

Technology Roadmap: Nanomaterials Applied to the Tertiary Treatment of Industrial Wastewater Contaminated by Synthetic Organic Dyes

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Industrial wastewater contaminated by synthetic organic dyes is a major environmental threat that needs treatment for its adequacy and, consequently, minimization of pollution of terrestrial water resources during its reintroduction into receiving water bodies. In recent decades, advances in nanotechnology have contributed to this path, allowing the application of nanomaterials (NMs) designed in different treatment techniques. Thus, the objective of this work includes the verification of trends related to the application of NMs to the tertiary treatment of industrial wastewater contaminated by synthetic organic dyes, using the Technology Roadmapping (TRM) method. Scientific articles and patent documents on the subject were extracted from the WIPO PatentScope, PatentInspiration, INPI and Scopus databases, with a total of 215 scientific articles, 27 granted patents and 52 requested patents considered relevant and analyzed. Through this study, it was possible to identify the main countries and universities in terms of technical-scientific production, such as China, India and Saudi Arabia, represented by the Chinese Academy of Sciences, Amity University and King Abdulaziz University. In the short, medium and long term, there is a tendency towards diversification of raw materials, with studies focusing on the use of mineral, synthetic, biological and residual inputs. In addition, there is also a propensity to search for hybrid and multifunctional NMs, to overcome the existing difficulties in their independent forms, impressively meeting market expectations.

1. Introduction

Contamination of water resources, a side effect of industrialization, is becoming a growing global problem with various organic and inorganic contaminants found in water bodies (Yadav et al., 2022). This is because the consumption of water resources available by the industrial sector implies the production of wastewater containing a wide range of compounds potentially harmful to the environment and which must be looked at carefully (Gangwar and Sebastian, 2021). Thus, the continuous growth of industrial activities, especially in developing countries, leads to an increase in demand for this resource and leverages the amount of aqueous effluents generated by production processes (Zanoni and Yamanaka, 2016).

In this context, the textile industry can be highlighted, as it is known worldwide as one of the largest consumers of water in its production processes and, consequently, one of the largest generators of industrial aqueous effluents contaminated by a variety of chemical products and synthetic organic dyes (Zanoni and Yamanaka, 2016). Due to the wide application of synthetic organic dyes in this segment and the massive losses of these substances during the stages of the industrial process (Sarayu and Sandhya, 2012), these complex and recalcitrant macromolecules become an important part of the industrial waste generated, with significant amounts being released daily in the environment without proper treatment (Papadoulou et al., 2013), which has the potential to cause severe environmental impacts and compromise water sources still available (Rauf and Ashraf, 2012).

In this way, the requirements of Environmental Agencies and Legislation, which establish the conditions and standards for the release of aqueous effluents for their adequacy, is a way of acting on the root cause of the problem, forcing industries to apply efficient treatment technologies to reach satisfactory levels of water quality,

which allows achieving the preservation of the environment (minimization of potential damage) and obtaining alternative sources of water, enabling the continuity of the development of countries and their industrial activities in a sustainable way (Kamali et al., 2019) .

With the advances in nanoscience and nanotechnology in recent decades, considered part of the 4th Industrial Revolution (Lazzaretti and Hupffer, 2019), the introduction of new materials in the market, nanomaterials (NMs), has revolutionized not only products, but also machines and equipment used in the most diverse sectors of the economy, being considered a highly promising market that grows exponentially. Although recent, research indicates NMs made up of different forms, namely nanoparticles (NPs), nanotubes (NTs), nanostructured, nanocomposites (NCs), nanofibers, for example, have excellent adsorptive and catalytic capabilities, in addition to a wide range of physical characteristics -chemicals that consider them highly attractive and promising for the removal of different contaminants present in water (Ahmed et al., 2021). Incidentally, nanoscale-based techniques could become extremely important to meet water quality standards, especially for the removal of emerging pollutants and low levels of contaminants (Adeleye et al., 2016). In this sense, the promising potential of nanotechnology is clear, enabling the evolution and improvement of treatment techniques for controlling pollution and reducing environmental damage generated by industrial activities (Adel et al., 2022).

Thus, in view of the relevance of nanotechnology in the world context, it is considered extremely useful to carry out diagnoses and studies related to these issues in developing countries, as is the case of Brazil, inferring the state of the art and identifying the materials, processes, technology and industrial sectors promising the use of technology, which can serve as a basis for decision-making, investments, implementation and direction of new studies in the area. In this sense, having a strategy for studying and understanding what is happening and what the future will be about nanotechnology; and its perspective of application in the treatment of wastewater contaminated by synthetic organic dyes is not only interesting, but extremely relevant, considering that one of the most important natural resources for humanity has its availability compromised and this nanoscience has a promising potential in the solution (Adel et al., 2022).

Based on this information, this article proposes a more detailed analysis of the technologies that involve the production and/or application of nanomaterials to the tertiary treatment of industrial wastewater contaminated by synthetic organic dyes, specifically treatment techniques that address the degradation/decomposition of contaminants. The main organizations operating in the sector will also be surveyed, delimiting which sources of raw materials are used, which products are obtained, which characteristics of the nanomaterial/treatment system are guaranteed and which trends are emerging in this area.

2. Technology prospection and technology roadmap

With the evolution of nanotechnology, conducting technological prospecting studies has become important to monitor technological development and help decision-making and planning in the area of nanotechnology and production of nanomaterials (NMs) (Porter and Detampel, 1995). In addition, since the main focus of the study is the temporal analysis, with a vision of the future, of the technologies and markets involved with the application of nanomaterials to the tertiary treatment of industrial wastewater contaminated by synthetic organic dyes, the use of the methodology of technology foresight lends itself well to this purpose.

Technological foresight, designated as a systematic way of mapping future technological and scientific developments, has the ability to substantially influence not only the industrial sector and the economy, but also society as a whole (Kupfer and Tigre, 2004).

Among the prospective techniques for technological monitoring, the application of technology roadmapping (TRM) stands out, or technological mapping, which is based on the analysis of technical-scientific publications, especially scientific articles and patent documents (Dang et al., 2010) , and is defined as a semi-quantitative method, that is, in which mathematical principles are applied to quantify or measure subjectivity, rational judgments, values and specialists' points of view (Popper, 2008). This technique is designated as a strategic approach for the management and planning of innovation in the short, medium and long term, which intends to understand the technological evolution of a product or process and which has as its main objective the construction of the technological roadmap that seeks to show, in simple and clear way, the possibilities of movement of an individual (or organization) in an established space of time (Kappel, 2001).

3. Methodology

The sources of technological information chosen for this work are scientific articles and patent documents (patents granted and requested) referring to NMs applied to the tertiary treatment of industrial wastewater contaminated by synthetic organic dyes and these documents were obtained through a bibliographical research in the Scopus, PatentInspiration, WIPO PatentScope and National Institute of Industrial Property (INPI) databases, taking into account the publications made in the last 11 years (2011 to 2021). The consideration of

the INPI base, linked to the Ministry of Economy of Brazil, aimed to guarantee the collection of patent information at the national level.

The research strategy and selection of documents for each of the databases used was carried out as follows:

- Database: Scopus
 - Survey date: September 2021;
 - Type of researched document: Scientific article;
 - Keywords used in the research: (nanomaterial* OR nanoparticle* OR nanocomposite* OR nanostructured) AND (wastewater OR waste water) AND treatment;
 - Search fields: Title, abstract and keywords;
 - Screening of documents extracted from the database: Identification of terms relevant to the scope and/or partial reading of the information;
 - Final number of documents selected: 215.
- Database: PatentInspiration
 - Survey date: October 2021;
 - Type of document searched: Patent;
 - Keywords used in the research: (nanomaterial* OR nanoparticle* OR nanostructured OR nanocomposite*) AND dye* AND (wastewater treatment OR waste water treatment);
 - Search fields: Title and abstract;
 - Screening of documents extracted from the database: Partial reading of information;
 - Final number of documents selected: 13.
- Database: WIPO PatentScope
 - Survey date: October 2021;
 - Type of document searched: Patent;
 - Keywords used in the research: (nanomaterial* OR nanoparticle* OR nanostructured OR nanocomposite*) AND dye* AND (wastewater treatment OR waste water treatment);
 - Search fields: All fields;
 - Screening of documents extracted from the database: Partial reading of information;
 - Final number of documents selected: 55.
- Database: INPI
 - Survey date: October 2021;
 - Type of document searched: Patent;
 - Keywords used in the research: nano* AND (water OR waste* OR effluent*) AND treatment;
 - Search fields: Summary;
 - Screening of documents extracted from the database: Partial reading of information;
 - Final number of documents selected: 11.

For the development of the study, the Microsoft® Excel® 2016 software, from the Microsoft® Office package, was used, which provided the organization of information from scientific articles and patents in spreadsheets, facilitating reading, establishing classifications and quantitative analyzes of the survey carried out.

Data analysis, carried out by reading the selected final documents (215 scientific articles, 27 patents granted and 52 requested), followed two different levels of depth, in which in the more general analysis (macro level) it was possible to verify the temporal evolution of publications, countries involved, universities/research centers and companies operating in the sector; and in the more detailed analysis on the subject (meso and micro levels) a categorization of the most expressive information found in them was established (Table 1), so that it was possible to identify which are the technological trends present in the granted patents (short term), requested patents (medium term) and scientific articles (long term).

4. Results

The results of the prospective study carried out will be presented, showing the most prominent information with the quantities obtained for each type of document (patent granted – short term (27), patent requested – medium term (52), scientific article – long term (215)), segmented into macro (Table 2) and meso/micro (Table 3) analyses.

It is noticed that China occupies a position of technological leadership in the long term and in a dominant way, with an expressive volume of articles published in the analyzed period. In the short and medium term, the technological leadership position is occupied by Saudi Arabia and India, respectively, with China in the second position in both terms.

Taking into account the types of institutions of origin, it can be seen, as expected, that universities are the majority in terms of patents and articles. The expressiveness of universities is greater in articles (79%), showing small reductions for requested patents (70%) and granted patents (65%). And reflecting this hegemony, the

institutions that have the highest number of publications in the analyzed period are universities of nationalities also consistent with the prominent countries.

Table 1: Categorization of meso and micro levels used in document analysis

Meso level	Micro level
Final product feature	Economic procurement: Low cost of raw materials and/or procurement techniques (simple, fast and leading to resource savings and lower operating costs) Recoverability: Application of procedures that guarantee the recovery of NM in the reaction medium or the disposition of NM in forms or structures that facilitate this removal Selectivity: Specific treatability of target contaminants, providing better use of catalysts, technique performance and lower operating costs Treatment efficiency: High percentages of contaminant removal (>50%) Fast treatment: Short treatment times for the aqueous effluent (order of magnitude = hours; < 24 hours) Stability: Chemical, physical, thermal and/or structural, ensuring the maintenance of the characteristics and properties of the nanomaterial Environmental advantages: Nanomaterials with low toxicity, biodegradable and/or reduced impacts/secondary contamination during use
Final product	Catalyst Microbiological Agent Electrode Adsorbent Membrane/filter
NM raw material	Biological: Plant, animal, algae or microbiological Mineral: Source of metallic components, either by occurrence as minerals, salts, oxides, hydroxides or acids Synthetic: Artificial polymers or other synthetic substances directly linked to the structure and final composition of nanomaterials, as well as for their functionalization Waste: Residual materials from different industrial or urban sectors, which can be of biological, mineral or synthetic origin

Table 2: Highlights with the highest number of publications verified by the macro analysis of the documents

Macro level	Short term (27)	Mid-term (52)	Long term (215)
Publication year	2020 (7)	2021 (13)	2021 (48)
Country of origin	Saudi Arabia (8), China (7), USA (3) and India (3)	India (18), China (11) and Brazil (9)	China (78), India (23) and Iran (19)
Types of home publishing institutions	65% University 5% Research Institute 5% Company 25% No bond	70% University 11% Research institute 11% Company 8% No bond	79% university 18% Research institute 3% Company
Institution	King Abdulaziz University (Saudi Arabia) (4), Imam Abdulrahman Bin Faisal University (Saudi Arabia) (3) and Soochow University (China) (3)	Amity University (India) (4), Federal University of Viçosa (Brazil) (3) and Technological University (Singapura) (2)	Chinese Academy of Sciences (China) (7) and Nanyang University of Kashan (Iran) (7)

The characteristics of the final product demonstrate that the developed materials deliver processes with excellent performances, either in relation to the efficiency of degradation of pollutants, as to the duration of the process. In addition, from economic and environmental aspects, there are more accessible products with low

toxicity components. Regarding the feasibility of reuse of NMs, the possibility of recovery and stability of materials is also guaranteed.

The most produced final products are catalysts, adsorbents and membranes in combined form, ensuring the synergistic effect of the catalytic, adsorptive and filtration processes, which have the advantage of overcoming the difficulties encountered in techniques used independently and improving the performance of the materials. With regard to the most used raw materials, the predominance of mineral and synthetic origin is perceived, but the presence of biological and residual origin can already be noticed both in articles and in patents, demonstrating the search for diversification of the inputs used in the acquisition of NMs.

Table 3: Representativeness of the categories considered in the meso/micro analysis of the documents

Meso level	Micro level	Short term (27)	Mid-term (52)	Long term (215)
Final product feature	Economic procurement	100%	100%	93%
	Recoverability	96%	92%	80%
	Selectivity	0%	4%	7%
	Treatment efficiency	100%	96%	100%
	Fast treatment	93%	86%	95%
	Stability	100%	100%	92%
	Environmental advantages	100%	98%	89%
Final product	Catalyst	100%	96%	99,5%
	Microbiological Agent	0%	6%	0,5%
	Electrode	0%	4%	4,7%
	Adsorbent	81%	71%	47,9%
	Membrane/filter	26%	10%	10,2%
NM raw material	Biological	33%	24%	30%
	Mineral	100%	100%	100%
	Synthetic	41%	37%	32%
	Waste	22%	10%	10%

5. Conclusions

Faced with the challenge of avoiding contamination and compromising available water resources by disposing wastewater contaminated by synthetic organic dyes, aqueous effluent treatment technologies have undergone great advances in recent years. Research and technical-scientific production in this area are shown to be highly boosted in countries such as China, India and Saudi Arabia, mainly through universities such as the Chinese Academy of Sciences, Amity University and King Abdulaziz University. Nanomaterials applied to treatment techniques are listed as the best alternative to guarantee the characteristics of efficiency, speed, economy and environmental advantages in the degradation processes of the evaluated contaminating organic species. In addition, it is noted that in the short, medium and long term there is a tendency to diversify the raw material used, through the use of mineral, synthetic, biological and residual inputs, and also a propensity for hybrid and multifunctional NMs, to overcome the difficulties existing in their independent forms. Thus, the potential of NM to become a better-performing substitute for larger-scale materials currently used has contributed to the increased interest of researchers and the market, as evidenced by the growing trend of studies and developments with the application of NMs in techniques of industrial wastewater treatment.

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