

## Article

# An Overview to Technical Solutions for Molybdenum Removal: Perspective from the Analysis of the Scientific Literature on Molybdenum and Drinking Water (1990–2019)

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**Abstract:** A bibliometric analysis using the Scopus database was performed to investigate the research documents published from 1990 to 2019 in scientific sources related to molybdenum in drinking water and determine the quantitative characteristics of the research in this period. The results from the analysis revealed that the number of publications was maintained at a regular production of around 5 papers per year until 2009, followed by a fast linear increase in the production in the period from 2010 to 2016 (29 papers in 2016), but the scientific production regarding this topic was reduced in 2017 and 2018 to recover the production obtained in 2016 once again in 2019. The total contribution of the three most productive countries (USA, China and India, respectively) accounted for around 50% of the total number of publications. Environmental Science was the most common subject (51.4% contribution), followed by Chemistry (26.7% contribution). The research efforts targeted toward the search for technical solutions for molybdenum removal from water are not as important as the ones focused on the identification of molybdenum-polluted water bodies and the analysis of the health effects of the intake of molybdenum. Nevertheless, examples of technological treatments to remove molybdenum from the aqueous solution include the use of adsorption and ion exchange; coagulation, flocculation and precipitation followed by filtration; membrane technologies and biological treatments.

**Keywords:** bibliometric analysis; drinking water; molybdenum; removal; research trends; treatments



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## 1. Introduction

Molybdenum (Mo), with atomic number 42, is located in the group 6 of the periodic table, between chromium and tungsten. In fact, the chemistries of molybdenum and tungsten are strongly similar. Until the final years of the 19th century, when molybdenum was first employed as steel additive, there were no industrial applications of this element [1]. The use of molybdenum in the development of special steels and other alloys was promoted during the First World War, and nowadays, around 75% of all molybdenum produced is used as an alloying element in steel [2].

Molybdenum is an essential element for both plants and animals. Despite its relatively low natural abundance (the element is not included in the list of the 50 most frequently occurring elements in the earth's crust), the amount of molybdenum available for plant uptake is enough in most soils [3], although molybdenum fertilization can effectively supplement molybdenum deficiencies when soils are not able to provide this essential micronutrient [4]. The range between toxicity and deficiency in animals is narrow, and careful control of molybdenum in animal diets is essential, particularly in ruminants, because molybdenum intake above certain critical levels produces molybdenosis, a form of intoxication that results in copper deficiency [5]. Because of this well-known toxic effect in animals, the possible adverse health consequences in humans caused by molybdenum have been investigated. Human molybdenosis is characterized by high levels of uric acid in both blood and urine, which cause gout-like diseases in people living in areas with high

molybdenum presence in soils. In addition, chronic exposure to excess molybdenum results in loss of appetite, listlessness, diarrhea and anemia [6–9]. Acute molybdenum toxicity is not frequent, and it can only occur due to industrial mining and metalworking exposure. Furthermore, more recent studies have pointed to molybdenum as a male reproductive toxicant, since there is evidence of an inverse association between molybdenum and human semen quality, which is consistent with animal data [10,11]. Safe and adequate intake levels have been defined for various segments of the population, for instance, 75–250 µg/day for all individuals above the age of 10 [12]. Regarding molybdenum presence in drinking water, the World Health Organization (WHO) recommended that it should not exceed 70 µg/L (although this element has been removed from its formal list of guideline values), while the United States Environmental Protection Agency (US EPA) determined that the “Lifetime Advisory Level” for molybdenum is 40 µg/L [13,14]. However, the European Union has not defined a threshold value to apply for molybdenum in drinking water [15], which gives a clear idea about the relatively little attention paid to environmental pollution caused by molybdenum and safe levels in drinking water [16].

This scarce concern about molybdenum when compared to other metals and metalloids, such as lead or arsenic, can be justified because most natural waters contain only very low levels of molybdenum dissolved. For instance, a very complete study about the occurrence of molybdenum in British surface waters and groundwaters demonstrated that the 90th percentile values for stream waters and groundwaters were below 3 and 2 µg/L, respectively [17]. These results indicate that water derived from these sources is unlikely to pose a major problem for drinking water supply, and the analysis of the concentration of molybdenum in drinking water from English and Welsh locations confirmed this hypothesis [18]. However, several studies have observed elevated molybdenum concentrations in surface waters and groundwaters across the world. Although surface waters and groundwaters may be naturally enriched when drainage waters pass through molybdenum-rich soils or strata [19], there has been a traditional direct linking of these high levels to the anthropogenic contribution to environmental media from mining and related industrial uses [20]. However, the contamination of groundwaters is not exclusively due to the impact of this direct anthropogenic contribution, since the mobilization of naturally occurring (geogenic) molybdenum induced by anthropogenic perturbations of the physicochemical conditions in aquifers also occurs [21]. Whatever the real cause, the fact is that elevated molybdenum concentrations in surface waters and groundwaters that exceed the 70 µg/L threshold have been registered across the world, with examples in Argentina, Chile, China, Jordan, Ethiopia, India or Florida, Nevada, California and Wisconsin in the USA [22–28]. Further information about this issue can be consulted in a review focused on the occurrence and distributions of molybdenum in surface waters and groundwaters and the corresponding environmental, health and water-supply implications [29]. Consequently, the inhabitants of these regions are exposed to molybdenum levels in the drinking water they consume that can imply a significant risk to their health [30,31].

As a transition element, molybdenum shows variable valency, with oxidation states from  $-2$  to  $+6$ . In addition, it can form many complexes compounds with most inorganic and organic ligands, with coordination numbers from 4 to 8 and ability to form binuclear and more complex polynuclear species involving bridging ligands [32]. Consequently, the aqueous chemistry of molybdenum is complex. It is dominated by oxo species, which are prone to dimerize and polymerize. Under common conditions, molybdate ion ( $\text{Mo}^{+6}$ ) is the most frequent chemical form of molybdenum in oxygenated freshwater and seawater systems, while reduced  $\text{Mo}^{+5}$  can appear in reducing environments due to reduction by organic acids, reduction in molybdenum in the nitrogen cycle or the presence of sulfate-reducing bacteria [33]. Under more strongly reducing conditions, molybdenum can be further reduced to  $\text{Mo}^{+4}$ , resulting in oxo molybdenum (IV) complexes or precipitates, such as  $\text{MoO}_2$  or  $\text{MoS}_2$ . The more reduced  $\text{Mo}^{+2}$  and  $\text{Mo}^{+3}$  are not common in aqueous systems [34]. Acid chemistry is important to understand the behavior of molybdenum in aqueous systems. It is well known that molybdic acid ( $\text{H}_2\text{MoO}_4$ ) has very similar first and

second acidity constants ( $\text{pK}_{a1} = 3.6\text{--}4.0$  and  $\text{pK}_{a2} = 3.9\text{--}4.4$ ), so the deprotonated molybdate ion ( $\text{MoO}_4^{2-}$ ) is the dominant form in basic, neutral and slightly acid solutions, whereas the protonated  $\text{H}_2\text{MoO}_4$  and  $\text{HMoO}_4^-$  forms are present only in acidic environments with pH values below 4 [35]. In these acidic conditions, the paramolybdate ion ( $\text{Mo}_7\text{O}_{24}^{-6}$ ), can also appear, and even most extreme pH values allow the formation of more complex polymolybdates, for instance, the octamolybdate ion ( $\text{Mo}_8\text{O}_{26}^{-4}$ ). In addition, in the presence of sulfidic bacteria, S atoms can replace the O atoms present in molybdate ion, forming thiomolybdate complexes [36].

The systematic management of the high number of scientific papers resulting from a bibliographic search regarding water pollution requires the use of specific tools to handle all this information, and bibliometric resources provide a valuable assistance. Bibliometrics was defined by Pritchard as the application of mathematical and statistical methods to books and other media of communication [37]. This research methodology, which has been extensively used in library and other information sciences, puts in application quantitative analysis and related statistical methods to define the distribution patterns of publications according to some given categories [38]. This methodology, which comprises components from mathematics, social sciences, natural sciences, engineering and even life sciences, allows the exploration, management, structuring and examination of a high number of scientific documents, and it is an effective tool for conducting methodological investigation of the role of science as a knowledge-generating and communication system [39,40]. This approach has been applied to identify relevant research trends, as demonstrated by numerous publications in the environmental and chemical engineering fields [41–45], including water contamination and wastewater aspects [46–50].

The main aim of this work was to investigate the scientific literature that covered the research on molybdenum and drinking water published from 1990 to 2019 in the sources considered by Scopus from a bibliometric approach. The documents found as a result of the bibliographic search were analyzed and classified according to several categories (annual production, most prolific countries and institutions, main journals and languages . . . ). Thereby, the quantitative features of the research on molybdenum removal and drinking water worldwide were obtained and applied to identify the most important hot topics in this field.

## 2. Data Sources and Methodology

The bibliographic search of the scientific literature related to molybdenum and drinking water was based on the employment of Scopus. This database compiles abstracts and citations of academic journal articles and other scientific documents, covering over 22,800 titles (more than 20,000 are peer-reviewed journals) from over 5000 international publishers. Taking into account the figures, Scopus can be considered the largest abstract and citation database of peer-reviewed literature [51]. More than 69 million abstracts with references back to 1969 and more than 6 million records before that year (as far back as 1823) are included. Scientific sources from all continents were considered, including non-English titles, when abstracts in English were provided. Furthermore, more than half of the publications included in Scopus come from outside North America, with relevant production by European, Latin American and Asian countries. As a result, Scopus offers an extensive offer of peer-reviewed literature across the fields of science, technology, engineering and mathematics (STEM). Nevertheless, other sources that could have provided valuable contributions to the studied field, such as the patent literature, monographs and potentially unindexed conference proceedings and other scientific documents, were not considered in this work.

The search within the Scopus database was completed in May 2020, with the choice of “molybdenum” and “drinking water” as keywords in the Article Title, Abstract, Keywords field of the search engine. The keywords *drinking* and *water* were introduced together with quotations to obtain only the papers that included both words in this exact sequence. This search was limited to 1990–2019 in order to find the scientific documents related to the

research on this topic published up to 2020 (just before the COVID-19 pandemic lock-down). The total number of documents resulting from the search was 296.

The analysis of the scientific literature obtained after the systematic bibliographic search must provide optimal conditions to achieve an improved understanding of the global research situation in a topic, which allows the discovery of past research gaps, the identification of present hot topics and the proposal of future long-term research strategies. Therefore, the investigated aspects included in this bibliometric article did not only cover the quantitative description of the publications (such as annual production, most prolific countries and institutions, main journals or most frequent languages), since it identified the most important research themes after the study of the corresponding keywords and most cited papers.

### 3. Results and discussion

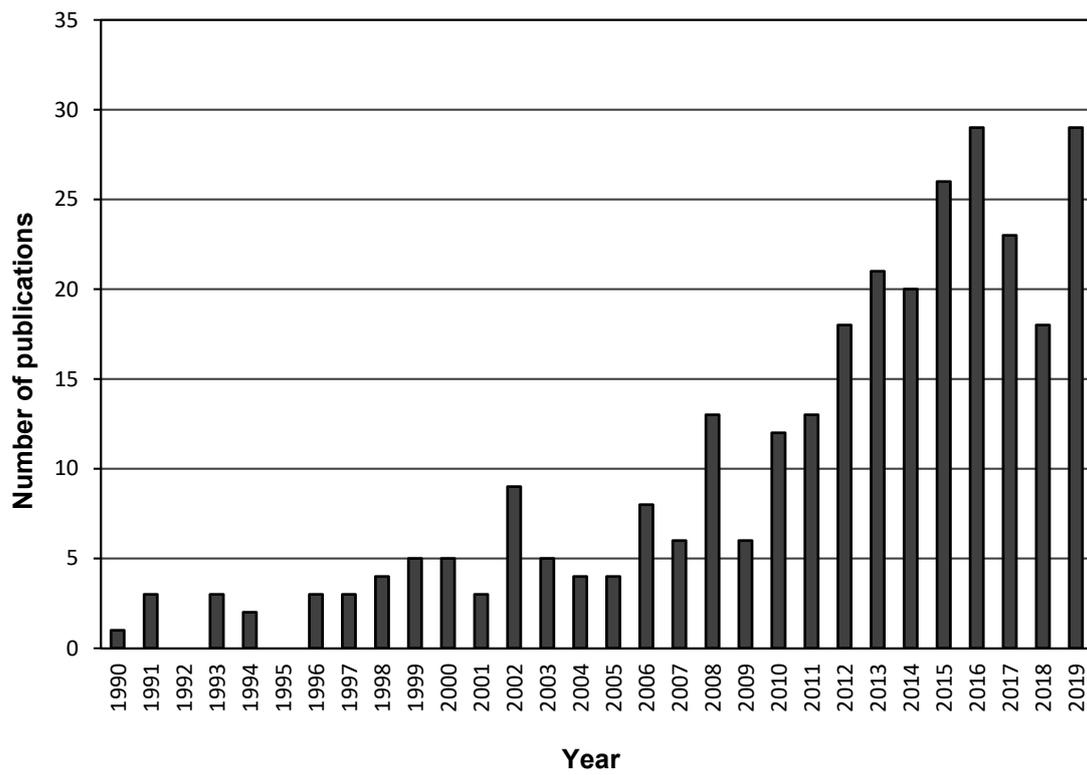
#### 3.1. Bibliometric Analysis of Research Trends on Molybdenum and Drinking Water (1990–2019)

##### 3.1.1. Publication Year, Document Type and Language of Publications

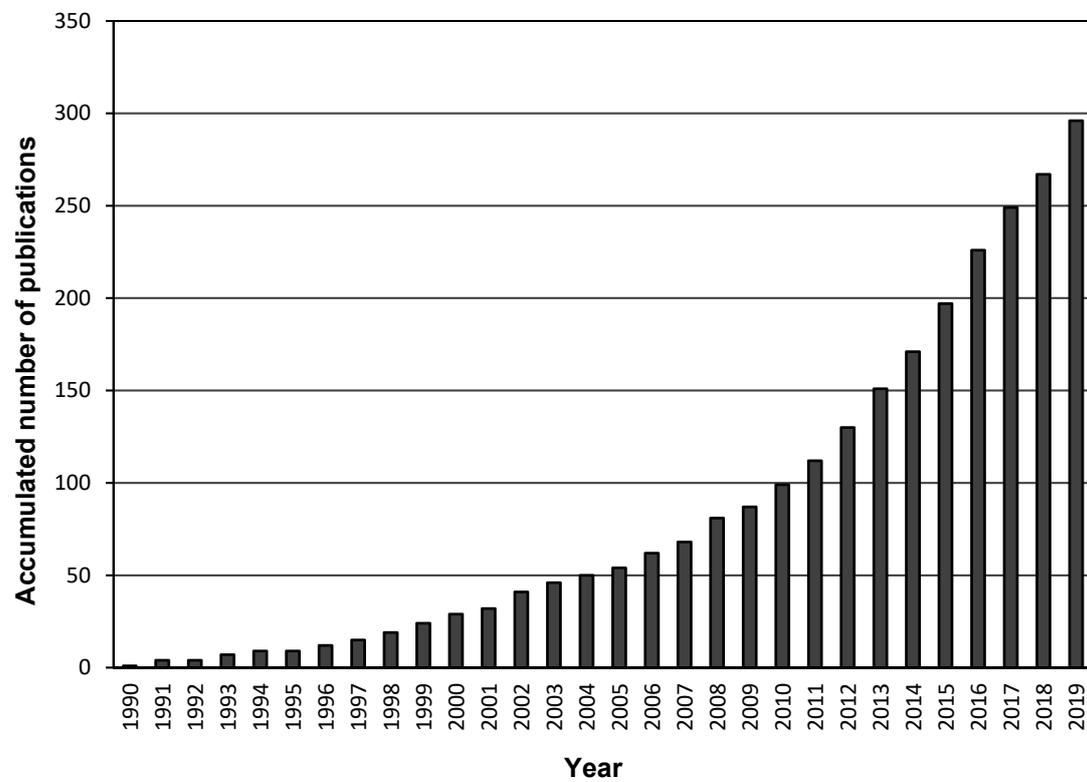
The evolution through time of the annual scientific production in the sources of Scopus and the total number of accumulated documents are graphed in Figure 1. Three different stages were distinguished. The first one covers the 1990–2009 period. Until 2009, the annual number of publications was maintained at a regular production of around 5 papers per year, and only 2008 contributed more than 10 papers. The second stage ranged from 2010 to 2016 and followed a linear increase in the annual production, starting at 12 documents and attaining 29 documents. Finally, the production was reduced in 2017 and 2018 (23 and 18 documents, respectively) to recover the value attained in 2016 again in 2019. Nonetheless, when the accumulated number of publications was analyzed, the corresponding evolution could be adjusted to a parabolic growth, and a quadratic regression model was applied to the data. The obtained equation was  $y = 0.475x^2 + 56.1x + 22.2$ , where  $y$  represents the number of accumulated documents and  $x$  the year (starting with 1 for the year 1990). The result exhibited a good fit, with an  $R^2$  value of 0.988.

The different types of documents were evaluated, and six types were identified. Nevertheless, article (265) was the most frequent document type, with 89.5% of total production, followed by review (15 documents and 5.1% contribution). Meanwhile, the number of proceedings papers was relatively low: just nine documents (3.0% contribution). The other less significant categories included book chapter (four), note (two) and letter (one). The clear preeminence of articles when compared to other types of publication was totally congruent with the results mentioned by other authors who investigated the research published regarding other water pollutants [48,49,52]. However, the relatively low contribution of proceedings papers is not as frequent, since the importance of the contributions in congress is significant in several engineering fields [53].

English was clearly the most frequently selected language in the scientific documents according to the search (93.6% of the documents were written in English). Several other languages were identified, including Russian and Chinese, as the second and third languages, respectively (1.7% and 1.4% of the total number of papers, respectively). The rest of the languages are compiled in Table 1, but they could be considered anecdotal, since no more than two documents were written in these languages. Once again, these results demonstrated that English has undoubtedly become the global lingua franca in the scientific research literature. Consequently, international communication has moved to a clear supremacy of English in this field, and more than 75% of the published documents in the social sciences and humanities and well over 90% in the natural sciences are written in English [54].



(a)



(b)

Figure 1. Annual (a) and accumulated (b) publication output.

**Table 1.** The languages employed by the publications.

Language	Publications	Contribution (%)
English	277	93.6
Russian	5	1.7
Chinese	4	1.4
French	2	0.7
Japanese	2	0.7
Turkish	2	0.7
German	1	0.3
Hungarian	1	0.3
Polish	1	0.3
Spanish	1	0.3

### 3.1.2. Publication Distribution of Countries and Institutions

The top 17 countries (the only ones that produced at least five documents) ranked by the total number of publications are compiled in Table 2. Since country affiliation is not an exclusive category (a document can be produced by authors from more than one country), some papers may be indexed in more than one country simultaneously due to international collaboration. As a consequence, the sum of the number of documents is higher than the total number of papers identified in the search. A reduced group of leading countries usually monopolize the worldwide scientific production. In this case, the joint contribution of the first three countries in the ranking (USA, China and India) accounts for around 50% of the total number of documents. The USA is the most prolific country, with 71 documents and a contribution percentage of 24.0%, very similar to the value obtained in another bibliometric analysis about selenium in drinking water [55]. This leader is followed by two Asian countries (China and India), which jointly contribute a percentage slightly higher than the American one (25.0%). Surprisingly, Turkey appears in the fourth position, before European countries, such as United Kingdom, France or Germany (sixth, seventh and eighth positions, respectively). The identification of molybdenum-rich groundwaters in arid regions of the Near East has been previously reported [29], so the concern about the presence of molybdenum in Turkish surface waters and groundwaters has promoted research in this area [56,57]. A similar explanation can justify the presence of another country in this region among the most productive ones, since Saudi Arabia occupies the last position in Table 2 thanks to the studies performed to gain a better understanding of the presence of heavy metals (including molybdenum) in the drinking water of different Arabian locations [58,59]. South American contribution was only represented by Argentina (eleventh position with nine documents) despite the high concentrations of molybdenum in the aquifers located in this subcontinent [60,61].

The top 12 institutions (the only ones with at least five documents) are shown in Table 3. Among these top 12 institutions, 4 were in China and only 2 in the USA, so although the USA was the most productive country, this production was greatly shared among the different institutions. In the case of China, its production was more concentrated, and the first (Chinese Academy of Sciences with 10 documents and 3.4% contribution) and the third (Ministry of Education China with 8 documents) institutions were Chinese. Surprisingly, the second position and the other shared third position corresponded to Turkish universities: Pamukkale Üniversitesi and Akdeniz Üniversitesi (nine and eight documents, respectively). A Latin American institution, the Argentinian Consejo Nacional de Investigaciones Científicas y Técnicas, contributed as much as the leading American institutions (United States Geological Survey and Norwich University), all of them with five documents.

**Table 2.** The top 17 most productive countries (at least five documents).

Ranking	Country	Publications	Contribution (%)
1	United States	71	24.0
2	China	49	16.6
3	India	25	8.4
4	Turkey	23	7.8
5	Canada	20	6.8
6	United Kingdom	18	6.1
7	France	14	4.7
8	Germany	13	4.4
8	Japan	13	4.4
10	Iran	10	3.4
11	Argentina	9	3.0
11	Italy	9	3.0
11	Sweden	9	3.0
14	Australia	8	2.7
15	Bangladesh	6	2.0
15	Russian Federation	6	2.0
17	Saudi Arabia	5	1.7

**Table 3.** The top 12 most productive institutions (at least five documents).

Ranking	Institution	Publications	Contribution (%)
1	Chinese Academy of Sciences (CHINA)	10	3.4
2	Pamukkale Üniversitesi (TURKEY)	9	3.0
3	Ministry of Education (CHINA)	8	2.7
4	Akdeniz Üniversitesi (TURKEY)	8	2.7
4	University of Toronto (CANADA)	6	2.0
6	Beijing Normal University (CHINA)	6	2.0
7	University of Chinese Academy of Sciences (CHINA)	6	2.0
7	Hospital for Sick Children-University of Toronto (CANADA)	6	2.0
9	Consejo Nacional de Investigaciones Científicas y Técnicas (ARGENTINA)	5	1.7
9	United States Geological Survey (USA)	5	1.7
9	Norwich University (USA)	5	1.7
9	British Geological Survey (UNITED KINGDOM)	5	1.7

### 3.1.3. Distribution of Output in Subject Categories and Journals

The distribution of subject categories is represented in Table 4, which shows the nine most popular categories (the only ones that produced at least 20 articles). Once again, some documents can be included in more than one subject, since it is not an exclusive category. The ranking indicates that Environmental Science was the most common subject (152 documents, which represents 51.4% contribution), followed by Chemistry (79 documents and 26.7% contribution). However, the relevance of biomedical sciences in research about molybdenum in drinking water is justified, since Medicine occupied the third position, followed by Biochemistry, Genetics and Molecular Biology and Pharmacology, Toxicology and Pharmaceutics in the fourth and fifth positions in the ranking, respectively. These results coincide with the ones obtained by bibliometric studies focused on the research trends on lead and selenium in drinking water [49,55], but they are not concordant with the trends identified in the case of a bibliometric analysis about arsenic in drinking water [48]. In the case of arsenic, the Engineering category occupied the second position in the ranking, while in this case, it occupied the eighth position (24 documents), just after Chemical Engineering, which shared the sixth position with 28 documents. These details give strong evidence of the important research efforts focused on the implementation of effective technical solutions that can alleviate the problems derived from the presence of arsenic in drinking water, while in the case of molybdenum, the research efforts point

to the analysis of the health effects of the intake of molybdenum and are not focused on technologies for its removal from drinking water.

**Table 4.** The top nine most popular subject categories (at least 20 documents).

Ranking	Subject	Publications	Contribution (%)
1	Environmental Science	152	51.4
2	Chemistry	79	26.7
3	Medicine	61	20.6
4	Biochemistry, Genetics and Molecular Biology	46	15.5
5	Pharmacology, Toxicology and Pharmaceutics	29	9.8
6	Agricultural and Biological Sciences	28	9.5
6	Chemical Engineering	28	9.5
8	Engineering	24	8.1
9	Earth and Planetary Sciences	21	7.1

The number of documents published in the most prolific journals is shown in Table 5. As an indicator of journal relevance, the corresponding Impact Factor (IF) and Scimago Journal Ranking (SJR) indicators of the top seven journals, the only ones that published at least five articles, were included. Only the leading journal *Environmental Monitoring and Assessment* contributed with more than 5% to the total scientific production (15 documents, which represents 5.1% contribution), so the published papers are highly shared among different sources. *Environmental Monitoring and Assessment* discusses technical developments and data arising from environmental monitoring and assessment, principles in the design of monitoring systems and the use of monitoring data in assessing the consequences of natural resource management and pollution risks. The relevance of the journals that published documents related to molybdenum and drinking water is demonstrated by the occurrence of four journals with IF values above 5: *Science of the Total Environment*, *Water Research*, *Environmental Science and Technology* and *Food Chemistry*. Furthermore, the presence of two journals related to the health effects of toxic elements, *Biological Trace Element Research* and *Journal of Environmental Science and Health: Part A Toxic Hazardous Substances and Environmental Engineering*, confirms the importance of the health aspects of the presence of molybdenum in drinking water.

**Table 5.** The top seven most popular journals (at least five documents).

Ranking	Source	IF 2018 (WoS)	SJR 2018 (Scopus)	Publications	Contribution (%)
1	<i>Environmental Monitoring and Assessment</i>	1.959	0.623	15	5.1
2	<i>Science of the Total Environment</i>	5.589	1.536	11	3.7
3	<i>Biological Trace Element Research</i>	2.431	0.693	9	3.0
4	<i>Water Research</i>	7.913	2.721	8	2.7
5	<i>Journal of Environmental Science and Health: Part A Toxic Hazardous Substances and Environmental Engineering</i>	1.536	0.480	7	2.4
6	<i>Environmental Science and Technology</i>	7.149	2.514	5	1.7
6	<i>Food Chemistry</i>	5.399	1.768	5	1.7

### 3.1.4. Most Frequently Cited Papers

The top 10 articles according to the number of times they were cited are presented in Table 6. The number of citations increases from 99 for the last article to 284 for the leading article, which occupied the first position in the ranking. Although more detailed comments regarding the identification of hot topics will be presented as a consequence of the analysis of the most frequently selected author keywords, the reading of the most cited publications gave an initial idea about some important aspects that deserve attention from researchers investigating molybdenum and drinking water.

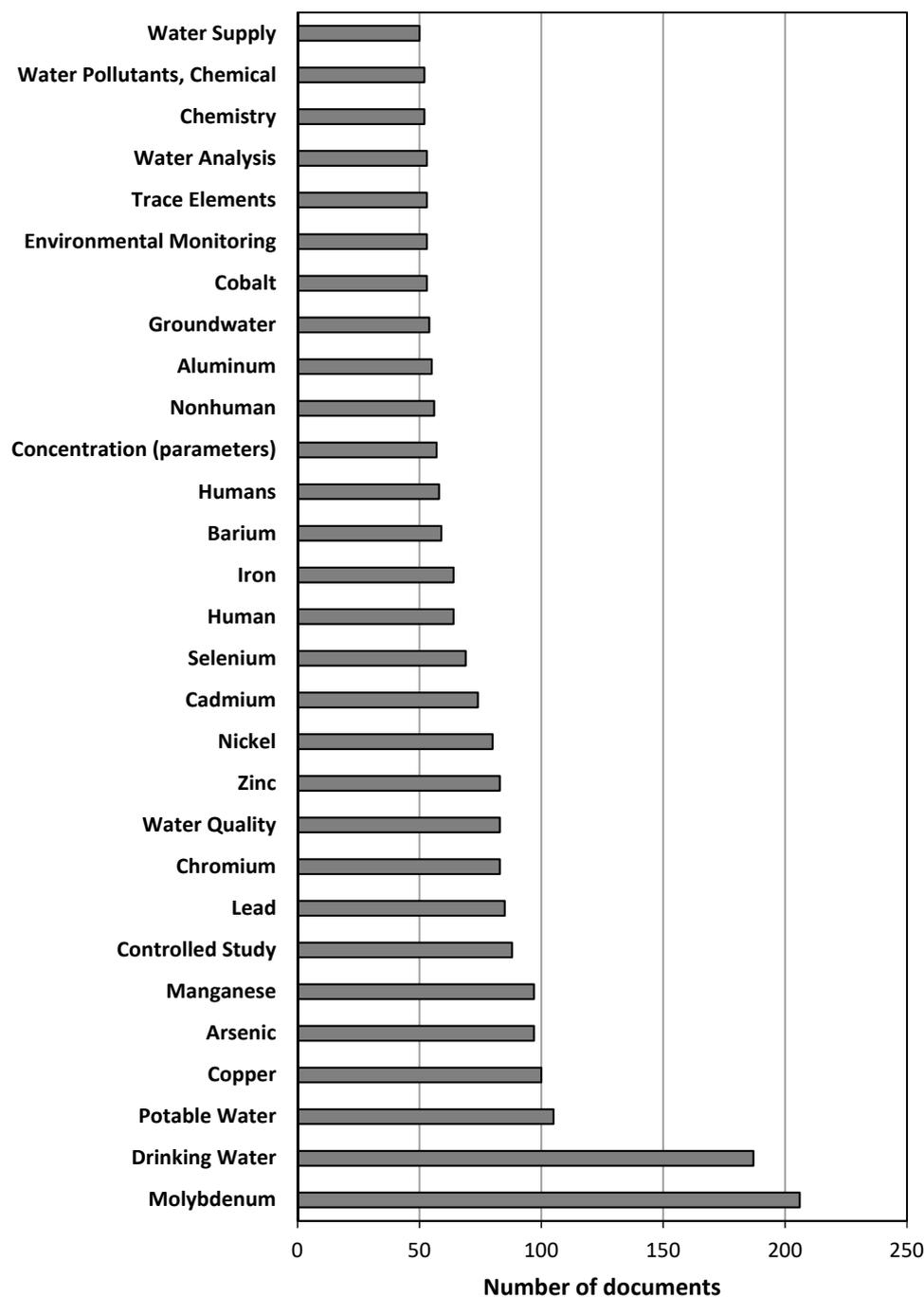
**Table 6.** The top 10 most cited papers.

Ranking	Articles	Times Cited
1	Title: <b>Rapid water disinfection using vertically aligned MoS<sub>2</sub> nanofilms and visible light</b> Authors: Liu, C., Kong, D., Hsu, P.-C., ( . . . ), Boehm, A.B., Cui, Y. Source: <i>Nature Nanotechnology</i> Published: 2016	284
2	Title: <b>One century of arsenic exposure in Latin America: A review of history and occurrence from 14 countries</b> Authors: Bundschuh, J., Litter, M.I., Parvez, F., ( . . . ), Cumbal, L., Toujaguez, R. Source: <i>Science of the Total Environment</i> Published: 2012	261
3	Title: <b>Removal of B, Cr, Mo, and Se from wastewater by incorporation into hydrocalumite and ettringite</b> Authors: Zhang, M., Reardon, E.J. Source: <i>Environmental Science and Technology</i> Published: 2003	187
4	Title: <b>In situ growing Bi<sub>2</sub>MoO<sub>6</sub> on g-C<sub>3</sub>N<sub>4</sub> nanosheets with enhanced photocatalytic hydrogen evolution and disinfection of bacteria under visible light irradiation</b> Authors: Li, J., Yin, Y., Liu, E., ( . . . ), Fan, J., Hu, X. Source: <i>Journal of Hazardous Materials</i> Published: 2017	140
5	Title: <b>MoS<sub>2</sub> nanosheets with widened interlayer spacing for high-efficiency removal of mercury in aquatic systems</b> Authors: Ai, K., Ruan, C., Shen, M., Lu, L. Source: <i>Advanced Functional Materials</i> Published: 2016	133
6	Title: <b>Leachability of elements from sub-bituminous coal fly ash from India</b> Authors: Praharaj, T., Powell, M.A., Hart, B.R., Tripathy, S. Source: <i>Environment International</i> Published: 2002	124
7	Title: <b>Treatment of arsenic-containing solutions using chitosan derivatives: Uptake mechanism and sorption performances</b> Authors: Dambies, L., Vincent, T., Guibal, E. Source: <i>Water Research</i> Published: 2002	119
8	Title: <b>Assessment of molybdenum toxicity in humans</b> Authors: Vyskočil, A., Viau, C. Source: <i>Journal of Applied Toxicology</i> Published: 1999	116
9	Title: <b>One-pot synthesis of multifunctional magnetic ferrite-MoS<sub>2</sub>-carbon dot nanohybrid adsorbent for efficient Pb(II) removal</b> Authors: Wang, J., Zhang, W., Yue, X., ( . . . ), Li, Z., Wang, J. Source: <i>Journal of Materials Chemistry A</i> Published: 2016	114
10	Title: <b>Arsenic(V) sorption on molybdate-impregnated chitosan beads</b> Authors: Dambies, L., Guibal, E., Roze, A. Source: <i>Colloids and Surfaces A: Physicochemical and Engineering Aspects</i> Published: 2000	99

Surprisingly, the most cited document explains the use of few-layered vertically aligned MoS<sub>2</sub> films for harvesting the whole spectrum of visible light and achieving highly efficient water disinfection [62]. Therefore, molybdenum is not a target to be removed from drinking water; it is part of a technological solution to remove other pollutants from drinking water instead. This approach is followed by several researchers among the most cited documents. The document in the fourth position in Table 6 presents another molybdenum compound, Bi<sub>2</sub>MoO<sub>6</sub>, which has been successfully employed to promote solar disinfection of water [63]. The documents in the fifth and ninth positions have also applied MoS<sub>2</sub> to water treatment, but in these cases, for the removal of mercury and lead, respectively [64,65]. In addition, the removal of arsenic from water by molybdate-impregnated chitosan beads has been deeply investigated by the documents in the seventh and tenth positions [66,67]. Regarding health and toxicological aspects of molybdenum, one article covers the assessment of molybdenum toxicity in humans and identifies the direct links between molybdenum intoxication and copper metabolism [68]. The remaining three papers in Table 6 are related to the identification of the presence and the quantification of the corresponding molybdenum concentrations in different water samples [69,70] and the proposal of a treatment alternative to remove molybdenum and other metals from water, simply by incorporation into hydrocalumite and ettringite [71]. Nevertheless, in both situations, molybdenum is not the main target of the research studies, and more attention is paid to other elements, such as arsenic, manganese or chromium.

### 3.1.5. Distribution Analysis of Author Keywords and Trending Topics of the Research

The list of the 29 most often used keywords (the only ones that were mentioned at least 50 times) is shown in Figure 2. Obviously, “*molybdenum*” was the most frequent keyword, as it was selected in 206 articles. The second position in the ranking corresponded to the other expression introduced in the Article Title, Abstract, Keywords field of the search engine database, “*drinking water*”, which appeared 187 times, followed by “*potable water*”, appearing 105 times. Indeed, these figures indicated that only 69.6% of all the identified documents used “*molybdenum*” as a keyword, while this percentage was reduced to 63.2% for “*drinking water*”. After a further look into the terms listed, the identification of several other metallic and metalloid elements in the first positions in the ranking must be highlighted: “*copper*” (100 times), “*arsenic*” (97 times), “*manganese*” (9 times), “*lead*” (85 times), “*chromium*” (83 times), “*zinc*” (80 times), “*cadmium*” (74 times), “*selenium*” (69 times), “*iron*” (64 times), “*barium*” (59 times), “*aluminum*” (55 times) and “*cobalt*” (53 times). Although other bibliometric analyses have identified the relevance of the toxicity interactions (synergistic and antagonistic effects) between metals [55], in the case of molybdenum, there is a lack of terms related to toxicological tests in the terms compiled in Table 2, and the presence of all these elements as frequent keywords should be explained by two alternative causes. On the one hand, the evaluation of the presence and the distribution of molybdenum in drinking water, water bodies or other samples of environmental interest implied a more complete water sampling and characterization, which included the assessment of the concentrations of all these elements in addition to molybdenum [72–74]. On the other hand, as mentioned in the previous section regarding the most cited documents, molybdenum can be useful for potabilization treatments and the removal of other elements from water. Finally, terms directly related to possible technologies for molybdenum removal from water or wastewater treatment were not frequently selected as keywords.



**Figure 2.** The top 29 most frequently used keywords (at least 50 times).

### 3.2. Review of Current Treatment Alternatives for Molybdenum Removal from Drinking Water

The list of commercially available and emerging technological alternatives for molybdenum removal from aqueous solution is extensive, but the most important options can be categorized into these four main categories:

- Adsorption and ion exchange.
- Coagulation–flocculation–precipitation.
- Membrane technologies.
- Biological processes.

A concise summary of each category is presented in the next subsections based on some of the most important references, but the aim of this work is not an extensive and meticulous

compilation of all the scientific papers published regarding the technical treatments to remove molybdenum from aqueous solution.

### 3.2.1. Adsorption and Ion Exchange

Adsorption and ion exchange are recurrently selected to remove metals and metalloids from aqueous solution. In fact, adsorption can be highlighted as the most relevant technology for arsenic or selenium removal from drinking water [48,55]. In the case of treatment of water samples with high molybdenum concentrations by adsorbents and ion exchangers, the number of scientific documents published is high as well.

Iron-based adsorbents can be mentioned among the most frequent materials tested to remove molybdenum from water. Zero-valent iron (ZVI), iron oxides, hydroxides and oxyhydroxides have demonstrated their efficacy to adsorb molybdenum for selenium oxyanions [75,76]. Other iron compounds, such as sulfide (pyrite), have been tested too, but their weak interactions with molybdate make other iron adsorbents more preferable [77]. The effects that pH, surface loading and ionic strength have on the adsorption mechanisms have been investigated, and the results have demonstrated that iron-based adsorbents can be effective in both acidic and alkaline conditions [78,79]. The most advanced approach proposes the employment of nanoparticles, nanocomposites and other nanomaterials for the intensification of molybdenum removal. For instance, polymer-functionalized nanocomposites were synthesized for selective adsorption of molybdate from aqueous solution by grafting hydrous ferric oxide nanoparticles into the porous structure of a polystyrene anion exchanger [80]. These nanocomposites exhibited greatly enhanced selectivity toward molybdate in the presence of competitive anions (such as chloride, carbonate, sulfate and phosphate), which can cause a significant reduction in the removal performance, since some of these ubiquitous anions, particularly phosphate, appear to be strong competitors of molybdate [81]. In addition, the presence of organic matter, even at low concentrations where no competition effect of adsorbed organic molecules can be observed, reduces molybdate adsorption, probably by decreasing the accessibility of diffusion pathways [82]. The removal of molybdenum from water by adsorbents based on other metallic compounds (mainly oxides and hydroxides) has been investigated. Activated alumina is known to be successfully applied in the removal of pollutants from drinking water, including molybdenum [83,84]. Other researchers have demonstrated the potential of other metallic compounds, such as titania [85,86] or chromium hydroxide [87].

Layered double hydroxides and zeolites are high-performance adsorbents that can be implemented in the treatment of drinking water. These materials have demonstrated that they can reduce molybdenum concentration significantly [88–90]. Nevertheless, specific conditions are required to optimize the adsorption process. For example, molybdate can be substantially adsorbed by some exchanged forms of clinoptilolite-rich tuff and natrolite, whereas the uptake by the natural forms of these zeolites can be considered negligible [91]. Therefore, the surface characteristics, the chemical composition and the ratio of the different ions determine the adsorption performance, so adequate mechano-chemical treatment is needed to assure maximal adsorption capacity [92].

Carbonaceous materials have been extensively employed as adsorbents, and activated carbon is the most illustrating example, which has been successfully applied in the removal of molybdenum [93]. The production of activated carbons from residual lignocellulosic wastes (for example coir pith) improves the sustainability of the process and fits the targets of circular economy. Moreover, in the case of molybdenum removal, the application of another adsorbent derived from natural biowastes has been deeply studied: chitosan. Chitosan is obtained by alkaline treatment of the chitin shells of shrimps and other crustaceans, and it has demonstrated a high molybdate adsorption capacity, attaining values above 250 mg/g [94]. The effects of the deacetylation degree and molecular weight of chitosan on molybdate sorption have been analyzed [95], and the optimal operation conditions have been defined [96]. The crosslinking of chitosan with glutaraldehyde improves the stability of the prepared adsorbent [97], which can even be used to prepare imprinted gel beads

with exceptional selectivity toward molybdate [98]. The sorption capacities of the main adsorbents employed for molybdenum removal are compiled in Table 7.

**Table 7.** Compilation of the sorption capacities of the main adsorbents tested for molybdenum removal from aqueous solutions.

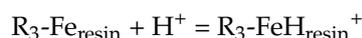
Treated Water	Adsorbent	Sorption Capacity (mg/g)	Reference
Synthetic solution	Akaganeite ( $\beta$ -FeOOH)	400	[76]
Synthetic solution	Pyrite ( $\text{FeS}_2$ )	21	[77]
Synthetic solution	Synthetic hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ )	6	[78]
Synthetic solution	Goethite ( $\alpha$ -FeO(OH))	26	[81]
Synthetic solution	Titania ( $\text{TiO}_2$ )	7	[85]
Synthetic solution	Alumina ( $\text{Al}_2\text{O}_3$ )	125	[86]
Synthetic solution	Fe(III)/Cr(III) hydroxide	12	[87]
Synthetic solution	Zn–Al sulphate layered double hydroxide	154	[88]
Synthetic solution	Hydrotalcite-like layered double hydroxide	10	[89]
Synthetic solution	Hydroxy-aluminum treated montmorillonite	5	[90]
Synthetic solution	Ag-exchanged clinoptilolite	100	[91]
Synthetic solution	ZnCl <sub>2</sub> activated coir pith carbon	17	[93]
Synthetic solution	Chitosan	265	[94]
Synthetic solution	Chitosan	750	[95]
Synthetic solution	Chitosan	820	[96]
Synthetic solution	Imprinted chitosan/triethanolamine gel	350	[98]

The use of commercially available ion exchange resins for molybdenum removal was investigated. Different works have evaluated the performance of strong and weak basic anionic resins (Table 8) for the removal of molybdate anion [99–105]. Results have shown that the adsorption capacity of some resins for molybdenum can be high, with values above 460 mg/g [99]. The pH plays a relevant role in the speciation of molybdenum and the rest of the chemicals present in aqueous solution and defines the performance and selectivity of the ion exchange process. In complex real matrices, the influence of the pH is modified by redox equilibria and the presence of ions that can take part in complexation reactions, so the definition of the optimal conditions for the treatment is not direct, and it must be investigated. For instance, on the one hand, in the case of Purolite A-170 resin for treatment of molybdenite dust leached solution, the adsorption efficiency of molybdenum was increased to 95% up to pH 4.0 but then sharply decreased to zero with an increase in the pH value above 9.0 [101]. It is clear that once the deprotonated molybdate ion ( $\text{MoO}_4^{2-}$ ) becomes the dominant form, which occurs at pH values around 4, the performance of the anionic ion exchange resin is highly increased. On the other hand, in the case of D290 resin from Bengbu Dongli Chemical for treatment of sulfurized tungstate solution (50 g/L W, 0.58 g/L Mo and 3 g/L  $\text{S}^{2-}$ ), over 99% removal of molybdenum was achieved at pH values above 8 [106]. Nevertheless, all the ion exchange processes based on the application of anionic resins have to deal with a very important drawback. The presence of other anions, such as nitrate, sulfate or chloride, implies a strong competition for the exchange sites in the resins. Since, in most cases, the concentrations of these competitive anions are much higher than the molybdate concentrations, the treatment with anionic ion exchange resins can turn out unproductive because of the depletion of the resins with these anions, which impede the effective removal of molybdenum.

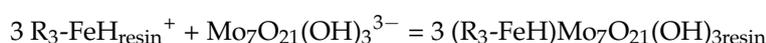
**Table 8.** Compilation of anionic ion exchange resins tested for molybdenum removal from aqueous solutions.

Resin	Manufacturer	Functional Group
D301	Tianjin Nankai Hecheng	Tertiary ammonium
D201	Hangzhou Zhengguang Chemical	Quaternary ammonium
D213	Hangzhou Zhengguang Chemical	Quaternary ammonium
D308	Hangzhou Zhengguang Chemical	Tertiary amine
D319	Hangzhou Zhengguang Chemical	Tertiary amine
D303	Hangzhou Zhengguang Chemical	Primary amine
D309	Hangzhou Zhengguang Chemical	Primary amine
D320	Hangzhou Zhengguang Chemical	Quaternary ammonium and tertiary amine
A-170	Purolite	Complex amine
A-172	Purolite	Complex amine
D3411	Purolite	Diethanol amine
AG 1 X-8	Bio-Rad	Quaternary ammonium
D290	Bengbu Dongli Chemical	Quaternary ammonium
VP OC 1065	Lewatit	Primary amine
MP 800	Lewatit	Quaternary ammonium
MP 62	Lewatit	Tertiary amine
M-43	Dowex	Tertiary amine

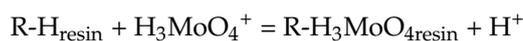
In order to improve the selectivity of the ion exchange resins for molybdenum removal and avoid the competition of other anions, innovative ligand and chelating resins have been suggested. The uptake of molybdenum from aqueous solutions can be facilitated by some commercially available bifunctional chelating cation exchange resins (polyampholites) [107]. The results demonstrated that the polyampholites containing carboxylic functional groups (Amberlite IRC718 and Amberlite IRC748 with iminodiacetic functional groups) were more susceptible toward the sorption of molybdenum-containing species from aqueous solutions than Duolite C467, which contains phosphonic acid groups. The ion exchange and formation of strong coordination complexes were favored at a weakly acidic to medium pH (3.5). Another example of the application of Amberlite IRC748 resin can be mentioned [108]. In this case, the chelating resin was employed to separate vanadium and molybdenum from an acidic sulfate solution of blue sludge. The loading of Mo from the leachate containing 40 mg/L Mo was found to be 2.9 g/L resin with a contact time of 100 min. The ion exchange resin Purolite D4123 (with 1-deoxy-1-(methylamino)-D-glucitol functional group) was tested for molybdate removal [102]. The maximum sorption capacity (1.22 mol/L) was determined from Langmuir isotherms and breakthrough capacity from dynamic column sorption. The study concluded that this special chelating resin showed higher breakthrough capacity and tolerance to competitive sorption of sulphates and chlorides than an anionic ion exchange resin with the diethanolamine functional group. Lastly, the use of strong cationic ion exchange resins, both in fresh or pretreated (metal loading) forms, can be applied in the removal of molybdenum too [103]. Diphonix (manufactured by EiChrom) is a strong cation exchanger functionalized with diphosphonic and sulfonic acid groups that has demonstrated its usefulness to capture both anionic and cationic complexes of molybdenum from aqueous solutions [104]. Some metals (iron as example) loaded into the Diphonix resin can become protonated in acidic medium:

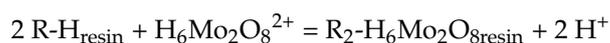


The above protonated iron can load anionic molybdenum species:



The reaction between cationic molybdenum species and fresh Diphonix resin can be represented as





Nevertheless, anionic resins presented better results than metal-loaded cationic resins for the removal of molybdenum, although the loading capacity value of Diphonix for molybdenum was found to be 90 mg/g, even in the presence of higher concentrations of copper and iron.

### 3.2.2. Coagulation–Flocculation–Precipitation

The use of iron and aluminum salts as coagulants is a common practice in water treatment because of its simplicity, wide availability, low price and avoidance of hazardous chemicals. As in the case of arsenic removal [48], ferric salts are the most preferred option. Both ferric chloride and ferric sulphate have been tested for molybdenum removal. A study that allowed a direct comparison concluded that the ferric sulphate showed a higher molybdenum removal efficiency at pH 4–5 than the chloride, but both chemicals demonstrated equal removal efficiency at pH 6–9 [109]. The synthesis of ferromagnetic nanoparticles derived from ferrous and ferric chlorides can improve the process performance and increase the removal efficiency from around 70% to more than 90% [110]. These ferromagnetic nanoclusters play a relevant role as core shells, which produce magnetic attraction and improve the gravitational and electrostatic attraction sedimentation. Ferromagnetic nanoparticles enhance the bridge and adsorption effects, leading to a larger floc size and giving, as a result, an enhanced filtration of the resulting ferromagnetic nanoclusters–ferric flocs. The selection of aluminum salts as a coagulant is less common, and the addition of coagulation aid chemicals, such as polyacrylamide, is suggested [111]. In fact, the application of commercially available formulations based on organic polyelectrolytes, which can achieve removal efficiencies around 90%, has gained attention in recent years [112,113]. The results obtained with the main coagulants employed for molybdenum removal are compiled in Table 9.

**Table 9.** Compilation of the main coagulants tested for molybdenum removal from aqueous solutions.

Treated Water	Coagulant	Dose (mg/L)	pH	Initial [Mo] (µg/L)	Removal (%)	Reference
Synthetic solution	FeCl <sub>3</sub> /Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	10	6	700	90/89	[109]
River reservoir	Ferromagnetic nanoparticles + FeCl <sub>3</sub>	35 + 97	7	500	97	[110]
Synthetic solution	Aluminum polychloride + polyacrylamide	40 + 0.8	-	1100	92	[111]
Mineral processing wastewater	BK-A (commercial formulation)	25	9	-	-	[112]
Nitric acid media doped with molybdenite	KlarAid products (commercial formulation)	20,000	-	615,000	88	[113]

Extractive metallurgy and hydrometallurgy have paid attention to the separation of molybdenum from other metals, and selective precipitation was investigated (Table 10). The results of the experiments carried out to investigate the precipitation behaviors of Mo and W with different divalent ions revealed that Mo was poorly precipitated by most of them (including Sr<sup>+2</sup>, Ca<sup>+2</sup>, Mn<sup>+2</sup>, Fe<sup>+2</sup>, Co<sup>+2</sup>, Ni<sup>+2</sup>, Zn<sup>+2</sup> or Cu<sup>+2</sup>), with precipitation percentages below 30% [114]. In fact, only Cd<sup>+2</sup>, Ba<sup>+2</sup> and Pb<sup>+2</sup> surpassed this value, with maximal 43% Mo precipitated in the case of Pb<sup>+2</sup>. Further detailed analysis of the precipitation of Mo in the presence of Co<sup>+2</sup> suggested that molybdenum was predominantly existent in the form of an anion group, which was physically adsorbed onto the precipitate, although some of the molybdenum was still chemically bound with cobalt [115]. However, the precipitation efficiency of molybdenum can be higher than 99% when precipitated with ammonium [116]. The formation of ammonium molybdate and tetraammonium octamolybdate is favored at pH values below 4 and is a more effective solution to precipitate molybdenum in aqueous solutions than the use of divalent cations [117].

Nevertheless, the mimesis of nature, where molybdenum is mainly present as molybdenite (MoS<sub>2</sub>), points to the fact that sulfide precipitation can be the most adequate way to remove molybdenum from solution. Among the precipitation methods, sulfide precipitation is commonly used in industry for many metals due to its advantages, which include

low solubilities of metal sulfide precipitates, possibility of selective metal removal, fast reaction rates, good settling properties and potential for reuse of sulfide precipitates by smelting [118]. In the case of Mo, oxidant conditions, such as the presence of concentrated  $H_2SO_4$ , rapidly oxidizes  $MoS_2$  into  $MoO_3$ . The precipitation of metals from synthetic leachates by addition of  $Na_2S$  resulted in the potential complete recovery of Mo at acidic pH values between 1 and 2 [119]. An adequate process design (optimal pH and temperature selection) can facilitate the selective precipitation of Mo in the presence of other metals, such as, V, Co or Cu [120], but complex sulfides, such as  $NH_4CuMoS_4$  and  $Cu_2MoS_4$ , may appear [121].

**Table 10.** Compilation of the main results of the precipitation conditions tested for molybdenum removal from aqueous solutions.

Treated Water	Precipitate	pH	Initial [Mo] ( $\mu\text{g/L}$ )	Removal (%)	Reference
Synthetic solution	$PbMoO_4$	-	4,800,000	43	[114]
Synthetic solution	$CoMoO_6 \cdot 0.9 H_2O$	7	23,000,000	>90	[115]
Synthetic alkali leaching solution	$(NH_4)_2Mo_4O_{13}$	2.5	22,100,000	99	[116]
Acidic leachate of mineral sludge	$MoO_3$	2	10,160,000	50	[118]
Acidic leachate of catalyst	$MoS$	2	17,300,000	98	[119]
Synthetic leachate of catalyst	Mo sulfides and oxides	2/6	38,000	72/87	[120]

### 3.2.3. Membrane-Based Processes

One of the main drawbacks of adsorption and ion exchange is the low performance in water samples with high salinity. The competence of other ions can reduce the removal of molybdenum significantly and result in an ineffective treatment. Equivalently, the presence of other chemical species in the molybdenum-rich water may interfere with the precipitation reactions, and the added reagent can be consumed without attaining molybdenum removal. Taking into account these considerations, membrane separations can provide a better solution for the treatment of high-salinity water streams, with simultaneous removal of a great variety of substances. Nevertheless, the selection of the most adequate pressure-assisted membrane technology must consider the balance between high molybdenum rejection and large permeate production. On the one hand, the least restrictive membrane technologies, such as microfiltration (MF) or ultrafiltration (UF), are characterized by high permeate production, but the removal rates can be unacceptably low. On the other hand, the most restrictive membrane technologies, such as reverse osmosis (RO) and nanofiltration (NF), can achieve satisfactory rejection percentages, but they also imply relatively low permeation fluxes and require high applied pressure [55].

Regarding the particular case of molybdenum removal, the use of MF and UF membranes has not achieved effective rejection percentages, since rejection values above 41% have not been reported [122]. Consequently, the implementation of auxiliary techniques has been proposed to improve the performance of UF membranes for this purpose. Micellar enhanced ultrafiltration (MEUF) has demonstrated to be a promising method to remove metal ions and organic compounds even at very low concentrations [123]. The addition of anionic and non-ionic surfactants (SDS and Tween 20 respectively) to the molybdenum solution (0.2–5.0  $Mo^{+6}$  mM) increased the rejection percentages to values above 90% [122]. Another example of the application of polymer-assisted ultrafiltration (PAUF) was identified. In this case, the use of water-soluble P(AAm-DDACI) as a polymeric sorbent for molybdenum significantly increased the performance of UF membranes of MWCO between 30 and 100 kDa when a reduced working pressure (2.0 bar) was applied [124]. Complete removal of molybdate ions (60 mg/L) was achieved at pH 3 with a polymer:metal molar ratio of 10:1.

Most documents related to the employment of commercially available NF and RO membranes for molybdenum removal refer to the application to wastewaters derived

from mining and metallurgical activities and groundwaters polluted by them (Table 11). Surface impoundments of tailings generated during uranium mining and milling often lead to groundwater contamination. Membrane filtration experiments designed to evaluate the capabilities of these processes to remove molybdenum, selenium, uranium, radium, thorium and other ions from contaminated groundwater have been proposed [125]. Three flat-sheet NF/RO membranes (PAC1 RO membrane from Ionics, TW30 LE RO membrane from Dow FilmTec and TFC-S NF membrane from Koch) were tested at a transmembrane pressure of 0.7 MPa, and all of them were highly effective in removing molybdenum, with rejection values in the range of 96–98%. The produced water is generated in the petroleum industry as a by-product of various processes in production and refining. The treatment of produced water using two commercial and highly hydrophilic NF and RO membranes (NF1 and RO-BW30 respectively) was able to successfully meet the regulatory quality standards for drinking water, with the exception of the parameters for ammonia and molybdenum [126]. In fact, the initial molybdenum concentration (815 µg/L) was reduced by 28% when treated by NF, while the RO membrane removal rate increased to 76%. Synthetic solutions that represent a leached secondary mining resource [127] or other molybdenum-rich material processing wastewaters [76] were treated by NF. In the first case, the polyamide NF membranes (NF99HF from Alfa Laval and UTC-60 from Toray) working at the applied pressures between 10 and 20 bar and pH 2 attained rejection values around 60% from an initial molybdenum concentration of 0.5 mg/L. In the latter case, the NF270-2540 membrane was tested at a lower pressure (5 bar) with 1 and 10 Mo mg/L solutions, and the achieved molybdenum rejection (98%) was clearly higher than the ones corresponding to chromium or vanadium. Finally, real Australian groundwaters were treated by four NF/RO membranes (BW30, ESPA4, NF90 and TFC-S) to investigate the effects of fluctuating energy and pH on the retention of dissolved metal contaminants using a photovoltaic-powered installation [128]. Molybdenum was present only in one of the groundwaters evaluated at 5 µg/L concentration. The work concluded that the rejection performance for most metals (copper, magnesium, manganese, molybdenum, nickel, uranium, vanadium and zinc) was highly dependent on the pH. These metals have insoluble and dominant species under certain pH conditions, which resulted in apparent retention values that varied significantly because of deposition on the membrane surface rather than charge or steric retention mechanisms. Nevertheless, pH values below 7 resulted in apparent retention percentages higher than 90%, with over 42% of the removed Mo accumulated in the membrane as precipitate.

**Table 11.** Compilation of the main results of the membrane technologies applied for molybdenum removal from aqueous solutions.

Treated Water	Membrane	ΔP (Bar)	Permeate Flux (m <sup>3</sup> /m <sup>2</sup> ·s)	Initial [Mo] (µg/L)	Removal (%)	Reference
Synthetic solution	NF270-2540 (Filmtec)	5	1.0 × 10 <sup>-3</sup>	1000	98	[76]
Groundwater contaminated by uranium mill tailings	PAC1 RO (Ionics) TW30 LE RO (FilmTec) TFC-S NF (Koch)	7	-	33,400	96–98	[125]
Produced water	NF1 and BW30 (Filmtec)	6 and 20	-	815	28 and 76	[126]
Synthetic solution	NF99HF (Alfa Laval) and UTC-60 (Toray)	20	1.7–3.7 × 10 <sup>-5</sup>	500	60–70	[127]
Brackish groundwater	BW30 (Filmtec)	14	1.4 × 10 <sup>-5</sup>	5	>95	[128]

### 3.2.4. Biological Treatments

Biological treatments for the removal of metals from water can be considered a solution with high potentiality, since they emerge as environmentally compatible treatment options (Table 12). Nevertheless, traditional biological and tertiary treatments in municipal wastew-

ater treatment plants are not effective for the removal of molybdenum from water [129]. Secondary treatment stage (activated sludge, biodisc and membrane bioreactor) can remove most metals (with removal rates above 70%), but molybdenum is included among the exceptions due to its low adsorption capacity, which results in removal rates below 10% with typical influent concentrations in the range between 1 and 10 µg/L. The consideration of tertiary treatment (polishing pond, rapid chemical settler, ozonation) did not contribute to the reduction in molybdenum content in water, since the corresponding removal rate was insignificant. Membrane bioreactors (MBRs) generally have a greater capacity for removing heavy metals from wastewater compared to conventional biological technologies due to a physical separation of the membrane with a significant removal of suspended solids. Two experimental full-scale MBRs (with microfiltration and ultrafiltration membranes) configured in pre-denitrification mode were able to reduce molybdenum concentration around 60–70% from the initial concentration of 3.6 µg/L [130]. However, this removal rate was clearly lower than the typical values for most metals analyzed. In order to increase the removal rate of molybdenum from water, specific microorganisms can be selected. For example, the removal of molybdenum and uranium in column bioreactors with immobilized *Desulfovibrio desulfuricans* has been investigated [131]. Intact cells of this bacterium were immobilized in polyacrylamide gel and used to remove soluble uranium and molybdenum species from water by enzymatically mediated reduction reactions. On the one hand, formate or lactate served as the electron donor, while, on the other hand, oxidized  $U^{+6}$  and  $Mo^{+6}$  species served as the electron acceptors. Over 99% removal percentages could be achieved for both elements with initial concentrations of 5 mg/L U and 10 mg/L Mo, respectively. Although sulfate concentrations as high as 2000 mg/L did not inhibit the biological treatment, nitrate inhibited molybdenum bio-reduction when its concentration was around 150 mg/L. Another study evaluated the potential of *Cupriavidus metallidurans* (strain CH34) to recover dissolved molybdenum [132]. This bacterium is known because of its adaptation to survive when exposed to several forms of heavy metal stress and was successfully employed in the selective recovery of molybdenum and vanadium from highly concentrated solutions derived from spent catalysts.

Algae have demonstrated efficient metal removal by either passive sorption to dead biomass or removal by living cells, and examples of this type of biosorbents have been tested for molybdenum treatment. Brown algae are adequate for this purpose, since they show high uptake capacities for various heavy metal ions due to the presence of biopolymers on the algae surface. *Petalonia fascia* is a brown seaweed that has been considered for  $Mo^{+6}$  removal from contaminated water [133]. The biosorbent prepared by immobilization of the biomass in an agar matrix was tested in batch and continuous sorption experiments. The main sorption mechanism was chemical sorption and resulted in high adsorption capacity (over 1300 mg/g). Another brown seaweed (*Cystoseria indica*) was investigated for molybdenum removal [134]. A packed bed column filled with algal biomass treated with 0.1 M  $CaCl_2$  solution was used for continuous biosorption of molybdate. The maximum biosorption capacity was found to be 18.32 mg/g, which allowed removal rates between 38 and 61% for solutions in the 30–95  $Mo^{+6}$  mg/L range. The waste biomass of *Posidonia oceanica* (a seagrass) accumulated on the beaches can be transformed to a resource when used as biosorbent for metals, including molybdenum [135]. After drying and rehydration of the seagrass biomass, batch tests were carried out with  $V^{+3}$  and  $Mo^{+5}$  solutions. Around 40% adsorption of molybdenum was attained with 5–80 mg/L initial concentrations. Very similar results were obtained when green seaweed biomass was employed instead of brown seaweed [136]. *Spongomorpha pacifica* biomass showed to be a good sorbent for molybdenum, and it has been used in continuous treatment of effluent polluted with molybdate ions, attaining a maximum sorption capacity over 1250 mg/g. Although most studies have focused on the use of dead biomass to remove metals, viable algae have shown promising results in metal removal from domestic and other wastewaters by living cells. The metal removal from oil sands tailings pond water by indigenous microalga *Parachlorella kessleri* is an example [137]. The indigenous algae were cultivated under

optimal conditions and applied for treatment of these industrial wastewaters. Some metals were successfully removed, such as zinc or manganese (removal rates close to 100%), but the case of molybdenum was not as effective. Removal rates in the range of only 2–27% were obtained from initial concentration levels between 50 and 125 µg/L.

Constructed wetlands have gained attention, as they can be considered a valid option for removal of heavy metals and emerging contaminants from water without high economic costs and provide additional ecological benefits. The selection among different filter media and plants is a key aspect to design an efficient constructed wetland specifically focused on molybdenum removal. Vertical-flow wetland filters with reed (*Phragmites australis*) and cattail (*Typha latifolia*) supported in humus, cinder, modified cinder or pyrite as filter media were investigated [138]. Synthetic solutions with concentrations of Mo<sup>+6</sup> from 2 to 40 mg/L were fed to the constructed wetland, and modified cinder and pyrite emerged as the best media, with adsorption capacities of 10.0 and 6.3 mg/g, respectively. In addition, cattail was more suitable for molybdenum absorption than reed, but the bioaccumulation accounted for only a very small portion of the total removal. Indeed, the largest fraction of molybdenum retained was the water-soluble fraction on the surface of the pyrite. The removal of selected risk metals (Pb, Cd, Cr, Mo, V, Be and Ba) from municipal wastewater using a horizontal-subsurface-flow constructed wetland was studied [139,140]. The system consisted of a storm overflow, a pretreatment (screens, horizontal sand trap and sedimentation basin) and two vegetated beds planted with common reed (*Phragmites australis*). The molybdenum concentration was reduced from 0.78 to 0.32 µg/L, which meant a 59% removal rate. Half of the molybdenum removal was produced during the pretreatment and approximately the same amount during the water flow through the first 5 m of the vegetation bed. Elevated concentrations of molybdenum in sediments taken from the front part of the wetland bed were observed.

**Table 12.** Compilation of the main results of the biological treatments applied for molybdenum removal from aqueous solutions.

Treated Water	Technology	Species	Initial [Mo] (µg/L)	Removal (%)	Sorption Capacity (mg/g)	Reference
Urban wastewater	Membrane bioreactor	Activated sludge	3.5	70	-	[130]
Synthetic solution	Column bioreactor	<i>Desulfovibrio desulfuricans</i>	10,000	99	-	[131]
Spent catalyst pulp	Bioleaching	<i>Cupriavidus metallidurans</i>	530,000	18	-	[132]
Synthetic solution	Biosorbent	<i>Petalonia fascia</i>	120,000	-	1376	[133]
Synthetic solution	Biosorbent	<i>Cystoseria indica</i>	95,000	-	30	[134]
Synthetic solution	Biosorbent	<i>Posidonia oceanica</i>	40,000	-	18	[135]
Synthetic solution	Biosorbent	<i>Spongomorpha pacifica</i>	3,200,000	-	1280	[136]
Oil sands tailings pond water	Biosorption	<i>Parachlorella kessleri</i>	50–125	2–27	-	[137]
Tap water doped with Mo	Constructed wetland	<i>Phragmites australis</i> and <i>Typha latifolia</i>	40,000	88	-	[138]
Municipal wastewater	Constructed wetland	<i>Phragmites australis</i>	1	59	-	[140]

#### 4. Conclusions

An overview of the research on molybdenum in drinking water was presented from the results of a bibliometric analysis (information about annual publications, document types, languages, countries, institutions, categories, journals and keywords). Although the number of accumulated publications on this topic increased according to a quadratic evolution during the 1990–2019 period, different periods were identified, including an initial stable phase until 2009, followed by a fast linear increase from 2010 to 2016, but an irregular production rate characterized the period after that year. The USA was the most productive country in terms of the total number of publications, followed by a couple of Asian countries (China and India). In fact, Chinese institutions appeared among the most productive ones. Although Environmental Science was the most frequent category, many studies in Medicine and Biochemistry, Genetics and Molecular Biology examined the identification of the health effects of the intake of molybdenum. Therefore, the research efforts targeted toward a search for technical solutions for molybdenum removal from water are not as important as the ones focused on the identification of molybdenum-polluted water bodies and the analysis of the health effects of the intake of molybdenum.

Nevertheless, although the investigation of new technological options to solve the problems caused by the presence of molybdenum in drinking water has been less intensive than the search for treatments to reduce the presence of other pollutants, such as arsenic or selenium, several research works have proposed adequate processes to remove molybdenum from aqueous media.

Adsorption and ion-exchange processes are the most frequently investigated treatment options. Several inorganic compounds, mainly iron oxides, hydroxides and oxyhydroxides, can be highlighted as the most promising sorbents under study, but other materials have been successfully applied too, such as layered double hydroxides, zeolites and carbonaceous materials. The use of strong and weak basic anionic resins has demonstrated good potential for reduction in molybdenum concentrations. Iron and aluminum salts have been successfully employed as coagulants, although the application of commercially available formulations based on organic polyelectrolytes, has gained attention in recent years. Pressure-assisted membrane technologies, such as nanofiltration (NF) and reverse osmosis (RO), must be considered as competitive solutions, but a balance between molybdenum rejection (higher in the case of RO) and permeate production (higher in the case of NF) is required. The most relevant biological treatments take advantage of the application of specific organisms known due to their adaptation to survive when exposed to high concentrations of heavy metals, such as bacteria *Desulfovibrio desulfuricans* and *Cupriavidus metallidurans*. Algal waste biomass is also a valuable biosorbent, and the design of adequate constructed wetlands can attain high removal of molybdenum.

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