Phosphate Conversion Coatings for Biomaterials: A Bibliometric Analysis

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Abstract. Finding solutions regarding the promotion of the biological response of metallic implants became thoroughly researched, especially by surface modification treatments, due to the high number of clinical demands and the advantageous commercial context. Most of the researchers focused on hydroxyapatite or metal oxide coatings deposited by different methods (electrodeposition, sol-gel, physical vapor deposition, etc.). However, in the last few years, chemical conversion coatings have increased attention in the field of biomaterials. The phosphate layers obtained by this technology have multiple benefits, among which are high adherence to the substrate, similar morphology with the bone, high corrosion resistance, etc. Also, the phosphate coatings present chemical stability and good wear resistance and don't have an impact on the mechanical properties of the substrate. Therefore, this paper aims to analyze the evolution of research in the field of coatings for metallic biomaterials, focusing on conversion coatings deposited on biomaterials, using bibliometric analysis. The results show an increase in the number of publications regarding the chemical conversion process since 2012, many of which are about the layers deposited on magnesium and titanium alloys.

Keywords: conversion coatings · biocompatibility · biomaterials · bibliometric analysis

1 Introduction

In 2020, USD 49.02 billion was spent on orthopaedic implants worldwide, anticipating brisk growth of 5.1% in the coming period. This development is mainly due to the increase in osteoporosis and osteoarthritis cases [1].

In the case of products made from biocompatible materials, worldwide, medical technology manufacturers are continuing to develop their products [2]. His evolution is due, first of all, to the significant increase in demand for these products but also to

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unprecedented technological progress. Thus, a growing number of companies focus their activity on the design, development, production, and marketing of human implants and prostheses [3].

Biomaterials can be classified according to several criteria, including material type such as: metallic, polymeric, ceramic, and composite [4].

Regarding the value of the global market for implants made of metallic biomaterials, it was valued at $86.3 billion in 2020 and is expected to grow by 5.4% by 2030 [5]. This data is based on reports of the number of people living with musculoskeletal diseases [6]. For example, according to the Romanian statistics office, in 2020, 15% of the population needed orthopaedic implants. This can be attributed to the increasing number of road accidents and trauma cases across the globe. In addition, there is an increasing demand for minimally invasive surgery among people [7]. Therefore, there is a lot of research on continuously improving the biological response of existing biomaterials on the market through surface treatments [8].

Biomaterials have diverse applications [9] and can be classified according to the systems in the body where they are used:

- For bone systems: bone prosthesis, implant;
- Muscular and digestive system: stitches;
- Circulatory system: valves or artificial vessels;
- Respiratory system: a device for artificial respiration;
- Urinary system: catheters, renal dialysis devices;
- Nervous system: hydrocephalic drain, cardiac pacemaker;
- Endocrine system: groups of encapsulated pancreatic cells;
- Reproductive system: mammoplasty, etc.

Regarding the metallic materials, which are used to replace joints, bone screws, and implants, they are based on titanium [10], stainless steel [11], Co-Cr alloys [12] and gold [13]. Their advantages are represented by superior mechanical properties (high mechanical resistance, elasticity), but the biggest disadvantage is represented by low resistance to corrosion when interacting with substances in the body (NaCl, HF, H_2O_2 etc.) [14].

Due to the low corrosion resistance properties that can eliminate toxic corrosion products in the body, as well as the bio-inert surface of the material, there is the possibility of an inflammatory reaction in the body, and this aspect often leads to the failure of the implant [14, 15]. Therefore, among the key conditions necessary for the efficient functioning of the implant are, among others, biocompatibility, biofunctionality, and biodegradability [16].

Therefore, there is a need to develop high-performance materials or coatings aimed at obtaining characteristics suitable for the human body.

Biometals can be encapsulated by depositing a thin film layer on their surface. This will enable the material to be accepted by the body after implanting it, due to its improved characteristics. Several techniques are used to coat bio-metallic material surfaces, including hydroxyapatite coatings, glass-ceramic coatings with tricalcium phosphate, oxide coatings, composite coatings, etc. [17, 18].

The most common metallic materials for biomedical uses in the world are titanium alloys. They are utilized in medicine for implants that replace damaged bones and tissues.

Examples include artificial hip joints, knee joints, and bone plates. In addition, artificial hearts, prosthetic heart valves, pacemakers, and screws for fracture fixation are also made from titanium and its alloys. [19, 20].

They show superior mechanical properties, chemical and mechanical stability, and favorable biocompatibility, having been used for many years as implant materials [21]. Due to corrosive properties and bio-inert surfaces, significant problems have arisen, including long-term failures and tissue necrosis as a result of them. Therefore, these defects must be substituted by surface treatments [19–21].

This paper analyzes the evolution of research in the field of coatings for metallic biomaterials, focusing on conversion coatings.

2 Methods

The evolution of research in the field of coatings used to improve biomaterial properties was carried out with the help of bibliometric analysis, with the implementation methodology being presented in Fig. 1.

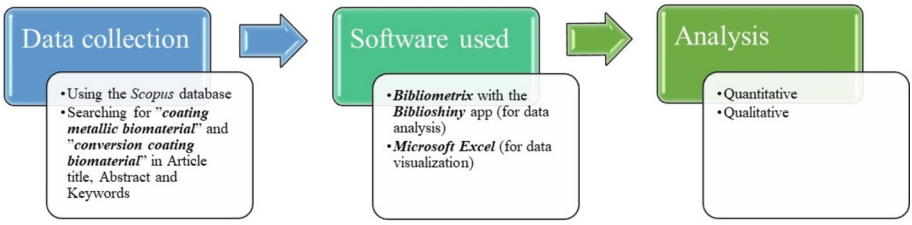

Fig. 1. The methodology of the study.

The data were extracted from Scopus, resulting in 978 research types published worldwide. This was done following the search for "coating metallic biomaterial" with the search query "Article Title, Abstract, Keywords". The papers published were written in English (95%), Chinese (1.84%), German and Spanish (0.51%), Russian (0.41%), Italian, Czech, Japanese, and Portuguese (0.31%), and Hungarian (0.2%). In terms of research on conversion coatings, the search was conducted for "conversion coating biomaterial" thus obtaining 202 papers, of which 96.04% are written in English, 2.97% in Chinese, and 1% in Japanese and Spanish.

The software chosen for the bibliometric analysis was Bibliometrix, with the Biblioshiny application [22]. Also, the data was visualized and verified in Microsoft Excel. The results were analyzed quantitatively and qualitatively. Publication years, types of research, writing languages, types of journals, and research constituent information (authors, countries, etc.) were analyzed quantitatively. Keyword mapping and thematic areas were considered in the qualitative analysis.

3 Results and Discussion

3.1 Data Obtained for "Coating Metallic Biomaterial"

The bibliometric analysis presents statistical information about publications, sources, citations, authors, frequency, etc. Table 1 presents a summary of the information related to research publications. Also, the number of sources from which publications were extracted is 455, and the number of documents is 978. This is with an average citation per document of 29.42 and 49878 references. The documents were articles (670), books (5), book chapters (58), conference papers (128), conference reviews (9), letters (1), retracted (1), and reviews (106).

Table 1. The main information about the data obtained between 1977 and 2022.

Document contents	
Keywords Plus	7595
Author's Keywords	2014
Authors	
Authors	3791
Authors of single-authored docs	54
Authors collaboration	
Single-authored docs	73
Co-Authors per Doc	4.8
International co-authorships %	23.72%

In Fig. 2, it is shown how interest in coatings used for metallic biomaterials has evolved over time. It can be observed that the annual growth rate is 8.72% in 2022. As can also be seen in the figure, the first research was published in 1977, and the number of studies increased exponentially from 2000 onward.

Regarding the first 10 sources according to the number of publications, these are presented in Table 2. As can be seen, most articles were published in top journals, with their impact factor exceeding 4. Also, these sources are significant journals in the fields of materials and bioengineering.

Regarding the distribution of publications according to the corresponding author's country of affiliation, it can be observed that research on improving biomaterial properties through surface treatments has been carried out on all continents. However, little research has been carried out in certain parts of South America, Northern and Eastern Europe, as well as Africa.

Table 3 shows the first 10 countries that produced scientific publications in the field of metallic biomaterial coatings. Over the years, 59 countries have been interested in this field, and 20 have published at least 10 articles in the field.

Among these countries, China and the USA are among the first to produce medical devices, explaining researchers' high interest.

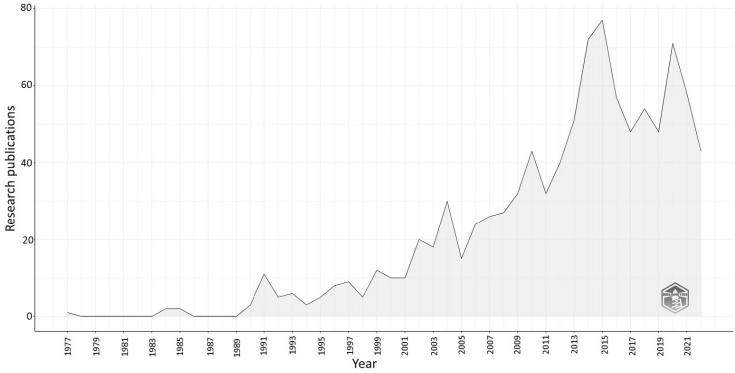

Fig. 2. Annual scientific production on coatings used for metallic biomaterials.

Table 2. Top 10 most relevant sources.

Sources	Publisher	Number of publication	IF 2021
Materials Science and Engineering C	Elsevier	46	7.328
Surface and Coatings Technology	Elsevier	27	4.865
Journal Of Biomedical Materials Research - Part A	Wiley	26	4.854
Biomaterials	Elsevier	23	15.304
Journal of Materials Science: Materials in Medicine	Springer Science + Business Media	19	4.727
Acta Biomaterialia	Elsevier	18	10.633
Acs Applied Materials and Interfaces	American Chemical Society (United States)	16	10.383
Colloids and Surfaces B: Biointerfaces	Elsevier	15	5.999
Journal of Biomedical Materials Research	Wiley	14	4.854
Applied Surface Science	Elsevier	13	7.392

The worldwide distribution of authors with publications in "coating metallic biomaterial" is shown in Fig. 3. The countries that don't have any authors affiliated with them are colored gray. The intensity of the blue color is related to the number of publications associated with that country. Joint publications by authors from different countries are

Table 3. Top 10 countries regarding the number of publications according to the corresponding author's country of affiliation on coatings used for metallic biomaterials.

Country	Number of publications	Frequency
USA	136	0.105
China	98	0.100
India	57	0.058
Germany	47	0.048
Brazil	41	0.042
Poland	41	0.042
Japan	37	0.038
France	34	0.035
Italy	33	0.034
United Kingdom	32	0.033

indicated with pink lines. Furthermore, no publication appears to be associated with authors from Russia or multiple African countries. European countries have at least one publication in this field.

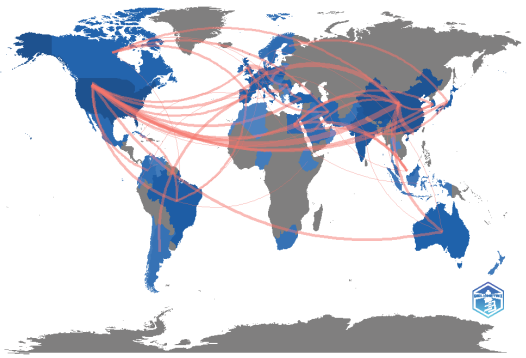

Fig. 3. The collaboration worldmap of authors with publication in the field of "coating metallic biomaterial".

Regarding the top 50 words as keywords, they are represented in Fig. 4. It can be observed that the subjects of the articles focus on the modification of biomaterial surfaces through biocompatible coatings. As a result, the most commonly used coatings are those based on hydroxyapatite. It also appears that most studies investigate corrosion resistance properties as well as antibacterial or toxicity properties. The most widely used biocompatible materials for research are titanium-based alloys, magnesium-based alloys, and stainless steels.

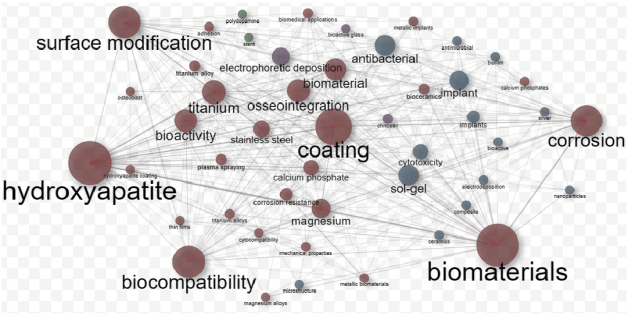

Fig. 4. Thematic map based on the author's keywords.

3.2 Data Obtained for "Conversion Coating Biomaterial"

From the bibliometric analysis carried out for the database obtained by searching the terms "conversion coating biomaterial" on Scopus, 111 sources were obtained from which publications were extracted, the number of documents being 202, with an average citation per document of 37.82 and 9670 references. The documents were articles (157), book chapters (3), conference papers (21), conference reviews (6), and reviews (15). Table 4 shows the main information about the data gathered between 1986 and 2022.

Table 4. The main information about the data obtained between 1986 and 2022.

Document contents	
Keywords Plus	3119
Author's Keywords	586
Authors	
Authors	889
Authors of single-authored docs	4
Authors collaboration	
Single-authored docs	9
Co-Authors per Doc	5.42
International co-authorships %	24.26%

The annual scientific production regarding publications about conversion coatings is presented in Fig. 5, where it can be seen that the annual growth rate is 6.29% in 2021. In addition, the first research was published in 1986, and from 2001 onward, research numbers increased exponentially between 2000 and 2018.

Depending on the number of publications, Table 5 shows the first 10 sources. Considering that most of the articles were published in prestigious journals (with an impact factor between 3 and 15), it can be seen that the field of deposition by chemical conversion is of great interest in terms of its use for improving the surface of biomaterials.

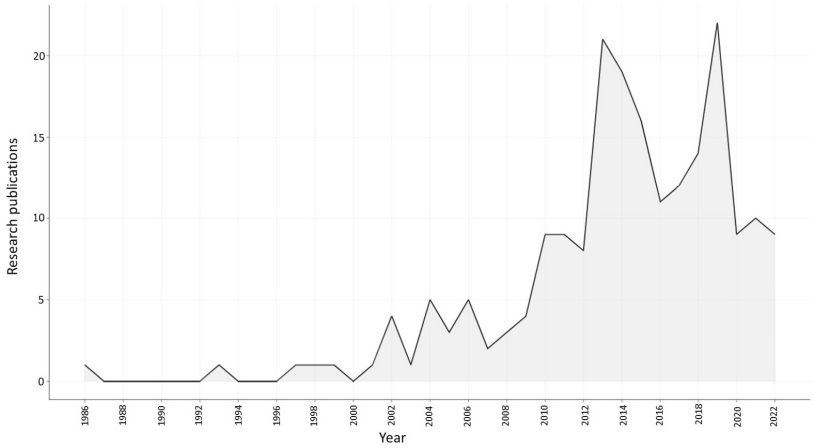

Fig. 5. Annual scientific production on conversion coatings.

Table 6 shows the first 10 countries with the most publications in the field of biomaterial conversion coatings.

Table 5. Top 10 most relevant sources.

Sources	Publisher	Number of publications	IF 2021
Acs Applied Materials and Interfaces	American Chemical Society (United States)	16	10.383
Biomaterials	Elsevier	9	15.304
Materials Science and Engineering C	Elsevier	9	7.328
Journal of Applied Polymer Science	Wiley	7	3.057
Acta Biomaterialia	Elsevier	6	10.633
Advanced Materials Research	Trans Tech Publications Ltd	6	0
Key Engineering Materials	Trans Tech Publications Ltd	4	0
Advanced Healthcare Materials	Wiley	3	9.933
Applied Surface Science	Elsevier	3	7.392
Acs Biomaterials Science and Engineering	American Chemical Society (United States)	3	14.310

Over the years, 30 countries have been interested in this field, and 9 of them have published at least 5 articles in the field.

Table 6. Top 10 countries regarding the number of publications according to the corresponding author's country of affiliation on conversion coatings.

Country	Number of publications	Frequency
China	76	0.376
USA	23	0.114
Australia	9	0.045
Germany	9	0.045
Brazil	7	0.035
Japan	7	0.035
Korea	6	0.030
India	5	0.025
Malaysia	5	0.025
United Kingdom	4	0.020

An analysis of the worldwide distribution of authors with publications in this field is presented in Fig. 6. The countries that do not have any publications in the analyzed field are presented in gray. While, depending on the number of publications, the blue color intensifies. Also, collaboration links between countries are indicated with pink lines. Regarding the distribution of publications according to the country of affiliation of the corresponding author, it can be observed that research on improving biomaterial properties through chemical conversion deposition has been carried out on all continents. However, not much research has been carried out in certain parts of Asia, Africa, and Eastern Europe.

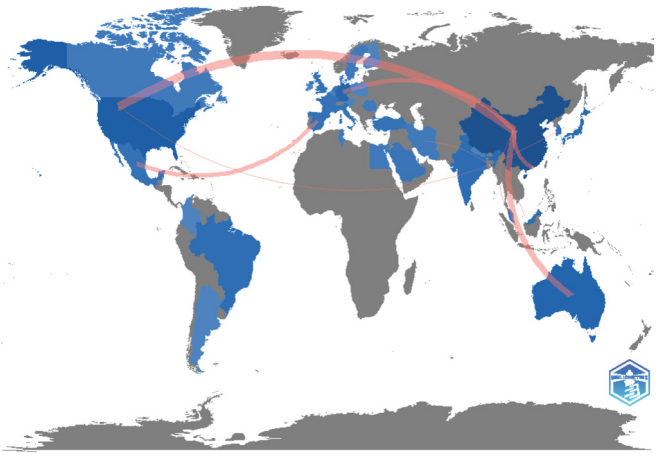

Fig. 6. The collaboration worldmap of authors with publication in the field of "conversion coating biomaterial".

Moreover, the 50 most frequent authors' keywords are presented in Fig. 7. It can be seen that research focuses mainly on improving the surface properties of magnesium alloys. Considering the properties obtained by coating biomaterials through chemical conversion, the corrosion properties, microstructure, cytocompatibility, osseointegration, and biodegradation are mainly studied.

Even in Fig. 7, it can be observed that the major material studied for chemical conversion coatings was magnesium alloy. There are studies regarding the improvement of the surface properties of the titanium alloys by depositing on their surface layers based on calcium-zinc phosphate [23], strontium-zinc phosphate [24], strontium-zinc-calcium [25] phosphate using chemical conversion process. The low number of publications regarding this subject is due to the bio-inert surface of titanium, which is difficult to activate to cause a chemical reaction between the phosphate solution and the metal.

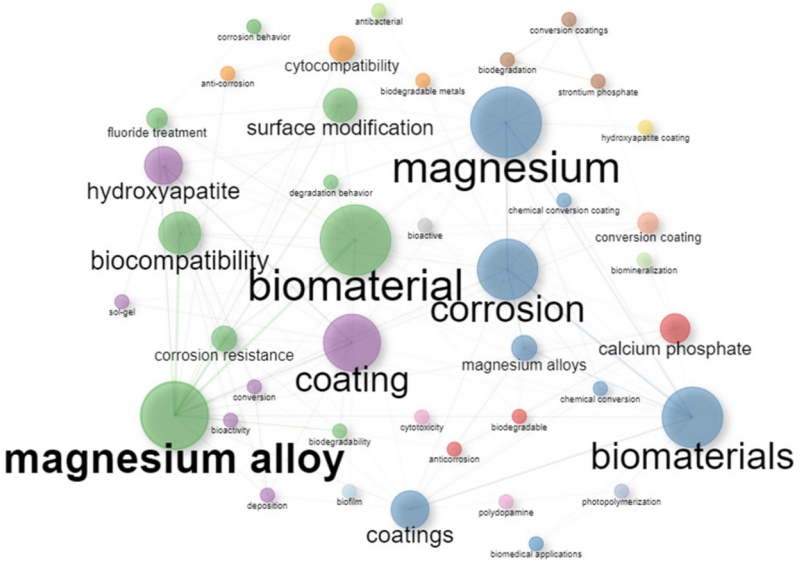

Fig. 7. Thematic-map.

4 Conclusions

Surface characteristics of biomaterials, such as roughness, chemical composition, and wettability, have a direct impact on the human body. These properties can be modified by coating the surfaces with various layers deposited by different methods.

Therefore, over time, many methods were studied to enhance the characteristics of the base biomaterial. These methods included electrochemical deposition, the sol-gel method, plasma spraying, etc. Many of them are used for hydroxyapatite deposition. As can be observed from the bibliometric analysis, the majority of studies were focused

on this type of coating. These studies were trying to improve the properties of the hydroxyapatite layer being deposited on various biomaterials.

Also, the bibliometric analysis shows that in the last few years, phosphate chemical conversion coatings have steadily drawn a lot of interest when it comes to the surface modification of biomaterials, especially magnesium alloys but also titanium and zinc alloys, and are one of the methods suitable for medical devices due to their advantages.

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