molibdato)	38	7738	13797	16927
Molybdate AND Photocataly* (Molibdatos AND Fotocatali*)	0	128	159	228

Source: Author's own table (2018)

Figure 1 – Patents filed by International Patent Classification (IPC) for the terms (a) "Molybdate" and (b) "Molybdate AND Photocataly*".



Source: Author's own figure (2018)

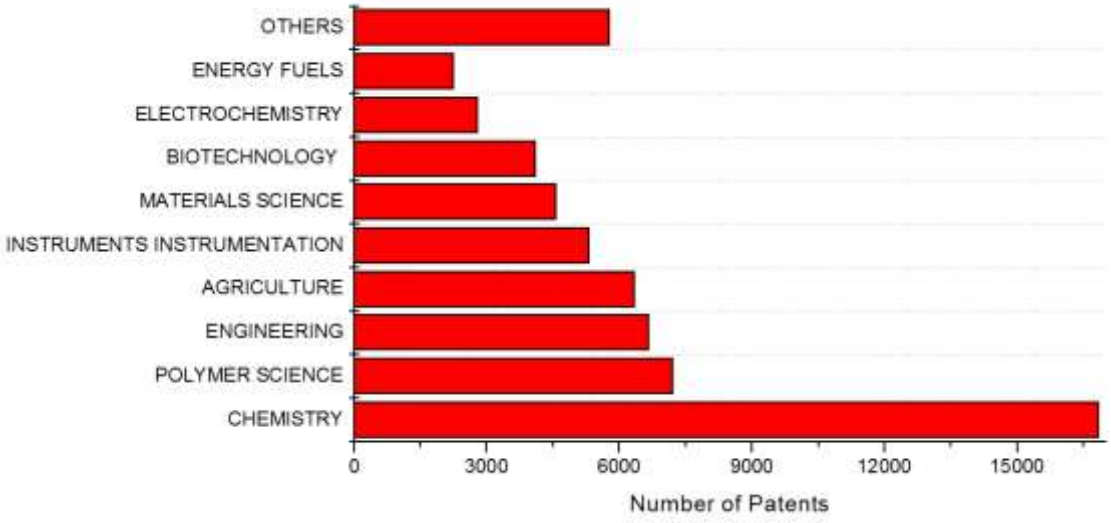
In Figure 1 (a) we can see that for the search term "Molybdate" the largest numbers of patents are in the classifications represented by the letters "C" and "A", which correspond to the classification Chemistry and Human Needs, respectively. The highlighted subclass for the term "Molybdate" was the "C05G", demonstrating that the deposited patents are mostly classified in Section C (Chemistry), Class C05 (Fertilizers) and Subclass C05G (Fertilizer Mixtures), indicating that molybdates have wide application in the chemical industry, in particular as an additive in the production of fertilizers (GUIA IPC, 2017). The use of molybdates as human needs appears as the second largest number of patents deposited in Section A (Human Needs), Class A01 (Agriculture) and Subclass A01G (Horticulture), showing together with Subclass C05G, which appeared in greater number, the great importance of molybdates in the production of agricultural inputs.

Subclass B01J appears with the highest number of patents deposited on the search using the combination "Molybdate AND Photocataly *" (Figure 1 (b)). This shows that most of the deposited patents regarding the use of molybdates as a photocatalyst classified in Section B (Processing operations), Class B01 (Physical or chemical processes or apparatus in general) and Subclass B01J (Chemical or physical processes). Subclass C02F (in Section C (Chemical), Class C02 (Water treatment) and Subclass C02F (Water treatment, wastewater, sewage or sludge and slime)) appears with the second largest number of patents deposited.

The subclasses B01J and C02F presented the majority of patents deposited when compared to the other subclasses, indicating the relevance of the photocatalytic application of molybdates in the chemical processes of water treatments and showing the great importance of this family of materials as environmental remediators. The use of molybdates as a photocatalytic agent appears in small numbers when compared to their use as in the chemical industry applied to agriculture (see Figure 1 (a) and (b)). However, although it has been neglected by the industry, the study of the applications of these materials as photocatalysts has increased in an extraordinary way in the last decade as we will see in the next section.

Figures 2 and 3 show the areas where most deposits patents based on a search using the terms "Molybdate" and "Molybdate AND Photocataly *" are found. The search using the term "Molybdate" (Figure 2) shows the vast application in the field of chemistry, as already evidenced by the International Patent Classification (IPC); the second largest area of application corresponds to the science of polymers, indicating possible application of the material in the form of composites.

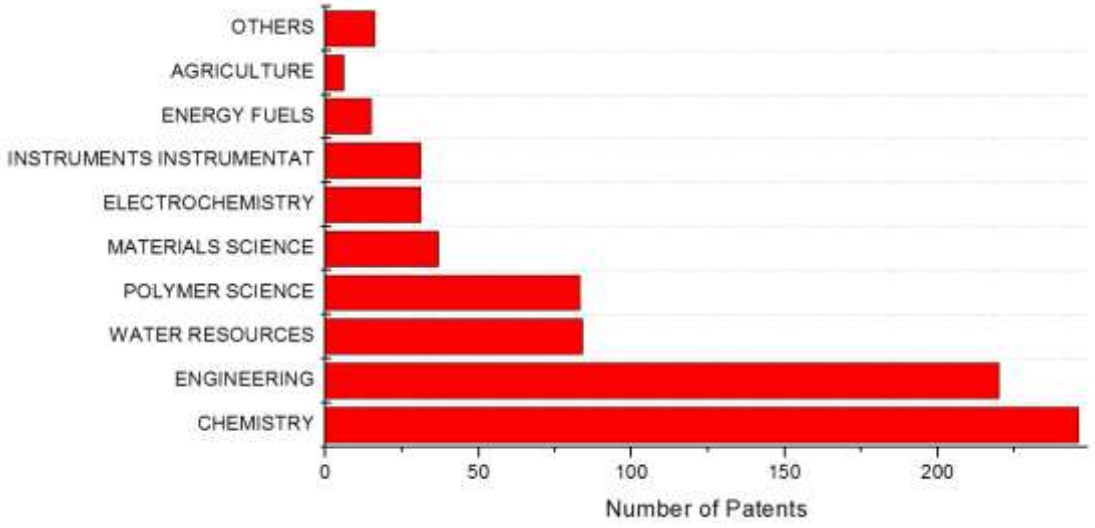
Figure 2 – Patents filed by application area for the term “Molybdate”.



Source: Author's own figure (2018)

Figure 3 shows the result of the number of patents according to the main areas of application using the combination of search "Molybdate and Photocataly *". As in the search using only the term "Molybdate", Figure 3 presents the area of Chemistry as the leading number of patent deposits of molybdates applied in photocatalysis, followed by the Engineering . The areas of chemistry related to the reactions occurring in the process of photocatalysis and the engineering by the mechanisms that govern the process of assembling and projects of environmental remediation stations are highlighted.

Figure 3 – Patents filed by application area for the terms “Molybdate AND Photocataly*”.



Source: Author's own figure (2018)

3.2. Articles

Table 2 shows the number of articles related to the keywords of the present study in journals as recorded in both Web of Science and SciELO.

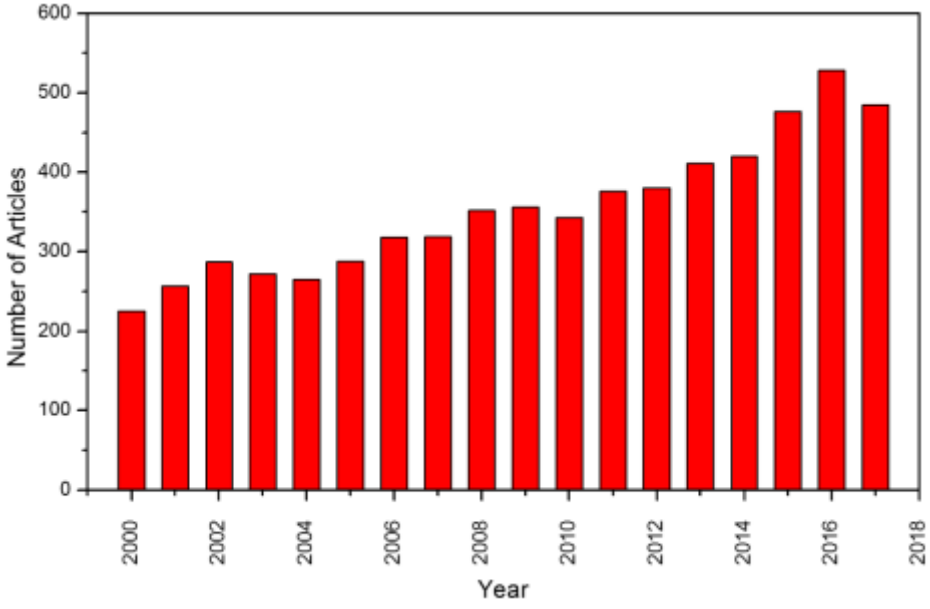
Table 2 – Article filed by database.

Search Terms	Web of Science	SciELO
Molybdate (Molibdato)	6361	56
Molybdate AND Photocataly* (Molibdatos AND Fotocatali*)	269	0

Source: Author's own table (2018)

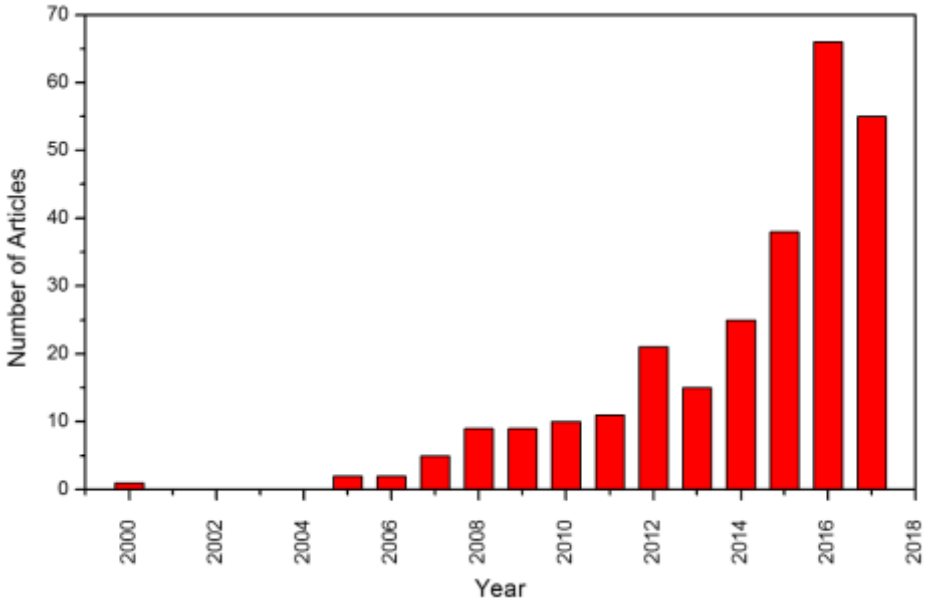
Due to the large number of articles, was used a search of results in the base of journals from Web of Science to perform a detailed analysis of the number of articles published per year, the countries with greater number of publications and the main research areas in which more articles have been published on the subject. Figure 4 shows the number of articles published per year, between 2000 and 2017, for a search using the term "Molybdate". The growing number of publications dealing with molybdates indicates the great importance of this family of materials to the scientific community. The search for the number of articles per year using the combination "Molybdate AND Photocataly *" is shown in Figure 5, where we observe an exponential growth of the number of publications per year, also revealing the importance that was given by the scientific community to the study of molybdates as photocatalysts, and indicating a possible rise of this area in the next years. However, it is worth to note that the number of articles published between 2000 and 2017 related to photocatalytic activity of molybdates is still very small when compared to the number of publications for the general term "Molybdates".

Figure 4 – Number of articles per year for the term “Molybdate”.



Source: Author's own figure (2018)

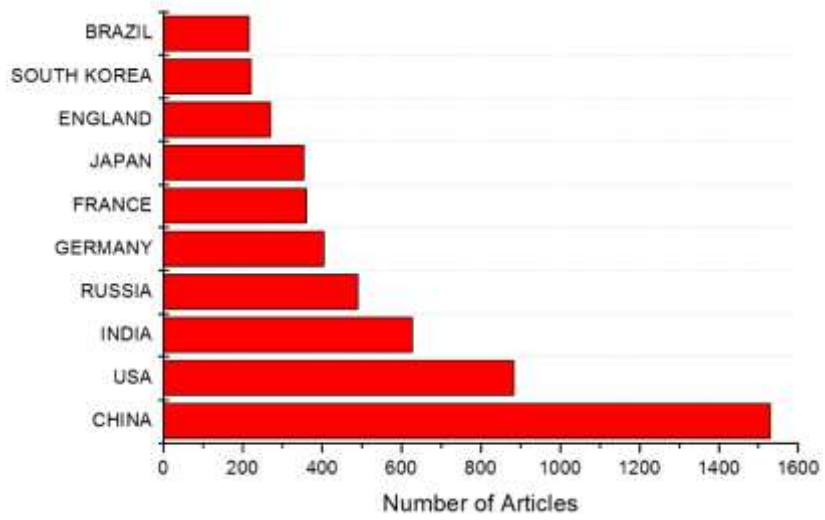
Figure 5 – Number of article per year for the terms “Molybdate AND Photocataly*”.



Source: Author's own figure (2018)

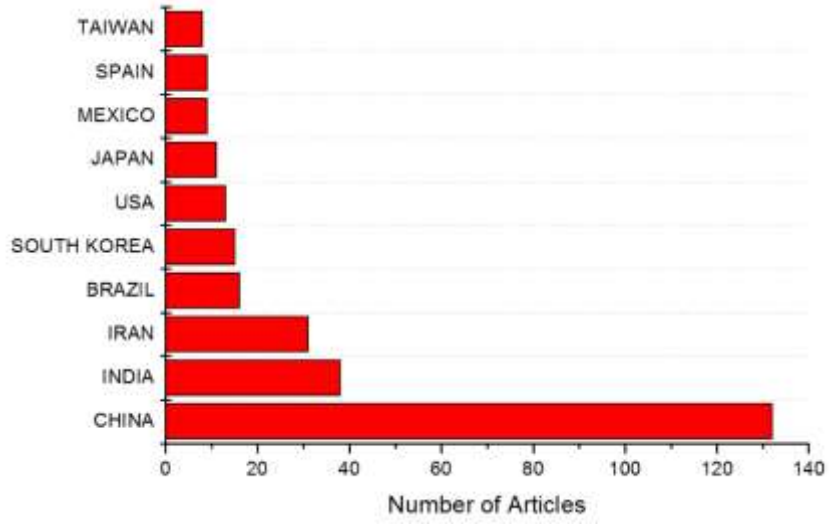
Among the countries that publish the largest number of articles related to the term "Molybdate" in the Web of Science base are China, the United States and India, as illustrated by Figure 6. Brazil appears among the ten countries with the largest number of scientific papers on molybdates, but it is still in a timid position, which emphasizes the need of the community of Brazilian researchers to work in this area. Figure 7 shows the number of papers published per year with the combination of the terms "Molibdate AND Photocataly *". China, India and Iran are at the top when the field of photocatalytic activity of molybdates is considered. Brazil is well positioned, soon after the Iran, showing itself as a country with a great research focus in the area of photocatalytic properties of molybdates. This fact apparently contradicts the results of the patent searches in the INPI database, but, in fact, reveals the main focus of the academic community on basic science, without interest in intellectual property for the theme of research.

Figure 6 – Number of articles by country of origin for the term “Molybdate”.



Source: Author's own figure (2018)

Figure 7 – Number of articles by country of origin for the terms “Molybdate AND Photocataly*”.

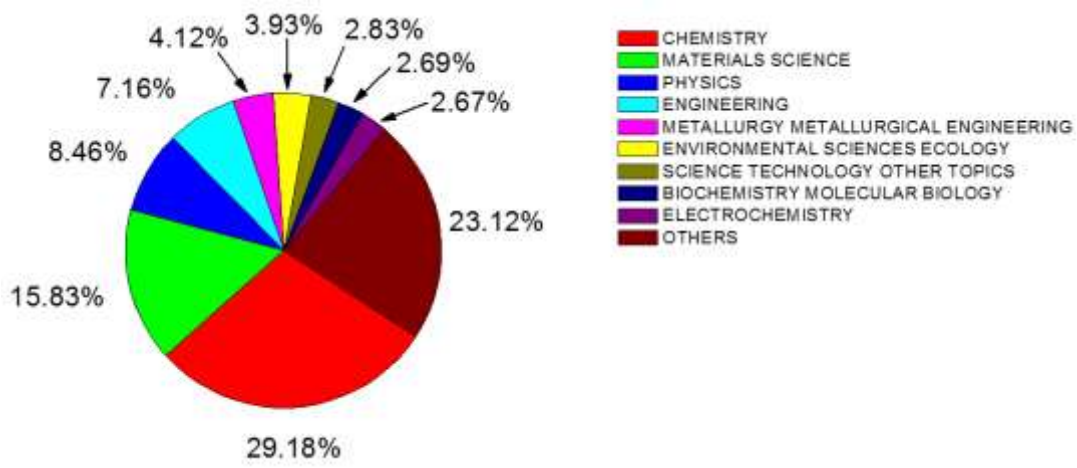


Source: Author's own figure (2018)

When evaluating the total number of publications in relation to the countries of origin (Figures 6 and 7), the ranking is expressively led by China, which is the major world power and has technologies and financing coming from the private sector, to direct research aimed at the discovery or the optimization of the photocatalytic properties of molybdates. Additionally, it was analyzed the areas in which more articles were published on the Web of Science journal base under the terms "Molybdate" and "Molybdate AND Photocataly *" (Figures 8 and 9). Based on Figure 8 we can see that the three areas that lead the ranking in numbers of publications are Chemistry (29.18%), Materials Science (15.83%) and Physics (8.46%), respectively. Chemistry leads 29.18% of the publication number because it studies new routes of synthesis of new molybdates with different chemical compositions, morphologies and structures as consequence of the great versatility of this family of material. Materials science appears in the second position because it focuses on the

optimization of molybdate applications. The physics area appears in the ranking because the molybdates are often studied due to their polymorphic properties under extreme conditions of pressure and/or temperature. These materials are investigated in order to understand the mechanisms that lead to the structural phase transitions. The large percentage of "other" category (23.12%) indicates the vast importance of molybdates in several areas of knowledge.

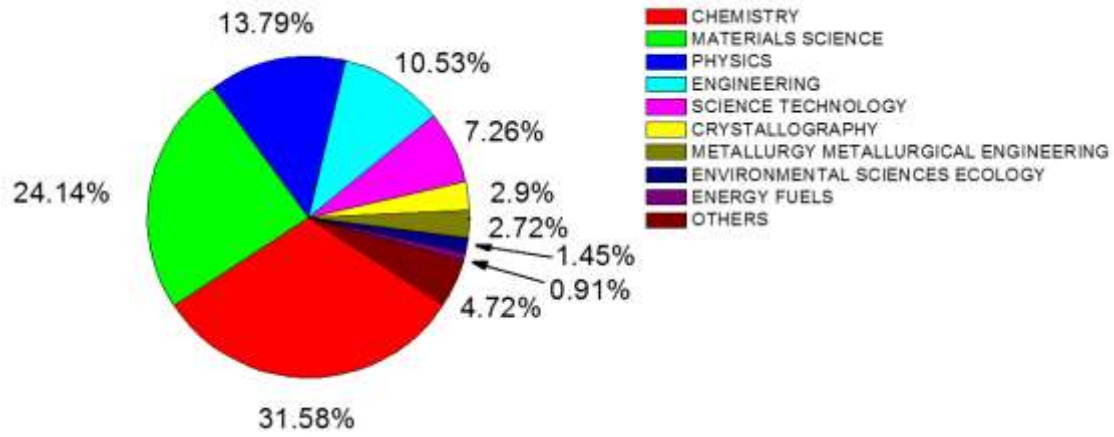
Figure 8 – Areas with the largest number of article publications for the term “Molybdate”.



Source: Author's own figure (2018)

Figure 9 illustrates the areas that most published with the combination "Molybdate AND Photocataly *". The areas that led the ranking in numbers of publications are Chemistry (31.58%), Materials Science (24.14%) and Physics (13.79%), the same result for the search using the term "Molybdate". Therefore, based on these results, we can see that chemistry, materials and physical sciences are interested both in the study of the physicochemical properties of molybdates and in the study of their photocatalytic properties. With such an investigation, researchers try to understandi the mechanisms that govern possible applications as well as to search the optimization of the photocatalytic reactions.

Figure 9 – Areas with the largest number of article publications for the terms “Molybdate AND Photocataly*”.



Source: Author's own figure (2018)

4. Conclusion

The survey of patents and scientific papers on molybdates and applications in photocatalysis demonstrated a very expressive result. It confirms a significant interest in the researches on processes of preparation of new materials with different morphologies, size and structures, improving its photocatalytic properties and adding economic value. However, in the records of the Brazilian Patent Database (INPI) it was observed the absence of patent deposits for the terms used in the search, contradicting the results regarding scientific articles, which reveal a good position of Brazil in the ranking of countries that presents the largest number of publish papers on the subject. It was noticed that chemistry, materials and physical sciences are interested both in the study of the physicochemical properties of molybdates and in the study of their photocatalytic properties, which shows a great interest of the academic environment by this class of material.

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