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Can absorbent polymers remove pesticides from the environment? A Data Mining study

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Abstract: Pesticides are essential for improving agriculture, which is required for global food security. Nowadays, with population growth, these chemistry products are more explored and improved to enhance food production. The excessive use of herbicides, insecticides, and fungicides prompts several environmental damages, besides causing lack of natural and clean resources, promoting the alarming contaminated food rate worldwide. In face of critical human health issues, researchers are racing to understand how to minimize the environmental effects through new or fixed methods to detect and remove pesticide residues from the environment. In addition to seeking to develop and implement rules on the use of agrochemical products, there are other promising strategies in which polymers with inherent adsorption activity are the main focus in view of their chemical properties and of reusability. Modern research on pesticide absorption polymers (PAP) and their employment in contaminated soil show that they can be used for pesticide detection or remotion, by chemical interaction mechanisms, which is more efficient than the latest. In view of all arguments, this paper shows the main issues covered in the articles on using polymers to detect agrochemical products from the environment. These analyses were made on the platforms Scopus and Web of Science. The results concluded that the principal search focus was on detecting high-hazard pesticides using polymers. The materials which were most mentioned were the methyl methacrylate polymer, the alkaline phosphatase biosensor and some metal coordination polymers, which can interact with complex groups of agrotoxics.

Keywords: Pesticides, polymers, detection, absorption, Data Mining.

Adherence to the BJEDIS' scope: Data Mining, Statistic Analysis and Data Analysis.

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1. INTRODUCTION

After the Green Revolution, agrochemical products were created and improved to certify more quality and quantity food. That is because of the growing population, explained by Malthus in your work (1), and the necessity for economic stability. Moreover, many chemical products used in the Second World War were studied and used for better reasons, like improving the harvest. One of the first pesticides applied was dichloro-diphenyl-trichloroethane (DDT), shown on molecule (a), an organochlorine product used as an insecticide to control insect-borne diseases or parasites that cause agricultural issues. This product was used until the 70s because it was cheaper than others. However, it was discovered that the DDT is a potential carcinogenic with a high level of toxicity and the high resistance for biological decomposition chlorine radicals. For this reason, most countries have banned DDT in agriculture.

After that, other pesticides were developed, divided in different chemical groups besides organochlorines.There's the carbamates, which has as fundamental structure the N-methylcarbomeric acid, an example is the insecticide Propoxur (shown on molecule b), a very toxic pesticide. Moreover, the organophosphorus is an organic compound which is derivative of phosphoric acid, thiophosphoric acid and dithiophosphoric acid. An example is the insecticide Chlorpyrifos (shown on molecule c), with level II of toxicology. Finally, there's the pyrethroids, which have a similar structure with the pyrethrins found at Chrysanthemum cinerariaefolium flowers, that are great to act as insecticides. Some materials used as pesticides molecular structure is shown in Figure 1. An example is the Cypermethrin (shown on molecule d), a synthetic pyrethroid with level II of toxicology, classified as dangerous if inhaled (2).

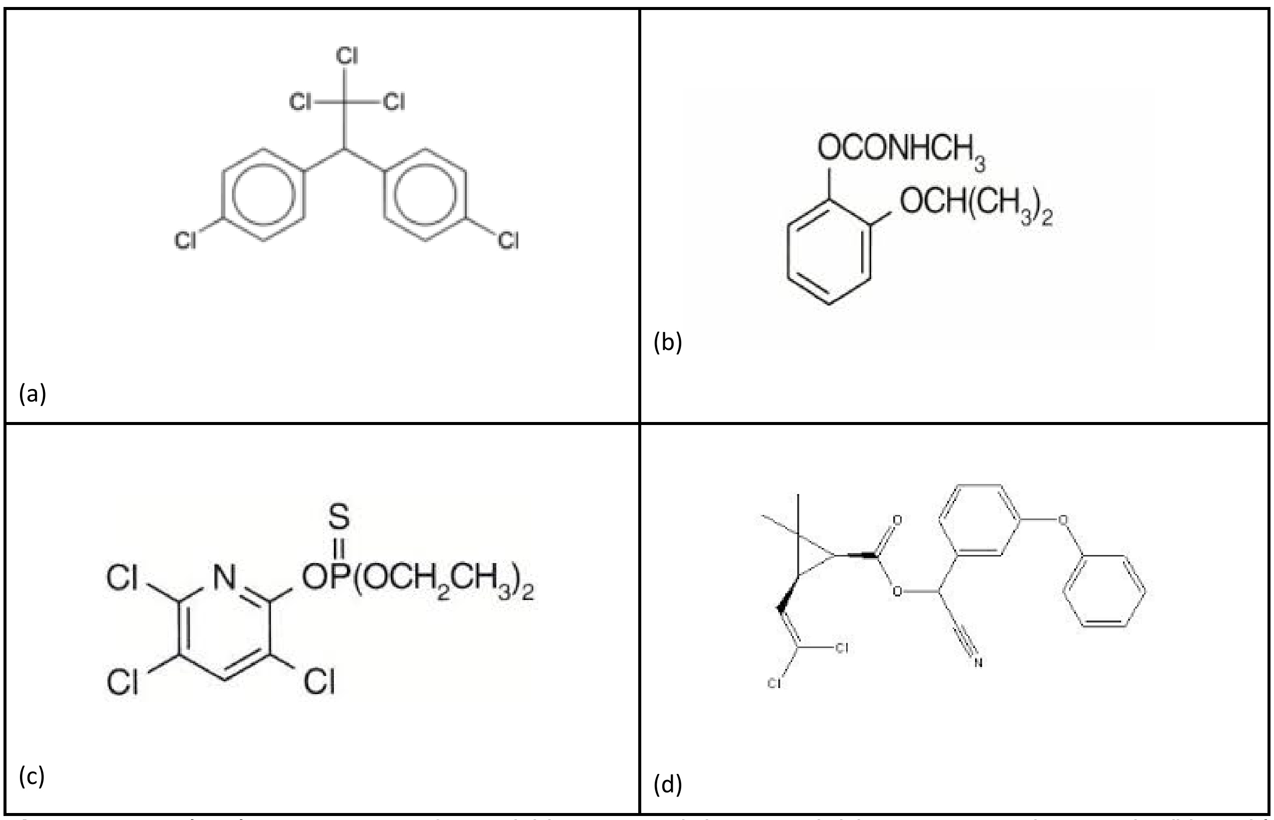

Figure 1. Molecular structure of pesticide: DDT (ChemDraw).(a), Propoxur (ANVISA) (b), Chlorpyrifos (www.gov.br).(c) and Cypermethrin (www.gov.br).(d).

According to the International Labor Organization, agrochemical products are responsible for seventy thousand intoxicated people cases per year (2). This disease's primary victims are by toxic product contact. Symptoms range from skin rashes to advanced stages of cancer. The excessive use of these compounds in the environment can expose them to different active substances, which causes air, soil and water pollution. Because of this, some laws were created to control the use of pesticides and their danger level. In "Silent Spring", by Rachel Carson, there's a study about the risks of the DDT discussed above and its impacts on flora and fauna. After this work, in 1972, this substance was banned from the United States. This action was considered one of the first regulations concerning agrochemicals (4).

In Brazil, the Agrotoxic Law (number 7,802) was approved in 1989, which in the first section said that the production, research, buying and selling, destination of waste, and classification, among others, would be regulated by guidelines described in this lawful standard. Regarding the publicity, a national law was created (number 9,294) that only accepts the pesticides publicity if it was directed to specific customers, like farm workers, and had an explanation about the use and dangers of this product (5).

However, waste removal for the maintenance of habitats is still a problem. The polymers' applications for detecting and removing agrochemicals are being studied. That is because of the low reactivity and low price, which encourages the synthesis of polymers with active substances that can remove or detect toxic substances. An example is a β-cyclodextrin polymer, which encapsulates pollutants and is more efficient than activated carbon (6).

Moreover, polymers with fluorescence properties (LNU-45 and LNU-47) provide the fluorescence effect when they interact with some pesticides. These materials are pyrene-based, a compound pilicyclic and antiaromatic with four fused benzene rings, with properties (like long fluorescence lifetime and high fluorescence quantum) that classify the pyrene as the most used chromophore. The LNU-45 and LNU-47 have presented effects on trifluralin and dicloran molecules because of the sensitivity by the substance with these compounds (7).

The examples above show the polymer's efficiency in removing pesticides. Research in databases are able to select and connect the requested information by an assembly system. Nowadays, a great repertory of research and discoveries are available on the Web. So, organizing, classifying and reviewing those contents is a database work. Moreover, databases have information like the publication year, number of citations and authors, which is essential to describe the scope and timeline of these materials application.

When the data selection is represented by a VOSviewer map, a program that can organize the bibliometric data about the information collected, it can show the most popular topics based on detector polymers and pesticides, the principal theme of this paper. Also, this map shows recent and more discussed topics interlinked. The examples above, gathered from Scopus and Web of Science databases, prove polymers efficiently remove pesticides. Now, VOSviewer maps were used to show relevant data regarding trends associations between polymers and pesticides, allowing for an understanding of how scientific efforts focus on them. It was made by two different researchers to collect more details about the subject. The results found some principal polymers used to detect pesticides. Driving to the conclusion that most scientific efforts converge towards the use of polymers as pesticide detection systems.

2. METHODOLOGY

A systematic literature search was used for an efficient and repeatable research process. Aiming that a guiding question was used: ***Can absorbent polymers remove pesticides from the environment?***

The keywords retrieved from this question are (i) Polymers, (ii) absorbent, (iii) pesticides, and (iv) environment. The papers coming from keywords were taken from the Scopus database. The research was based on the papers' titles. The information required for searching the papers was the keywords and a code created with them to form sets which can satisfy the limits of research, being more specifical. After exporting these pieces of information to a bibliographic file in RIS file format, the app VOSviewer translates the archive using clustering techniques to make a graph-based map based on the most critical terms, telling the year publication and the number of occurrences of each term. For better understanding, "Cluster" is a group of related terms, while "nodes" are the terms on each cluster. These nodes can relate to others and show different subjects.

The VOSviewer uses the information about the paper's title, the citations of each paper, the relation between the terms (if they appear on the same paper), the number of occurrences and the publication year to create a map with nodes as the terms and lines which link one text to another one (8). The results were split into two new archives in text format (*.txt). One of them, called MAP archive, can be moved to a spreadsheet for analyzing the data. Moreover, Tuckey HSD and ANOVA tests were performed using the Statistics Kingdom web-tool, clarifying clusters statistically similar regarding their publication years.

The first search in the Scopus database was done using the Research key: TITLE-ABS-KEY (Polym* AND pesticide). This search returned 3,062 documents. All titles and abstracts of these documents were saved in a RIS file, which was further analyzed using VOSviewer. The MAP file generated by the software was saved and studied using an electronic spreadsheet, which made it possible to group the labels (nodes) by clusters or by average year of publication. These clusters could then be saved separately as new MAP files, allowing to present partial results referring to each of the clusters individually.

A second search in the Web of Science database was performed using the Research key: ((TI=(polym*)) AND TI=(pestici*)) AND TI=(detection). This search was based on the main terms from Cluster 1. This search returned 68 documents, which created five Clusters. All titles and abstracts of these documents were saved in a RIS file, which was further analyzed using VOSviewer.

3. RESULTS

The first research, made by Scopus database, returned a more significant number of terms than the second one, made on Web of Science. The terms are not necessarily interconnected, in other words, some nodes don't have lines between other terms. Figure 2 presents the most frequent terms (on the top) and the average year of publication (on the bottom). The first map (Figure 1 - on the top) shows that cluster 1 (colored in red) has the biggest number of terms that was expected from the keywords.

Also, the average year of publication's map (Figure 1 - on the bottom) presents, in a visual way, that the most terms were published between 2012 and 2014. However, when the map is approximate, there are some terms with publication year in different periods. That is because data was presented in Table 2, where the confidence limit of each cluster was calculated.

Figure 3 shows the density of total link strength, related to the number occurrences on each cluster. As was mentioned before, the most cited terms "determination", "detection limit", "resistance" and "expression" are still in evidence. However, it isn't possible to identify the total link strength differences between all clusters, as well as the cluster's colors with the smallest number of terms, such as clusters 5 and 6.

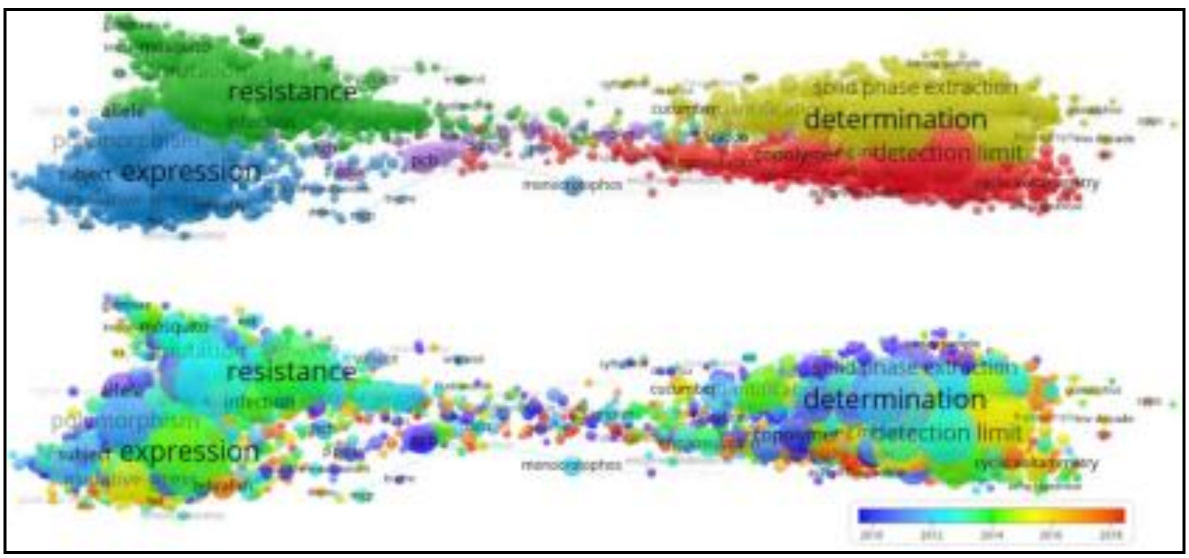

Figure 2. Map taken from VOSviewer: Network (top) and Overlay (bottom) visualizations.

Figure 3. Density visualization.

However, for a specific analysis, the use of spreadsheets dividing each Cluster is more efficient (Figure 4 and Table 1). In Figure 4, each cluster is present with five more occurrence terms. Although cluster 1 showed the highest number of terms, cluster 4 has more total link strength (TLS), of which the term "determination" was the highest TLS.

In Table 1 the map organized the information into six clusters, and Cluster 1 (colored in red) has the most extensive number of terms as can be observed. It was observed that Cluster 1 showed pesticides detection as the main topics around 2014, while their top node is "detection limit". In addition,

Figure 4. Principal nodes of each cluster and Total Link Strength (TLS). The colors are the same as the map.

Cluster#1		Cluster#2		Cluster#3	
Nodes	TLS	Nodes	TLS	Nodes	TLS
detection limit	8519	resistance	12918	expression	12184
sensor	6631	population	11767	polymorphism	7080
selectivity	6538	mutation	5954	genotype	6055
spectroscopy	5963	frequency	4855	gene expression	5490
fourier	5657	allele	4022	association	5460

Cluster#4		Cluster#5		Cluster#6	
Nodes	TLS	Nodes	TLS	Nodes	TLS
determination	15234	polychlorinated biphenyl	1414	high selectivity	1408
limit	11018	pcb	1373	target molecule	987
recovery	10289	pcbs	1259	mmip	696
extraction	8493	persistent organic pollutant	1236	filtration	607
mip	8196	pop	886	mmips	417

For the year publication found in each cluster, there is a spreadsheet (Table 1) that can define the confidence interval of the clusters about the year publication.

Table 1. Ranges, pub. year, number of terms and principal nodes

	Average year	TI95%	Inferior limit	Average	Superior limit	Principal nodes	number of terms
Cluster#1	2014.1	0.279903	2013.82	2014.096789	2014.376693	detection	886
Cluster#2	2013.2	0.202905	2013.03	2013.234829	2013.437733	resistance	821
Cluster#3	2014.0	0.1907	2013.83	2014.017222	2014.207923	expression	783
Cluster#4	2012.5	0.371283	2012.10	2012.472002	2012.843286	determination	486
Cluster#5	2011.5	0.87251	2010.60	2011.47629	2012.348801	pcb	62
Cluster#6	2016.5	1.541142	2014.96	2016.504688	2018.045829	high selectivity	24

After organizing the years and nodes, ANOVA and Tuckey HSD tests were performed. A relation was found between clusters 1 and 3 and clusters 4 and 5, the average year was near each other, as well as the limit statistically calculated that delimit the year of publication about a certain term. The conclusion is that clusters 1 and 3, such as clusters 4 and 5, have statistically similar ages.

The first research has, as a result, a specific map about cluster 1 shown in the Figure 5, as described in the section "Methods", it's a map created from the data of cluster 1, which is the most consistent to satisfy the goal of this study. Besides the terms already mentioned in the Figure 4, in this map can be observed several relevant terms, such as bisensor xrd and copolymers, indicating that these studies were developed around 2012, and between 2014 and 2016, respectively.

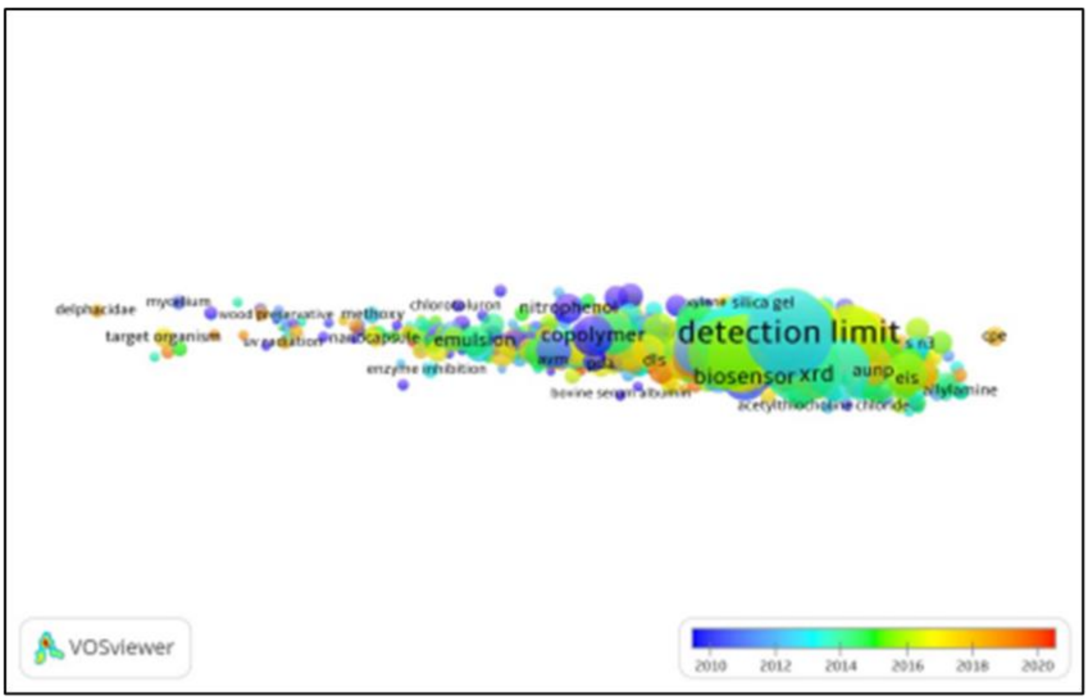

Figure 5. Overlay visualization of Cluster 1.

The second data analysis based on Cluster 1 was network visualization found in Figure 6, which observed the most significant number of related terms to the principal theme. In this map a minimum number of occurrences equal to one, resulting in 18 numbers of terms divided into five clusters. The main focus in these data analysis has the terms observed in the map (Figure 6), directing the research to articles about detector polymers of agrochemicals. It's clear that "detect limit" has the biggest density and the terms with red nodes are more recent than the others. So, the term with big density can also appear with other terms, mainly pesticide detection and polymer sensor.

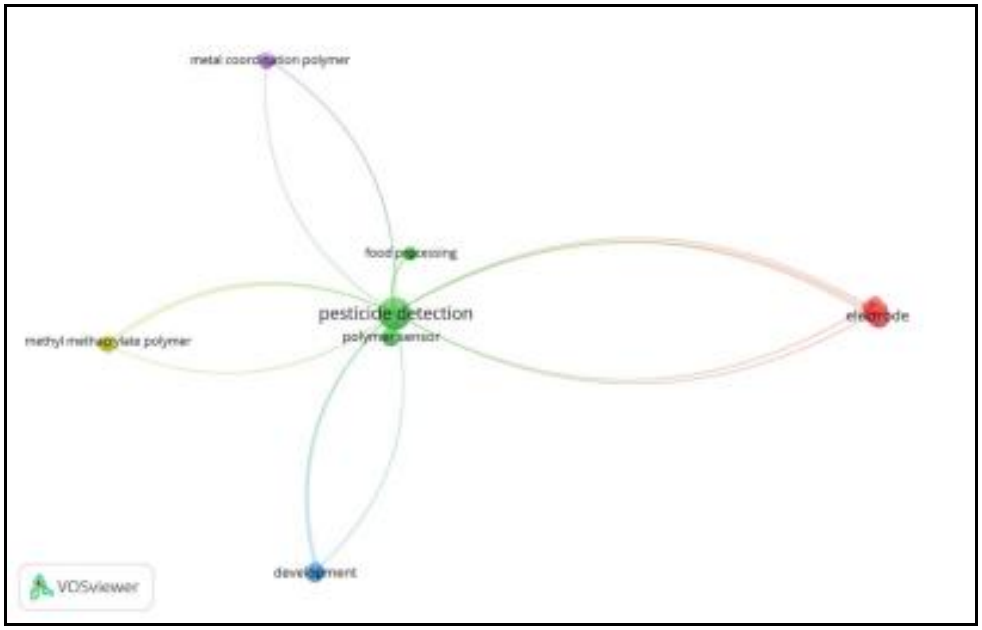

Figure 6. Network visualization (keyword: ((TI=(polym*)) AND TI=(pestici*)) AND TI=(detection)).

Figure 7 (overlay visualization map) shows the year publication proximity, which means that it improves on the terms connection and the less variability of year publication. Moreover, this information is evidence that pesticide detection using polymers is recent, so it is in current terms. Besides, polymers based on methyl methacrylate and polymers capable of coordinating metals appear highlighted with values from more recent years, indicating that research in these fields deserves attention.

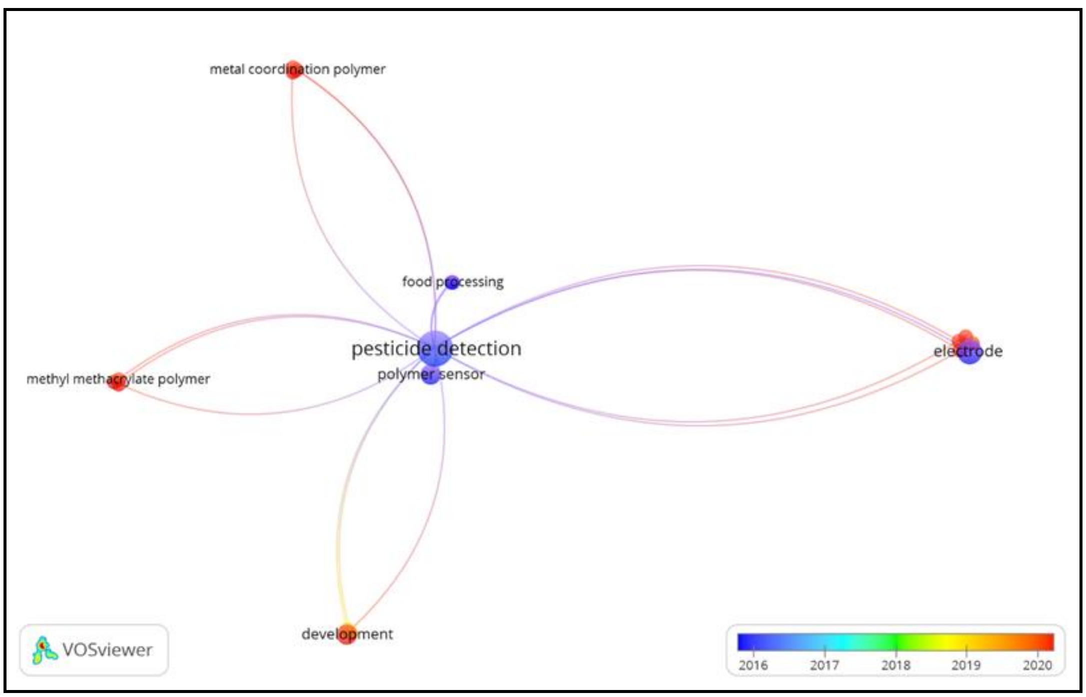

Figure 7. Overlay Visualization.

Figure 8, which is shown the density visualization maps, was another relevant analysis related to cluster 1, which can be shown quantitative datas. This map highlights the term with more occurrences such as "pesticide detection", which is a method to solve environmental and health problems about pesticide contamination. As said before, researchers are looking for manners to remove or detect pesticides using polymers with properties that can be useful, cheap and efficient. However, it is possible to see more deeply the occurrences of each cluster in Table 2.

Table 2 shows that "alkaline phosphatase biosensor" and "pesticide detection" are the principal terms that appear during the years; instead, the terms "methyl methacrylate polymer" and "metal coordination polymer" only appear in 2020, indicates that these theme is more recent, comparing with “alkaline phosphatase biosensor”.

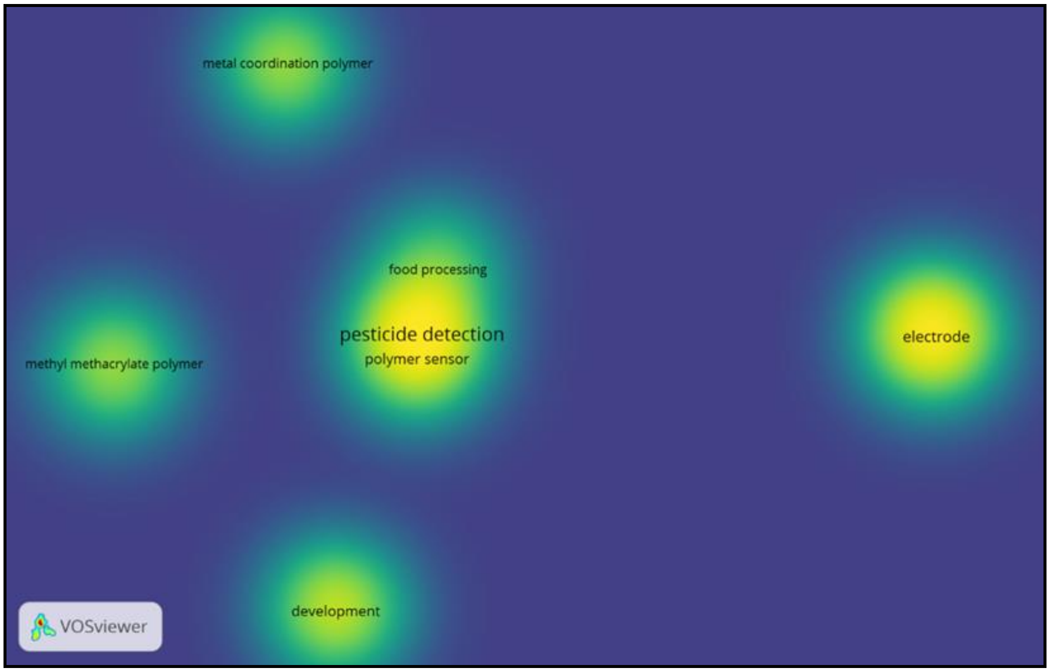

Figure 8. Density Visualization.

Table 2. Table talking about the second research with year pub., principal nodes and number of terms.

	Average year	TI95%	Inferior limit	Average	Superior limit	Principal nodes	number of terms
Cluster#1	2018.27	3.397	2014.9	2018.3	2021.7	alkaline phosphatase biosensor	5
Cluster#2	2012.42	7.133	2005.3	2012.4	2019.5	pesticide detection	4
Cluster#3	2019.33	0.653	2018.7	2019.3	2020.0	development	3
Cluster#4	2020	0	2020.0	2020.0	2020.0	methyl methacrylate polymer	3
Cluster#5	2020	0	2020.0	2020.0	2020.0	metal coordination polymer	3

The second research analyzed evidence that their principal terms were about detection by biosensors and metal conductor polymers, which have toxic agents detection properties. The term "alkaline phosphatase biosensor" is a toxic detector enzyme that can evidence some intoxication by agrochemicals, for instance. It can be found on human tissue, but a study made this material using a covalent binding at a modified electrode to develop biosensors which are able to detect organophosphorus pesticides (9).

The term “methyl methacrylate Polymer” (PMMA) is about application of this polymer in the main goal (pesticide detection), which developed the molecularly imprinted polymer (MIP), used to make a selective electrode for pesticide detection, like the Cypermethrin, which show high toxic level (10).

Other examples of metal coordination polymer are the cerium-based coordination polymer nanoparticles (CPNs) for fluorescent and colorimetric methods used to detect multiple pesticides (11). The luminescent coordination polymer with cadmium ions, 1,10-phenanthroline, and benzene-1,3,5-tricarboxylic acid ligands can detect and remove the pesticide diclofenac, too (12). Finally, a nanozyme (Sm-CeO2) with metal coordination polymers(Ce^{3+} with adenosine triphosphate (ATP)) is sensitive to the pesticides and gives fluorescence caused by Ce^{3+} (13)

4. CONCLUSION

Furthermore, regarding the critical question of this research, "Can absorbent polymers remove pesticides from the environment?", the results show that the foremost and noblest use of polymeric materials in this scenario relies upon detector devices. So, data mining has contributed to directing the research about pesticide detection methods using polymers and their efficiency based on their properties, like the active center or electric conduction, which can react with different substances.

Sample CRediT author statement

Izabel Marques Machado: Data analysis, and Writing-Original draft preparation. **Fernando G. de Souza Junior**: Conceptualization, Supervision, Reviewing and Editing.

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