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Theme

Chitosan and its derivatives for adsorption of heavy metals from wastewater: Bibliometric evaluation of Scopus database.

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Dedications

This dissertation is dedicated to my most important people in my life:

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To all of you, I dedicate this work.

Aicha

ae is activity of metal in solution at equilibrium.

Ce is metal concentration in equilibrium solution (mg/L).

Cs is metal adsorbed on CP- LC (mg/g).

ΔG ° (kJ / mol) are free energy of Gibbs or free adsorption enthalpy due to the transfer of one mole of solute from the solution to the solid / liquid interface.

ΔH ° (kJ / mol) the adsorption enthalpy.

k_1 (1/min) is the rate constant of pseudo-first order model.

K_2 (g/mg/ min) is the rate constant of pseudo-second order model.

Kc is the distribution constant.

K_L is the equilibrium constant (L/mg).

q_t and **qe** is the Biosorption capacity (mg/g) at equilibrium and at time t (min).

ΔS ° (J / mol / K) the adsorption entropy.

[USEPA] is The United States Environmental Protection Agency. is activity coefficient of Pb (II) in equilibrium solution.

Ys is activity coefficient of adsorbed metal.

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GENERAL

INTODUCTION

Introduction

Rapid pace of industrialization and tremendous increase of human population in last few decades have caused serious environmental pollution. Water pollution due to the presence of elevated concentrations of wide varieties of contaminants or pollutants such as, toxic heavy metal ions, inorganic anions, micro pollutants, organic compounds such as dyes, phenols, pesticides, humic substances, detergents and other persistent organic pollutants, has been widely reported in different parts of the world in recent decades **[1]** . Established chemical manufacturers release vast quantities of polluted wastewater containing heavy metal ions, including cadmium, cobalt, nickel, arsenic, lead, mercury, chromium, and zinc, which are significant hazardous substance **[2]** . Pollution due to heavy metals has been a cause of concern across the globe, posing a threat to human health because of their toxic nature even at low concentrations **[3]**. The toxic proprieties of heavy metal ions are presented as follows: (1) the degree of toxicity can last for a longtime in the environment; (2) some heavy metals could be transformed from a low toxic element into high toxic forms in a certain environment;(3) the bioaccumulation and bio- augmentation of these metals by the food chain in living species could damage normal physiological activity and endangering human life; (4) heavy metals can only be changed and transformed in valence and species, but cannot be degraded by any methods;(5) the toxicity of heavy metal ions occurs even in very low concentration of about 1.0–10 mg/L .**[4]**

Due to their increasing application and the above immutable nature, the heavy metal pollution has naturally become one of the most serious environmental problems today. Conventional methods for removing metal ions from aqueous solution have been studied in detail, such as chemical precipitation, adsorption, ion exchange, electrochemical treatment, membrane technologies, lectro-coagulation, ultra-filtration, flocculation, etc. **[5]**. Among of these technologies, adsorption has been regarded as a cost-effective way of remediating heavy metals water and wastewater **[6]**. Also, in consort with adsorption, low-cost adsorbents are quite in trend in the present time. Different types of materials such as clay, zeolite, lignocellulosic materials, agricultural waste, bio-polymers, metal oxides, microorganisms, biopolymers, sewage waste, fly ash, activated carbon, zero valence iron, are successfully used as effective adsorbent **[7]**. Chitosan and its derivatives, as biocompatible polymers, have attracted considerable attention for applications in the adsorption technology due to suitable physical and mechanical properties. Chitosan naturally develops functionality, flexibility, and high specific strength by exploiting hierarchical structure **[8]**. It also has low density, low price, as well as biodegradability **[9]**. Chitosan materials enable tuning of porosity and interconnectivity desirable for targeting water treatment applications **[10]**. Furthermore, chitosan can be chemically modified by substitution of its native hydroxyl groups with functional groups, such as specific acids, chlorides, and oxides, to improve the adsorption properties or to develop new desired characteristic **[11]**. Overall, chemically modified chitosan exhibited about 40%–80% higher adsorption capacities for various aquatic pollutants than their unmodified forms. Numerous chemicals have been used for chitosan modifications, which include mineral and organic acids, bases, oxidizing agent, organic compounds, etc. **[7]**

To better understand the evaluation of chitosan & heavy metals adsorption research and display a board panorama of the field this paper draws on bibliometric analysis to visualize the research thermes and trends **[12]**. Bibliometric analysis is a term introduced by Pritchard in 1969 **[13]** which means quantitative analysis of research articles and reviews **[14]**. This analysis was used to examine patterns of collaboration among authors, scientific outputs and their contributions, impact, national collaboration and contribution, and country contributions to research **[15]**. This analysis became popular due to the availability and accessibility of analytical software and increasing electronic indexing databases. According to pit chard’s original book, Bibliometrics can be defined as “the application of mathematical and statistical methods to books and other communication media” **[13].**

This thesis is structured into three main chapters. The first chapter presents the fundamental concepts of adsorption, laying the groundwork for understanding its mechanisms and applications. The second chapter describes the methodology, focusing on the use of bibliometric tools such as VOSviewer, Bibliometrix, and Cite Space for data analysis. The third chapter discusses the results obtained from the bibliometric study and provides an in-depth analysis of trends, key contributors, and research directions in the field of adsorption.

CHAPTER I

HEAVY METALS AND ITS REMOVAL

I.1 Heavy metals pollution

Heavy Metal pollutants are among the major toxic and persistent effluents in aquatic environment **[16].** Metal pollution occurs directly or indirectly by effluent outfalls from neo-industries. Unfortunately, many aquatic ecosystems face metal ions concentrations that exceed aqueous media criteria designed to preserve the natural environment, humans and animals. Most metals are transition substances with incompletely filled *d* orbital's [**17].** These orbitals allow heavy metal cations in solutions with the ability to form complex substances, which may or may not be redox-active **[17].** Heavy Metal cations play a major roleas groups of trace elements in sophisticated bio-chemical reaction, though some of them are necessary for many organisms **[18].** Consequently, heavy metals are extremely dangerous to plants, animals and human and because of their augmentation and accumulation (over at various limiting concentration levels depending of the heavy metal). The toxicity of metal ions occurs even in very low concentrations of about 1.0-10 ppm, which are classified based on toxicity are presented in **table I. 1. [19]**

Table I.1: Classification of heavy metals based on toxicity. **[20]**

Heavy metals	Toxicity
Mn, Fe, Mo	Low toxicity
Cr , Zn, Ni, V, Co, W, Cu	Average toxicity
As, Ag, Sb, Cd, Hg, Pb, U	High toxicity

I.2 toxicity of Heavy metals

Heavy metals can produce side effects on soil, on water, on air, but also on plants, animals and humans **[17].** In soil, high levels of heavy metals can produce alteration of soil quality through modification of pH, color, porosity and natural composition, but also low crop production, loss of many types of normal flora and habitat **[16]**. Metal ions can be accumulated into food chains and concentrated in aquatic media to a level that impacts their physiological state. Due to their non-biodegradable characteristics, carcinogenicity and toxicity to living organisms, many heavy metals are regarded as priority effluents. Among them, the toxic heavy metals of particular concern in treatment of industrial wastewaters include, copper, lead, cadmium, arsenic, chromium, mercury, Selenium, zinc, nickel. Some of the common sources and impact of heavy metals are present in **table. I.2 [21]**. Their accumulation into the water imposes serious problems on humans and ecosystems, due to decreasing of drinking water quality and purity, decreasing water supplies for all living organisms. High levels of heavy metals in air can lead to harmful health problems, including respiratory infections, cardiovascular disease, premature mortality, eyes and skin irritation, but also can cause infrastructure deterioration, acid rain increasing, corrosion, eutrophication and haze, low yields of the crop, not enough oxygen. In plants, they can produce damage of roots or leaves interfere in important biochemical process, such as photosynthesis, alteration of minerals absorption, and damage of chlorophyll, reduce the growth and development of the roots, which leading to reduction of overall growth of the plant **[22]**.

The toxicity of heavy metals in animal is manifested through decreased body weight, kidney damage, liver affections, shortened life span, increased oxidative stress, modifications of cells composition, DNA damage. In humans, they can produce kidney damage, liver affections, pulmonary effects, several types of cancer **[23]**.

Heavy metals became toxic when are not metabolized by the body and accumulates in organs and soft tissues. They reach the human body by ingesting contaminated water or food, inhalation of absorption through the skin. Among the pathways, ingestion in the common route that helps the heavy metals to enter to the animal bodies. The effect of this metals can be inhibitory, stimulatory and toxic for some biochemical processes, being able to produce various health problems on nervous system (Alzheimer, Parkinsoma, depression, dementia), on bone system (bone mineralization) an on reproductive system. Also, can produce DNA damage, RNA affection, or cancer of lungs, skin, bladder, due to production of ROS. Their toxicity depends the dose of exposure, time of exposure, pollutant concentration, organism which are exposed to it, nature and oxidation state of the metal **[23].**

Based on that, the sequestration of heavy metals from aqueous media has attracted attention by researchers, for the preservation of public health and ecosystems, so, it is essential to remove these toxic metals before discharge.

Table I. 2: Sources and impact of heavy metals. **[20]**

Sl.	**Heavy metals**	**Sources of Metal contamination**	**Adverse health effects**	**Allowed limits WHO (ppm)**
1	Copper	Dental products, Corrosion of household, plumbing, erosion of natural deposits , alloy, electroplating,	Gastrointestinal (GI) irritation and Liver toxicity, lung neoplasm's, , kidney damage	1.0-1.3
2	Lead	Lead-acid battery production, Plumbing systems, pigment, pesticides industry	Delayed development in children, anemia, vomiting, kidney damage, high blood pressure	0.005-0.015
4	Arsenic	Electroplating, industrial fuel, mining, battery manufacturing Erosion of natural deposits, runoff, pigment	Cancer, skin damage, circulatory system problems	0.01
5	Chromium	Steel industry, Electro plating, pulp mills, erosion leather tannery facilities, steel welding, paints, chromate and ferrochrome production	Diarrhea, skin and eye irritation, kidney dysfunction, ulcer, irritation in respiratory track Allergic dermatites, hemolysais, rénal failure	0.05-0.25
6	Antimony	Petroleum refineries, fire retardants, ceramics, electronics, solder	Increased blood cholesterol, decreased blood sugar	0.006
7	Mercury	Erosion of natural deposits, discharge from refineries and factories, runoff from landfills, croplands	Hypersensitivity, fever, vomiting, neurasthenia	0.002
8	Mercury	Petroleum refineries, erosion, discharge from mines	Hair and finger nail loss, red skin, numbness in fingers and toes, caustic burns,	0.01-0.05
9	Zinc	Electroplating industry, galvanized metal surfaces, motor oil and hydraulic fluid, tire dust	Corrosive to skin and eye, zinc pox, sweet taste, throat dryness, cough, weakness, generalized	5

I.3 Adsorption Technique for Removal of Heavy Metals

Adsorption is usually considered a cost-effective and reliable method for wastewater treatment. Adsorption is basically a process of mass transfer in which solute or removable species are transported from a runny phase onto the surface of a solid phase. By physiochemical interactions, adsorbed species are bounded to the solid surface. The removal efficiency of adsorption can range up to 99.9%. The United States Environmental Protection Agency (USEPA) declared the adsorption process as one of the most excellent and best wastewater treatment techniques, among others. **[24]**

Adsorption is considered a well-developed process for removing heavy metals from wastewater due to its simplicity and cost effectiveness compared with the other approaches. In this process, generally, adsorbate migration occurs in three sequential steps: (1) migration of adsorbate to the border shell of the adsorbent, (2) in trap article diffusion into pores, and (3) adsorption and desorption of solute. The characteristics of adsorbate, adsorbent, and matrix control the rate of all these steps. In order to determine the maximum adsorption capacity of the material, adsorption isotherms are utilized. Adsorption isotherms are structured by plotting the adsorbed molecules per unit area of the interface versus the gas pressure or the liquid solution's concentration in equilibrium. Langmuir and Freundlich isotherms are the most commonly used models to assess pollutant adsorption. **[24]**

I.3.1Adsorption phenomenon

Adsorption is a surface phenomenon where molecules or ions from a fluid (liquid or gas) adhere to the surface of a solid or liquid (the adsorbent) due to attractive forces. This process involves the accumulation of the adsorbate on the surface of the adsorbent rather than penetration into the material itself. Adsorption can occur due to physical forces (physical adsorption) or chemical interactions (chemical adsorption) between the adsorbate and adsorbent. **[25]**

Applications of Adsorption are commonly employed in the following fields:

- Environmental Remediation: Removal of pollutants such as heavy metals, dyes, and organic contaminants from wastewater.
- Gas Separation: Separation of gases based on their affinity for specific adsorbents.
- Catalysis: Adsorption of reactants onto catalyst surfaces to enhance chemical reactions.
- Purification: Purification of liquids and gases by removing impurities.

In summary, adsorption is a versatile phenomenon utilized across various industries and applications, offering efficient ways to manipulate and separate substances based on their surface interactions with adsorbent materials [**26]**.

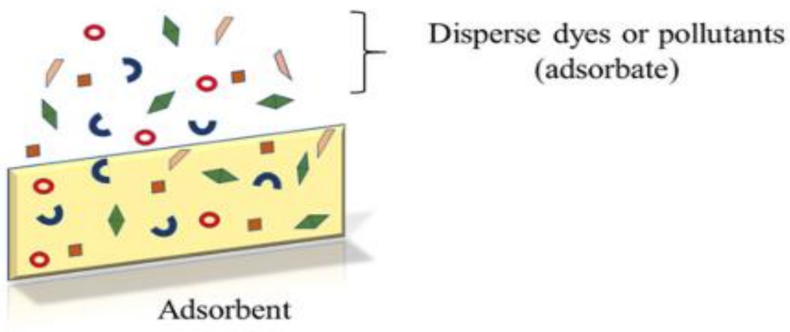


Fig I.1: General mechanism of adsorption to remove contaminant. **[23]**

I.3.2 Types of Adsorption

Adsorption is a process in which a substance (adsorbate), in gas or liquid phase, accumulates on a solid surface. It is based on the capability of porous materials with large surfaces to selectively retain compounds on the surface of the solid (adsorbent). There are two types of adsorption; physical and chemical adsorption, the difference between them is shown in **Fig.I.2 [20]**.

1. **Physical Adsorption (Physisorption)**

Van der Waals forces, dipole interactions, and hydrogen binding achieve physical adsorption. There is no electron exchange between adsorbent and adsorbate. Because there is no activation, energy required for physical adsorption, the time needed to reach equilibrium is very short. Physical adsorption is a non–specific and a reversible process. [**27]**

2. **Chemical Adsorption**

Chemical adsorption results from the chemical link between adsorbent and adsorbate molecule, therefore it is specific as well as irreversible and chemical as well as electronic properties of adsorbent are changed. Binding between adsorbent and adsorbate by covalent bond is called weak chemical adsorption, and that by ionic bonds is called strong chemical adsorption. **[27]**

3. Differences between Physical and Chemical Adsorption

- Bonding: Physical adsorption involves weak van der Waals forces, while chemical adsorption involves stronger chemical bonds.
- Reversibility: Physical adsorption is generally reversible with changes in temperature or pressure, whereas chemical adsorption is often irreversible under normal conditions.
- Temperature Dependence: Physical adsorption occurs at lower temperatures, while chemical adsorption typically requires higher temperatures.
- Multilayer Formation: Physical adsorption can form multilayer of adsorbate molecules, whereas chemical adsorption usually forms a monolayer due to stronger bonding. **[28]**

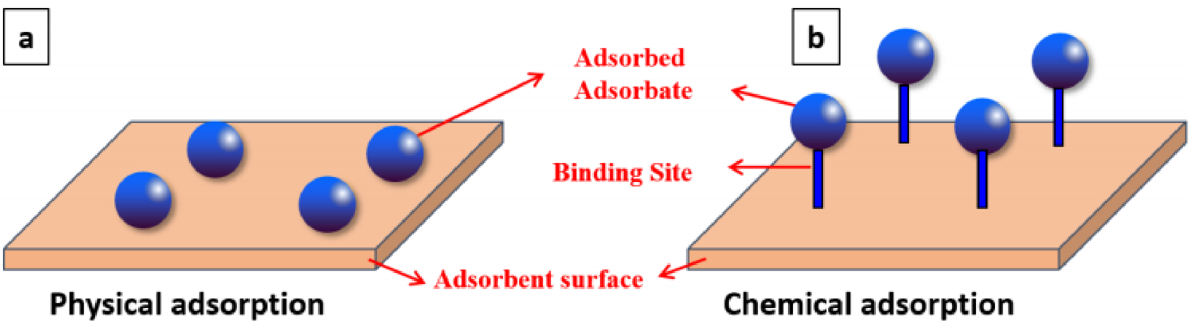


Fig I.2: Illustration of interaction between adsorbate and adsorbent surface. Figures **(a)** and **(b)** are the physical **(a)** and the chemical **(b)** adsorption. **[20]**

I.3.3 Adsorption Mechanisms

The adsorption process forms a layer of adsorbate (metal ions) on the surface of adsorbents. Adsorption can be reproduced for multiple applications via a desorption method (reverse adsorption in which adsorbate ions are transported from the adsorbent surface) because adsorption is a reversible process in certain circumstances. Adsorption onto a solid adsorbent includes three major steps: transportation of the pollutant to the adsorbent surface from aqueous solution, adsorption onto the solid surface, and transport within the adsorbent particle. Generally, electrostatic attraction causes charged pollutants to adsorb on differently charged adsorbents because heavy metals have a vigorous affinity for hydroxyl (OH^-) or other functional group surfaces. **[29]**

The adsorption process of the adsorbate molecules from the bulk liquid phase into the adsorbent surface is presumed to involve the following stages:

1. Mass transfer of the adsorbate molecules across the external boundary layer towards the solid particle.
2. Adsorbate molecules transport from the particle surface into the active sites by diffusion within the pore–filled liquid and migrate along the solid surface of the pore.
3. Solute molecules adsorption on the active sites on the interior surfaces of the pores.
4. Once the molecule adsorbed, it may migrate on the pore surface trough surface diffusion.**[20]**

I.3.4 Isotherm models

Isotherm models are mathematical representations used to describe the adsorption process, which is the accumulation of molecules of a substance at a surface or interface. There are several commonly used isotherm models in adsorption studies, each with its own assumptions and applications. Here are a few key ones **[30]**:

1. **Langmuir Isotherm:**

The simplest and still the most useful isotherm, for both physical and chemical adsorption, is the Langmuir isotherm. This model assumes that adsorption is limited to a monolayer: only a single layer of molecules on the adsorbent surface are absorbed, adsorbent surface is homogeneous and adsorption energy is uniform for all sites and there is no transmigration of adsorbate in the plane of the surface. Based on previous research studies, the Langmuir model has the best fitness quality with experimental data between two parameter monolayer adsorption isotherm models. The mathematical expression of Langmuir isotherm models are given as: [**31]**

$$qe = \frac{q_{max} K_l C_e}{1 + K_L C_e}$$

K_L is the equilibrium constant (L/mg), which is a criterion of the tendency of the adsorbate to adsorb onto the active sites of the adsorbent surface. A larger b value represents higher adsorption.

2. **Freundlich Isotherm**

Freundlich isotherms the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. At present, Freundlich isotherm is widely applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves. The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies chemisorption process where 1/n above one is an indicative of cooperative adsorption. The equation of Freundlich isotherm models are given as **[31]**:

$$q_e = K_F C_e^{(\frac{1}{n_F})}$$

3. **Timken model**

Timken isotherm is the early model describing the adsorption of hydrogen onto platinum electrodes within the acidic solutions. The isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies. The Temkin isotherm model is given as **[32]**:

$$q_e = \frac{RT}{b_T} lnA_T C_e$$

4. **Elovich model**

The Elovich is model based on a kinetic principle with the assumption of adsorption sites increasing exponentially with adsorption, which represents multilayer adsorption. The Elovich isotherm model is expressed as **[17]:**

$$C_e = \frac{q_e}{\mathrm{q_{mE} K_E} \exp(\frac{-q_e}{q_m})}$$

I.3.5 Adsorption Kinetics

The kinetic behavior of adsorbates on adsorbents has been studied using the effect of time on sorption. Due to the large collection of kinetic models, the selection of suitable models for the analysis of sorption data is quite challenging. Scientific reports have shown how mathematical models were proposed and used to describe adsorption experiments. Thus, adsorption kinetic models have been classified into two groups namely; adsorption reaction models and adsorption diffusion models. Adsorption reaction models reveal the rate of adsorbate uptake by adsorbents but they do not show the actual cause of adsorption. On the contrary adsorption diffusion models take into cognizance external diffusion, internal (pore) diffusion and effect of mass action (i.e. adsorption/desorption between adsorbates and active sites of adsorbents.

Pursuant to the aforementioned adsorption reaction models should be consistent with proposed mechanisms defined by fitting adsorption diffusion models **[33].** Non-linear form and linear form equations of kinetic models are given in **Table I.3**.

Table I.3: Illustration of the linear forms, nonlinear forms and plot of kinetic models analyzed for optimization studies.

Kinetics model	Non-linear form	linear form	Refs
pseudo-first order	$q_t = q_e(1 - e^{-k_1 t})$	$\log(q_e - q_t) = \log q_e - K_I.t/2.303$	**[22]**
pseudo-second order	$q_t = \frac{K_2 q_e^2}{1 + K_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	**[24]**

Where q_t and qe is the Bio sorption capacity (mg/g) at equilibrium and at time t (min), respectively and k_1 (1/min) is the rate constant of pseudo-first order model K_2 (g/mg/ min) is the rate constant of pseudo-second order model.

I.3.6 Adsorption Thermodynamics

The thermodynamic parameters that shall be taken into consideration in order to qualify the adsorption processes are free energy of Gibbs or free adsorption enthalpy ΔG ° (kJ / mol) due to the transfer of one mole of solute from the solution to the solid / liquid interface, the adsorption enthalpy; ΔH ° (kJ / mol) as well as the adsorption entropy; ΔS ° (J / mol / K). These quantities were calculated according to the following equations **[32]**:

$$\Delta G^0 = -RTlnKc$$

$$InK_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$K_c = \frac{as}{ae} = \frac{Ys}{Ye} = \frac{Cs}{Ce}$$

Where Kc is the distribution constant, as is activity of adsorbed metal, ae is activity of metal in solution at equilibrium, Ys is activity coefficient of adsorbed metal, Ye is activity coefficient of Pb (II) in equilibrium solution, Cs is metal adsorbed on CP-LC (mg/g), and Ce is metal concentration in equilibrium solution (mg/L). (ΔH◦) (ΔS◦) and (ΔG◦) are enthalpy (kJ/mol), entropy (J/mol K) and change in Gibbs free energy (kJ/mol), respectively. R is the universal gas constant (8.314 J/mol K) and T is the temperature in Kelvin.

I.4 Recent advances in heavy metal removal by chitosan based adsorbents

Recent advancements in the field of heavy metal removal using chitosan-based adsorbents have shown promising results. Chitosan, a biopolymer derived from chitin, has gained attention due to its excellent adsorption capacity, biodegradability, and non-toxicity. Researchers have been exploring various modifications and composite materials to enhance its efficiency and selectivity in removing heavy metals from contaminated water sources.

- ❖ **Modification Techniques:** Chitosan can be modified through chemical methods (e.g., cross-linking, grafting) or physical methods (e.g., blending with other materials) to improve its surface area, porosity, and metal binding sites. These modifications aim to maximize its adsorption capacity and stability under different environmental conditions.
- ❖ **Composite Materials**: Researchers have developed chitosan-based composite materials by incorporating nanoparticles (e.g., grapheme oxide, carbon nanotubes) or other organic/inorganic substances. These composites often exhibit synergistic effects, combining the advantages of chitosan (such as biocompatibility) with enhanced adsorption properties of the added materials.
- ❖ **Adsorption Mechanisms:** The adsorption mechanisms of chitosan-based adsorbents involve complex interactions such as electrostatic attraction, ion exchange, chelation, and surface complexation. Understanding these mechanisms is crucial for optimizing adsorption processes and designing efficient adsorbents.
- ❖ **Application in Wastewater Treatment**: Chitosan-based adsorbents have been extensively studied for the removal of various heavy metals (e.g., lead, cadmium, copper, chromium) from industrial effluents and contaminated water bodies. Their effectiveness in reducing metal concentrations to meet regulatory standards highlights their potential for large-scale applications in wastewater treatment.
- ❖ **Regeneration and Reusability:** One of the challenges in using adsorbents is their regeneration and reusability. Researchers are exploring methods to regenerate chitosan-

based adsorbents, such as desorption techniques using appropriate eluents, to maintain their adsorption capacity over multiple cycles. **[34]**

Overall, the ongoing research and development in chitosan-based adsorbents for heavy metal removal hold promise for addressing environmental pollution challenges effectively. Continued advancements in material science and process engineering are expected to further enhance the performance and practical application of these adsorbents in water treatment technologies.

CHAPTER II:

METHODOLOGY

II Introduction

This study aims to provide a comprehensive bibliometric analysis of chitosan & heavy metals research. First, relevant publications are retrieved in the corresponding database following the retrieval strategy . Next, the fundamental characteristics of the publications are described in terms of annual indicators, types and research areas of publications, and highly cited publications. Afterward, influential and highly productive countries/regions, institutions, authors, and their collaborative relationships are studied through several complementary bibliometric methods and tools. Meanwhile, research frontiers, hot spots, and future trends are identified. In the end, current topical issues, future trends and challenges, and limitations are further discussed. The research framework of the methodology of this study is shown in **Fig II. 1**. **[35]**

II.1 Data source and retrieval strategy

Scopus is the most comprehensive information resource globally, covering many disciplines owned by the Thomson & Reuters Corporation . It provide

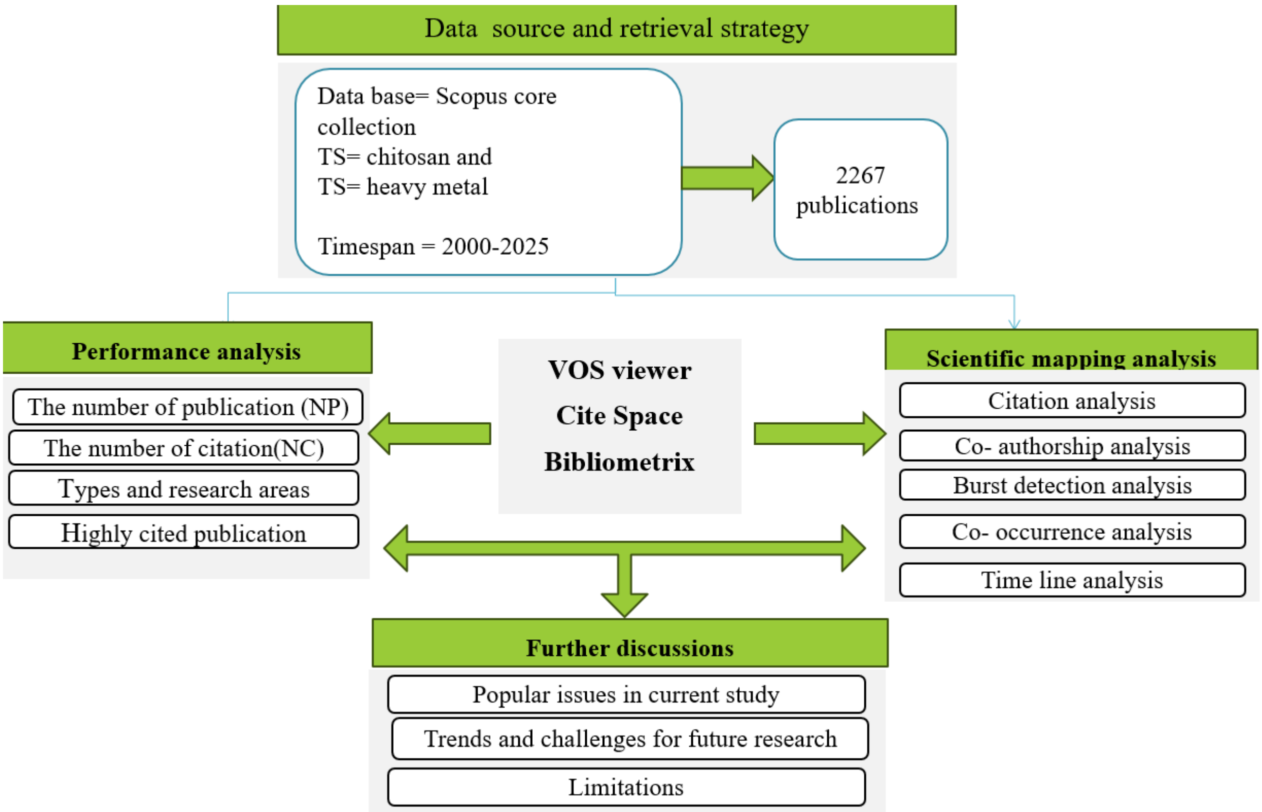


Fig II.1: The research framework of the methodology. **[35]**

Scholars with high quality and reliable academic information and has gradually become the mainstream data source for bibliometric analysis. To retrieve and collect reliable literatures, Scopus core collection is used as the data source in this study. The retrieval settings are as follows: TS = ‘chitosan’ and TS = 'heavy metal', Time span = 2000–2025, Database = Scopus Core Collection. As of 2025.03.01, a total of 2276 publications were retrieved. Then, the relevant information was exported in plain text format for bibliometric analysis , including titles, abstracts, keywords, etc.

II.2 Bibliometric methods

Bibliometrics belongs to the discipline of scientometrics, which can be applied to evaluate the scientific activities of a field of research) or a specific journal. Meanwhile, the primary characteristics are highlighted in a structural approach **.** In this study, the bibliometric analysis focuses on performance analysis and scientific mapping analysis to reveal the development of chitosan & heavy metals research. Performance analysis is based on activity indicators to measure the productivity and influence of publications through item Ana (country/region, institution, author, etc.). The basic characteristics can be measured by several recognized bibliometric indicators, including the number of publications (NP), the number of citations (NC), and the average number of citations per publication (AC). Scientific mapping analysis shows the knowledge structure and dynamic organization of a particular research subject or journal. The analysis in this part mainly involves the following aspects: citation analysis, co-authorship analysis, burst detection analysis, co- occurrence analysis, and timeline analysis. In this paper, three powerful visualization software tools, VOS viewer, Cite Space, and Bibliometrix are adopted to excavate and analyze the data. VOS viewer provides network and density visualization for scientific mapping. Cite Space allows searching for emerging trends and transient patterns in the scientific literature. Bibliometrics is an open-source tool for scientific mapping analysis based on the R language. **[35]**

II.2.1 VOS viewer

VOS viewer is a powerful bibliometric software tool used to analyze and visualize scientific landscapes, aiding in identifying trends, relationships between keywords and authors, and knowledge gaps in various research fields. It allows for the clustering of related publications, enabling users to pinpoint accurate keywords for searching, identify collaboration partners, seminal papers, and key factors in the emergence of modern issues like emerging infections. VOS viewer facilitates the construction and display of bibliometric relationships among different variables, making it a valuable resource for conducting exploratory research, generating new research avenues, and shaping subsequent formal studies based on preliminary findings. Overall, VOS viewer serves as a multifunctional tool for organizing, analyzing, and visualizing information in any field of research, making it an essential asset for researchers seeking to navigate the scientific landscape effectively. **[36]**

II.2.2 Cite Space

Cite Space is a freely available computer program written in Java for visualizing and analyzing literature of a scientific domain. A knowledge domain is broadly defined in order to capture the notion of a logically and cohesively organized body of knowledge. It may range from specific topics such as post-traumatic stress disorder to fields of study lacking clear-cut boundaries, such as research on terrorism or regenerative medicine.

Cite Space takes bibliographic information, especially citation information from the Web of Science, and generates interactive visualizations. Users can explore various patterns and trends uncovered from scientific publications, and develop a good understanding of scientific literature much more efficiently than they would from an unguided search through literature. The full text of many scientific publications can be accessed with a single click through the interactive visualization in Cite Space. At the end of a session, Cite Space can generate a summary report to summarize key information about the literature analyzed. **[37]**

II.2.3 Bibliometrix

The Bibliometrics is gradually extending to all disciplines. It is particularly suitable for science mapping at a time when the emphasis on empirical contributions is producing voluminous, fragmented, and controversial research streams. Science mapping is complex and unwieldy because it is multi-step and frequently requires numerous and diverse software tools, which are not all necessarily freeware. Although automated workflows that integrate these software tools into an organized data flow are emerging, in this paper we propose a unique open-source tool, designed by the authors, called *Bibliometrix*, for performing comprehensive science mapping analysis. *Bibliometrix* supports a recommended workflow to perform bibliometric analyses. As it is programmed in R, the proposed tool is flexible and can be rapidly upgraded and integrated with other statistical R-packages. It is therefore useful in a constantly changing science such as Bibliometrics. **[38]**

II.3 Data sources

Scopus ((https ://www.scopus.com) the most extensive database for research articles in the field of science and engineering and covers a wide variety of all the recent research areas. It provides scholars with high quality and reliable academic information and has gradually become the mainstream data source for bibliometric analysis. To retrieve and collect reliable literatures, the Scopus core collection is used as the data source in this paper. Hence, we execute relevant research by selecting appropriate texts from the Scopus database and collecting data. The field for searching for this study includes the title, abstract, and keywords. These articles were published in English between the years 2000 and 2025. TITLE-ABS-KEY (adsorption AND chitosan AND heavy AND metals) AND (LIMIT-TO (EXACTKEYWORD , "Chitosan") OR LIMIT-TO (EXACTKEYWORD , "Adsorption") OR LIMIT-TO (EXACTKEYWORD , "Heavy Metals") OR LIMIT-TO (EXACTKEYWORD , "Metal Ions") OR LIMIT-TO (EXACTKEYWORD , "Heavy Metal")).

CHAPTER III:

RESULTS AND DISCUSSION

III.1. Performance Analysis

III.1.1 Data description

A total of 2267 articles were published across 589 sources during the survey period from 2000 to 2025 (up to January 01, 2025); the characteristics of these articles are detailed in **Table III.1**. A total of 6103 authors contributed to the studies, which comprised 48 single-authored documents and an average of 4.98 co-authors per article. The average number of citations per article is 53.79 while the average age of the documents stands at 6.7 years, reflecting an annual growth rate of 7.45%. In SCOPUS, all publications can be categorized by different types. It should be noted that some documents belong to two or more types simultaneously. Therefore, the sum of the number of documents corresponding to each type is greater than the number of documents retrieved. The distribution of document types is shown in **Fig III. 1**. Four publication types are obtained, with Articles accounting for the largest share (85%). This is followed closely by conference Papers (4%), Review Articles (9%), and book chapter (2%). **[39]**

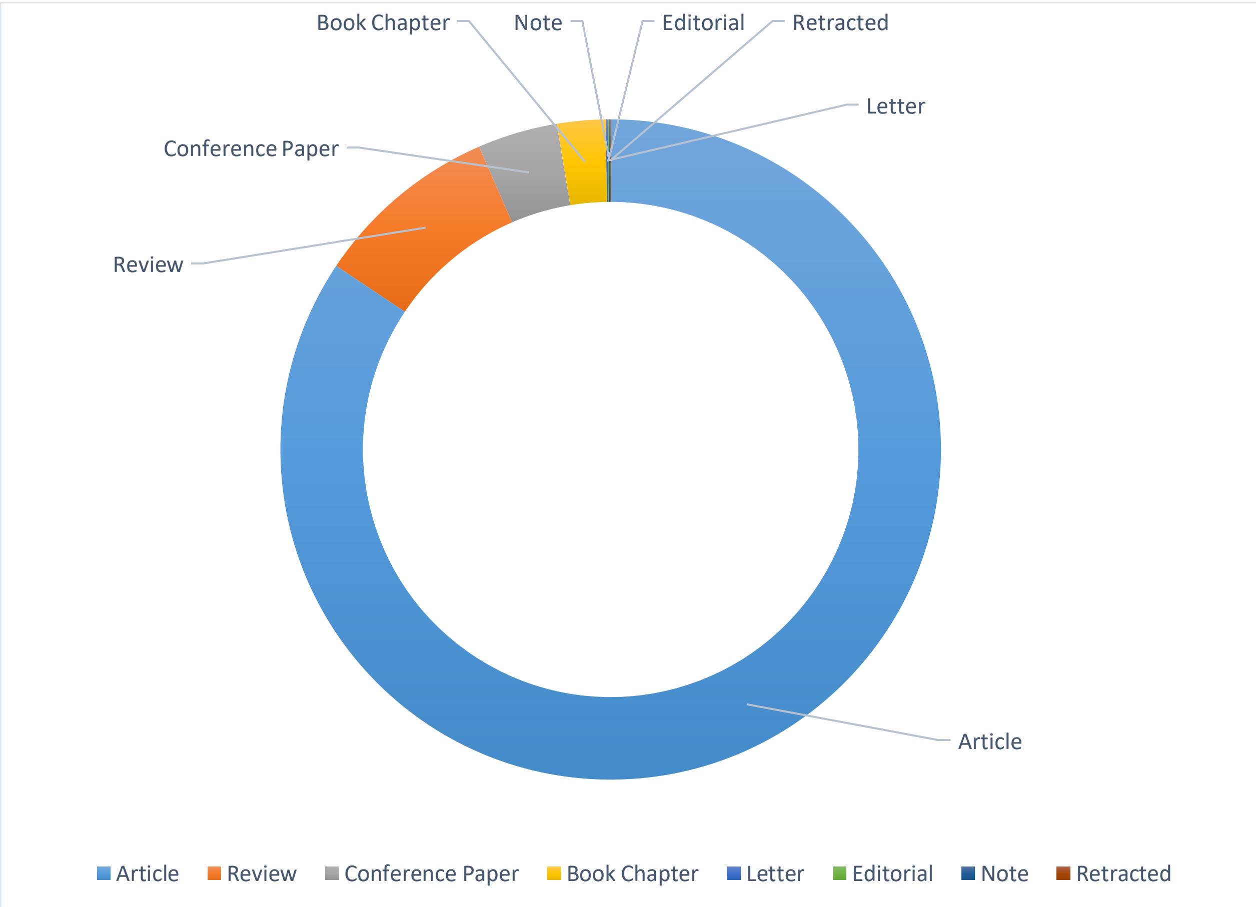


Fig III. 1: presents the Documents by type concerning the adsorption of heavy metals from aqueous medium via chitosan adsorbent.

Table III.1: Core information of the articles related to the Chitosan and heavy metals.

Main information about data		**2000 :**
Times pan		**2025**
1	Sources (Journals, Books, etc.)	589
2	Documents	2267
3	Annual Growth Rate %	7.45
4	Document Average Age	6.7
5	Average citations per doc%	53.79
6	References	0
7	Keywords Plus (ID)	10099
8	Author's Keywords (DE)	3596
9	Authors	6103
10	Authors of single-authored docs	45
11	Single-authored docs	48
12	Co-Authors per Doc %	4.98
13	International Co- authorships %	21.69

III.1. 2 Documents by year

Fig.III.2 illustrates the yearly publication count and research trends concerning the adsorption of heavy metals from aqueous medium via chitosan adsorbent. The quantity of yearly publications from 2000 to 2025 increased consistently, with an annual growth rate of 23, 05%. The publication trend during the last 25 years may be categorized into three distinct phases: the initial phase, the intermediate phase, and the exponential phase. Between 2000 and 2015, it constituted an initial period, characterized by an average publishing rate of 20, 34. This trend steadily escalates from 2016 to 2020, characterized as an intermediate or main growth phase with an average publishing rate of 29,934. Nonetheless, the quantity of published publications throughout this period exhibited persistent volatility. The subsequent phase, the exponential phase from 2020 to the present, saw a fast escalation in the publishing trend, averaging 46,073 articles year. A significant connection (y = 8,3915 x-16809; R^2 = 0.7087) was identified between the publication year and the quantity of published papers from 2000 to 2025. The average citation count per article is shown in **Fig.III.2 (A)**, with the peak citation count recorded at 252 in 2024.

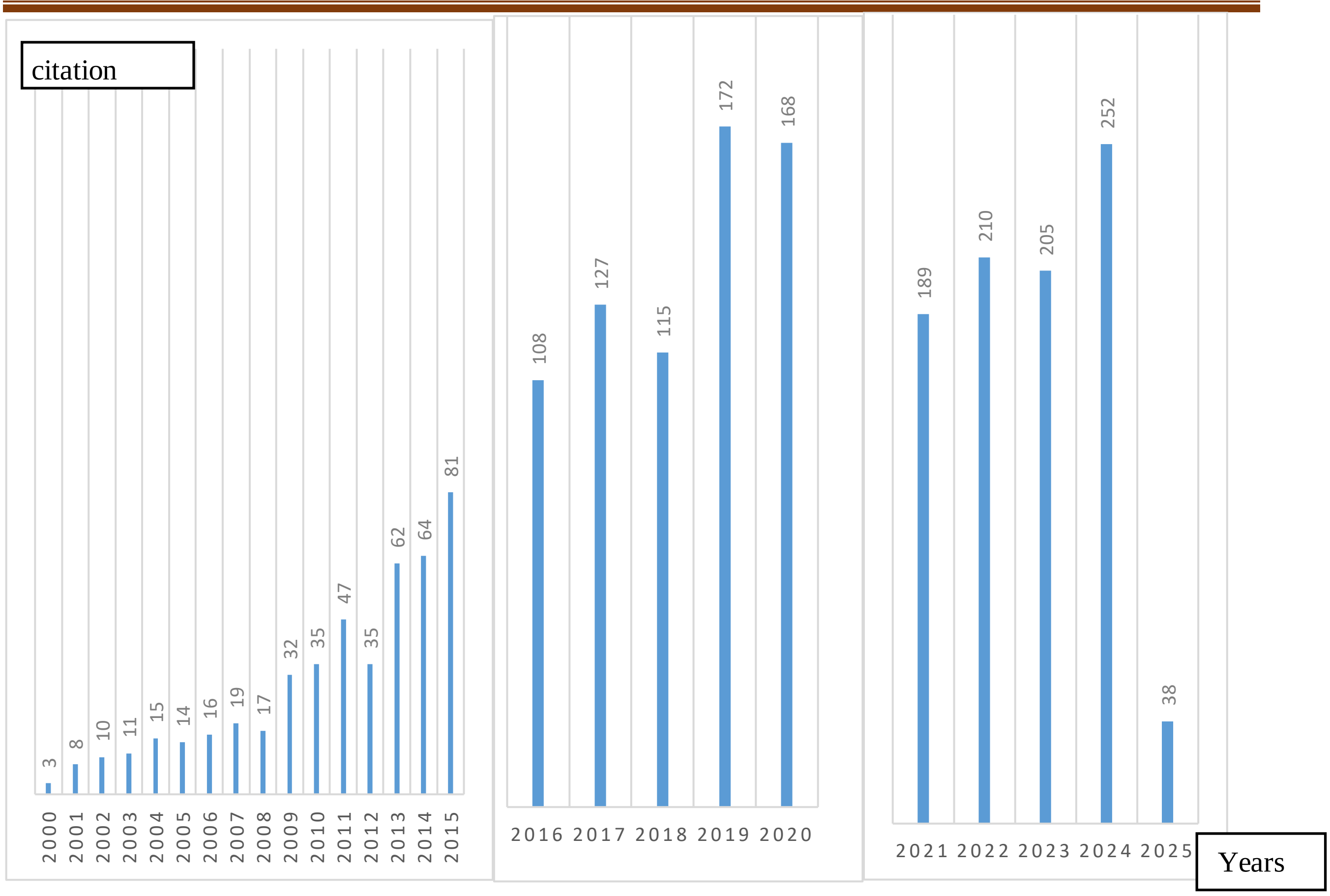


Fig.III.02 (A): Annual global scientific production of research articles.

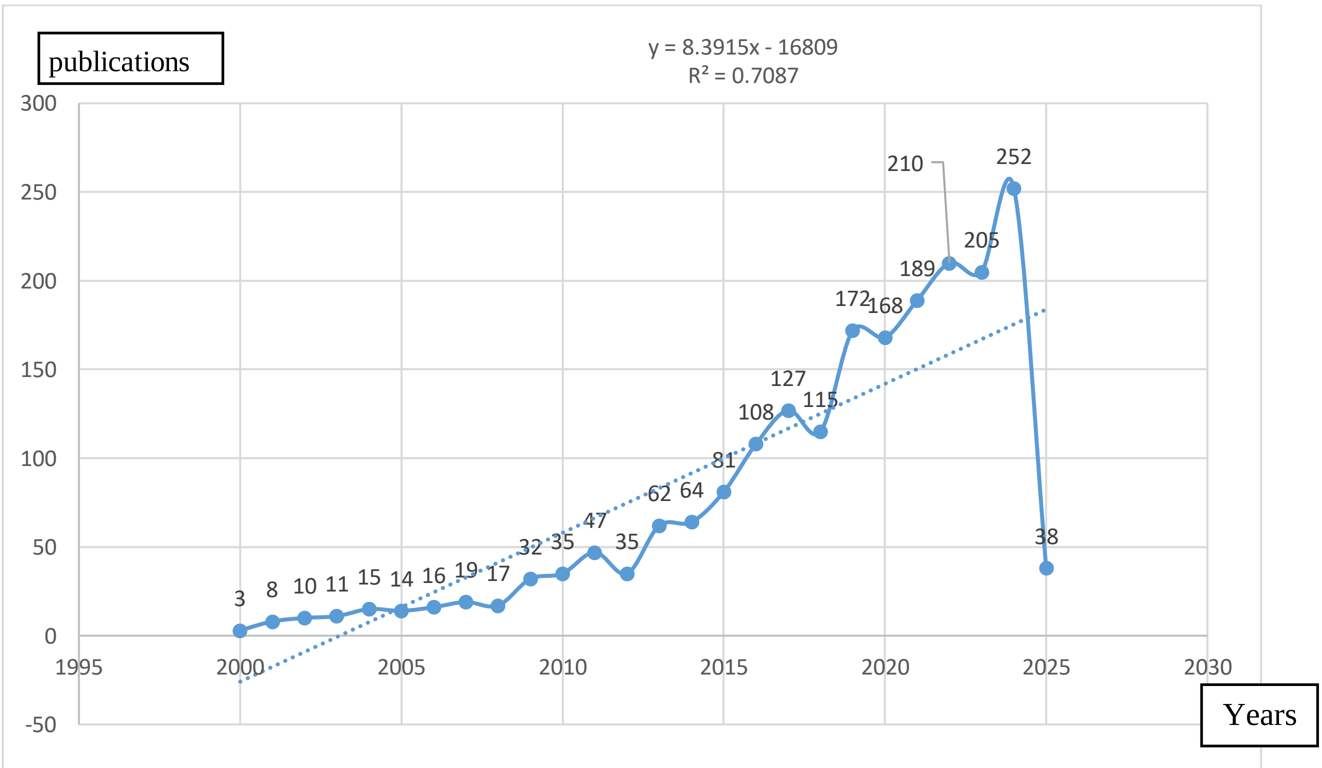


Fig.III.2: presents illustrate the yearly publication count and research trends concerning the adsorption of heavy metals from aqueous medium via chitosan adsorbent.

III.1. 3 Documents by author

Fig. III.3 illustrates the contribution of authors according to the quantity of papers published on the adsorption of heavy metals from aqueous solutions using chitosan as an adsorbent. Establishing a criterion of nine or more publications per author. This strategy may accidentally exacerbate the Matthew Effect by prioritising writers with a greater publication count. The analysis reveals ten primary authors who have published a minimum of nine publications in this subject domain. Based on the results presented in **Fig. III.3**, Sundha, P.N. emerges as the preeminent author with the highest number of publications (25 documents), indicating a significant interest and promotion of research regarding the adsorption of heavy metals from aqueous media using chitosan adsorbent. Likewise, the writers Gomathi, T and Zheng, H, ranked second and third, have published 15 and 14 documents, respectively. The first three writers with the highest output in this domain account for a cumulative total of 42.857%. This also implies that research on the adsorption of heavy metals from aqueous media using chitosan, as an adsorbent is a joint effort among several authors. These data indicate that these three writers have had considerable impact on this study. **[40]**

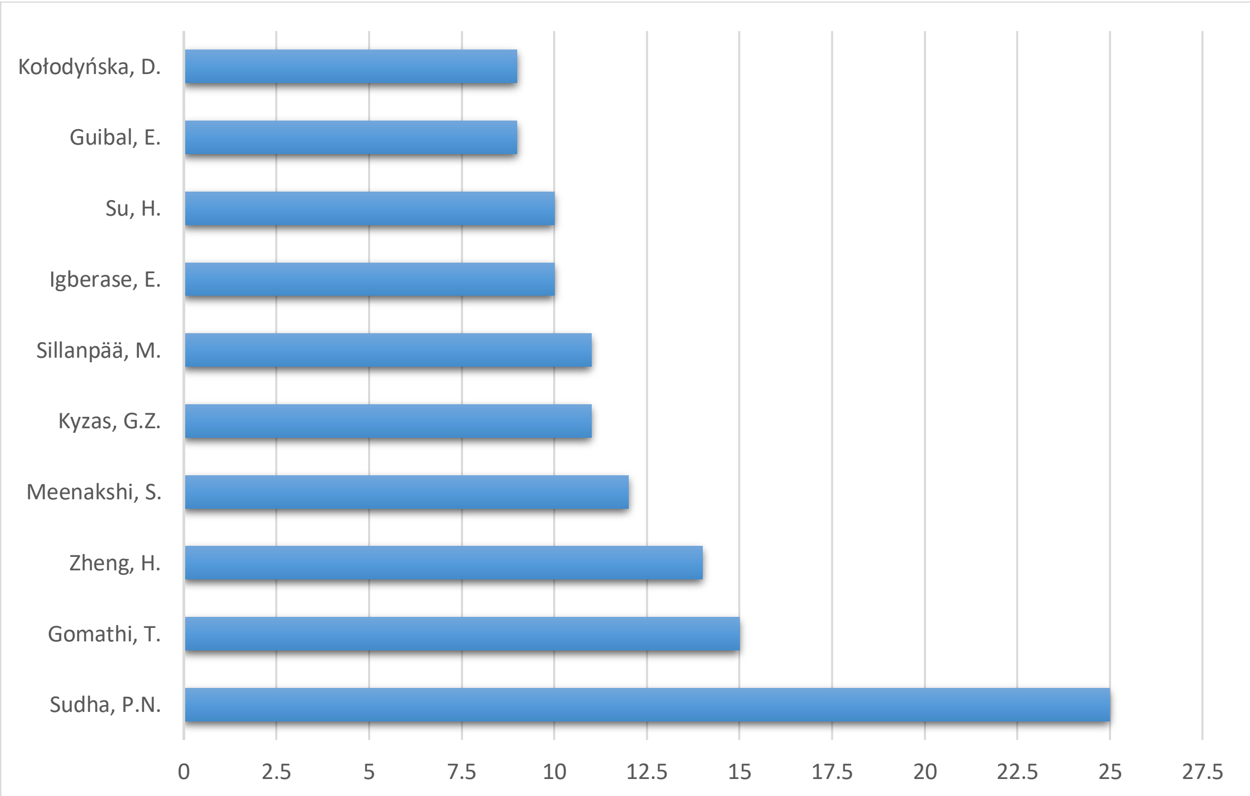


Fig .III. 3: presents the participation of authors based on the number of documents published concerning the adsorption of heavy metals from aqueous medium via chitosan adsorbent.

III.1.4 Documents by affiliation

Fig III. 4 presents the results analysis of institutions related to various studies on concerning the adsorption of heavy metals from aqueous medium via chitosan adsorbent. From this analysis, a total of 164 affiliations were shown to have participated in scientific publications based on the adsorption of heavy metals from aqueous medium via chitosan adsorbent. Considering affiliates that had at least 22 documents, only 10 affiliates participated in this study. Ministry of Education of the People's Republic of China is the affiliation with the highest number of documents, namely 112 documents. Chinese Academy of Sciences and Dhanabhagiyam Krishnasamy Mudaliar College for Women occupying the second and third positions have published 59 and 27 documents. **[40]**

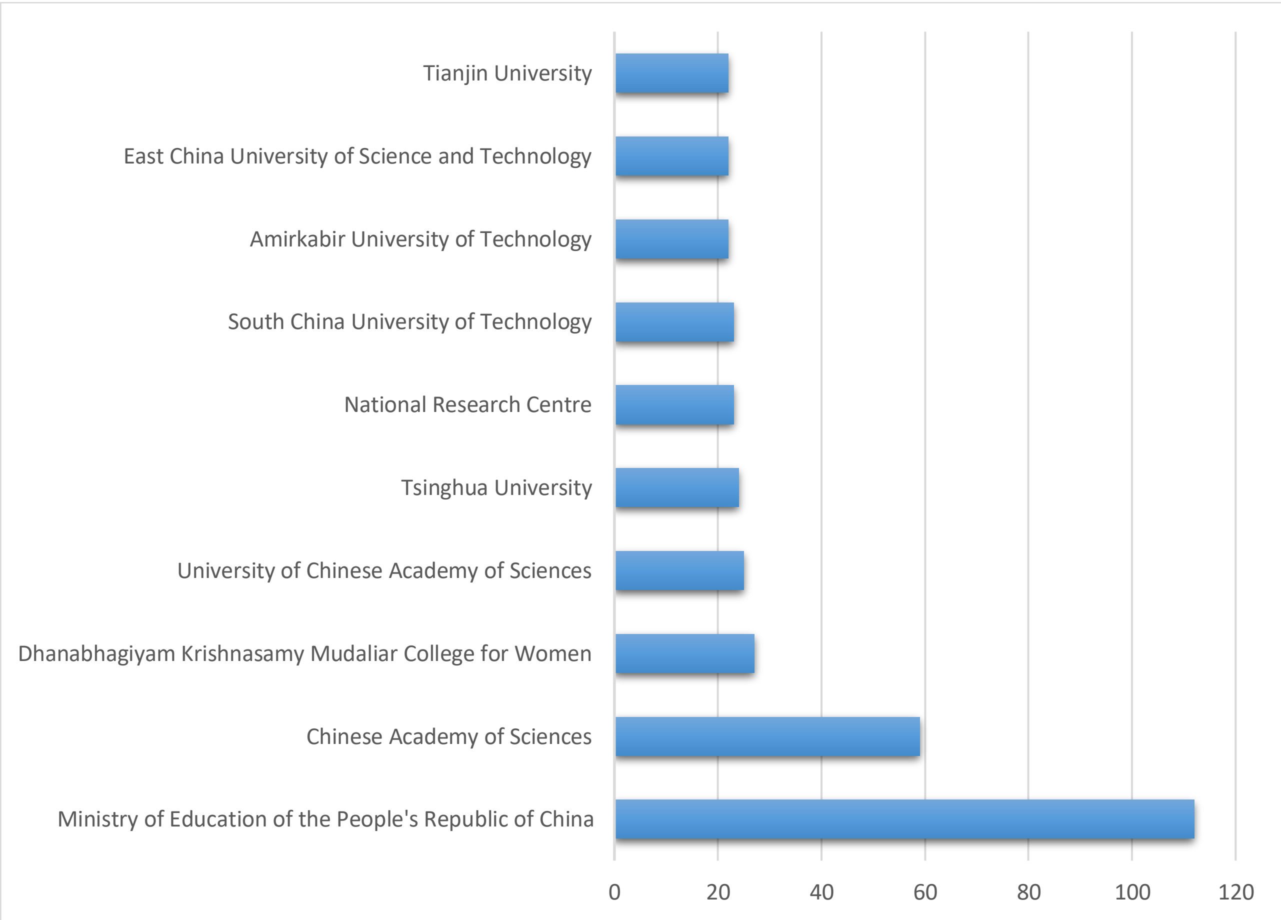


Fig .III. 4: presents the results analysis of institutions related to various studies on concerning the adsorption of heavy metals from aqueous medium via chitosan adsorbent.

III.1. 5 Documents by country or territory

Fig III. 5 (a) presents the Documents by country or territory concerning the adsorption of heavy metals from aqueous medium via chitosan adsorbent. It can be observed that, according to the Scopus database, china is the most active country in the production of studies related to the adsorption of heavy metals from aqueous medium via chitosan adsorbent from 2000 to 2025. Researchers from China contributed 813 of 1791 articles related to this field, which represents 45, 39 %. Meanwhile, researchers from India contributed 274 articles, representing 15.298 %. Researchers from Iran contributed 148 articles, which represents 8, 26 %. The top 10 countries ranked listed in **Fig III.5**. Compared with other countries, the prominence of china, India and Iran in the country's cooperation network is notable. According to the Scopus database, these three countries have made significant progress in the adsorption of heavy metals from aqueous medium via chitosan adsorbent. These countries have produced more than 1235 publications. **[41]**

The total number of publications serves as a clear indicator of a country or region's output in relation to a specific research topic. **Fig.III.5** present an overview of collaboration between countries/regions. The density map of publications in various countries/regions, as illustrated in **Fig.III. 5 (b),** provides a visual representation of the geographical distribution of highly productive nations. A total of 98 countries and regions took part in the study, with the varying shades of red reflecting the number of publications. A deeper shade of red indicates a greater quantity of publications in the respective country or region. According to **Fig.III. 5 (b)**, China leads with 813 publications, followed by India with 274 publications. Subsequently, Iran and Egypt are noted, with 148 and 130 publications, respectively. Publications are predominantly found in the United States, Saudi Arabia, Malaysia, and South Korea, indicating a clear geographical concentration of research on Chitosan and heavy metals.

Fig III. 6 illustrates the cooperation globe map, with the thickness of the linkages indicating the degree of collaboration across various nations and regions. This figure delineates distinct cooperation patterns and illustrates the countries/regions with the most proximate collaborative links in this domain. China has a high frequency of collaborative partnerships; data analysis indicates a significant level of academic collaboration between china and USA in this domain. Malaysia, Egypt, India, and Soudia Arabia have strong alliances with many nations and areas. China has a significant proportion of domestic partnerships, suggesting that the majority of research is conducted autonomously. Conversely, most collaborations in USA are international partnerships.

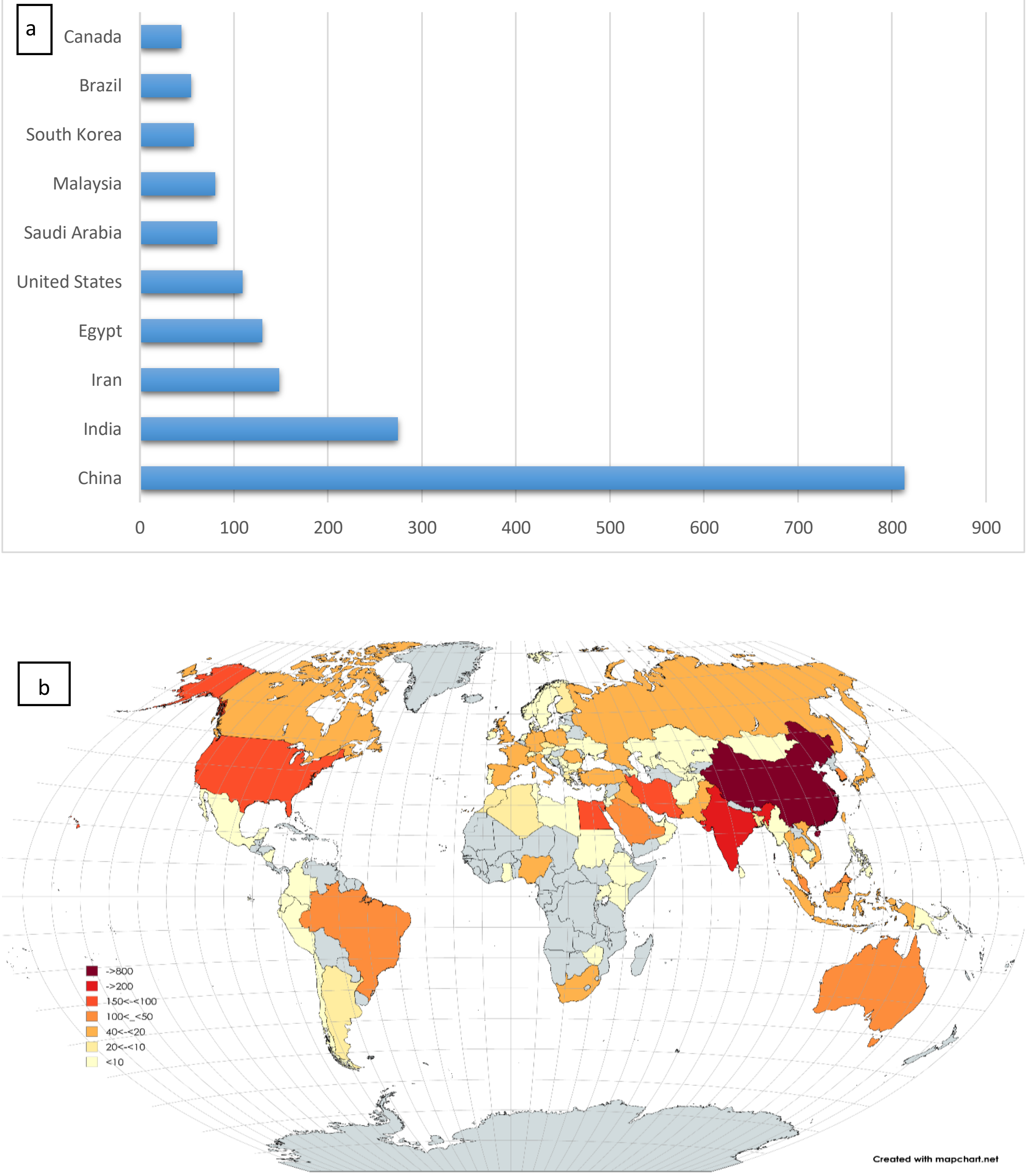


Fig. III. 5 The overview of collaboration between countries/regions. (a) Presents the Documents by country or territory concerning the adsorption of heavy metals from aqueous medium via chitosan adsorbent. (b)The collaboration world map.

Fig. III.6: The specific collaboration pattern.

III.1. 6 Documents by subject area

Each publication addresses at least one area of research. The top 10 research areas are presented in **Fig III.7**. The top 10 research areas are presented in **Fig III.7**. In **Fig III.7**, the most popular research areas are engineering science (810) chemistry (762), with 20% and 18 %, respectively. I t is followed by chemical engineering (14%), Materials Science (13%), and biochemistry, genetics and molecular biology (10%). The remaining five research areas are engineering (8%), Physics and astronomy (5%), energy (4%), pharmacology toxicology and pharmaceutics (2%), and Medicine (2%). **[40]**

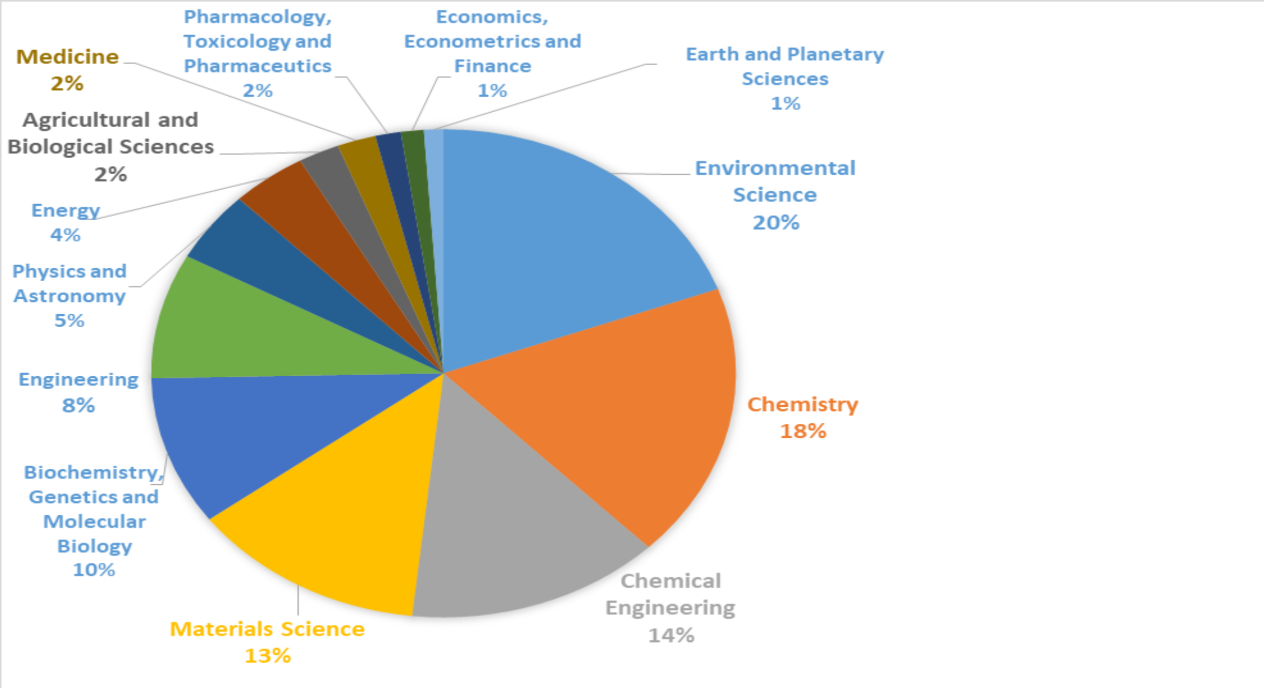


Fig III.7: presents the Documents by subject area.

III.1.7 Documents by funding sponsor

International scientific collaborations play a crucial role in integrating into the global research community. From 2000 to 2025, total of165 institutions are involved in the selected research articles on concerning the adsorption of heavy metals from aqueous medium via chitosan adsorbent. **Fig.III.8** presents a compilation of the ten most productive institutions based on their productivity. National Natural Science Foundation of China; n = 403) in China holds the top position, followed by Ministry of Science and Technology of the People's Republic of China (n =124), National Key Research and Development Program of China (n = 58), Fundamental Research Funds for the Central Universities (n = 37), and Ministry of Education of the People's Republic of China (n = 33).

India "Department of Science and Technology, Ministry of Science and Technology", being a significant partici-pant, had the number of institutions (n = 20) among the top ten research institutions studying adsorption of heavy metals from aqueous medium via chitosan adsorbent.

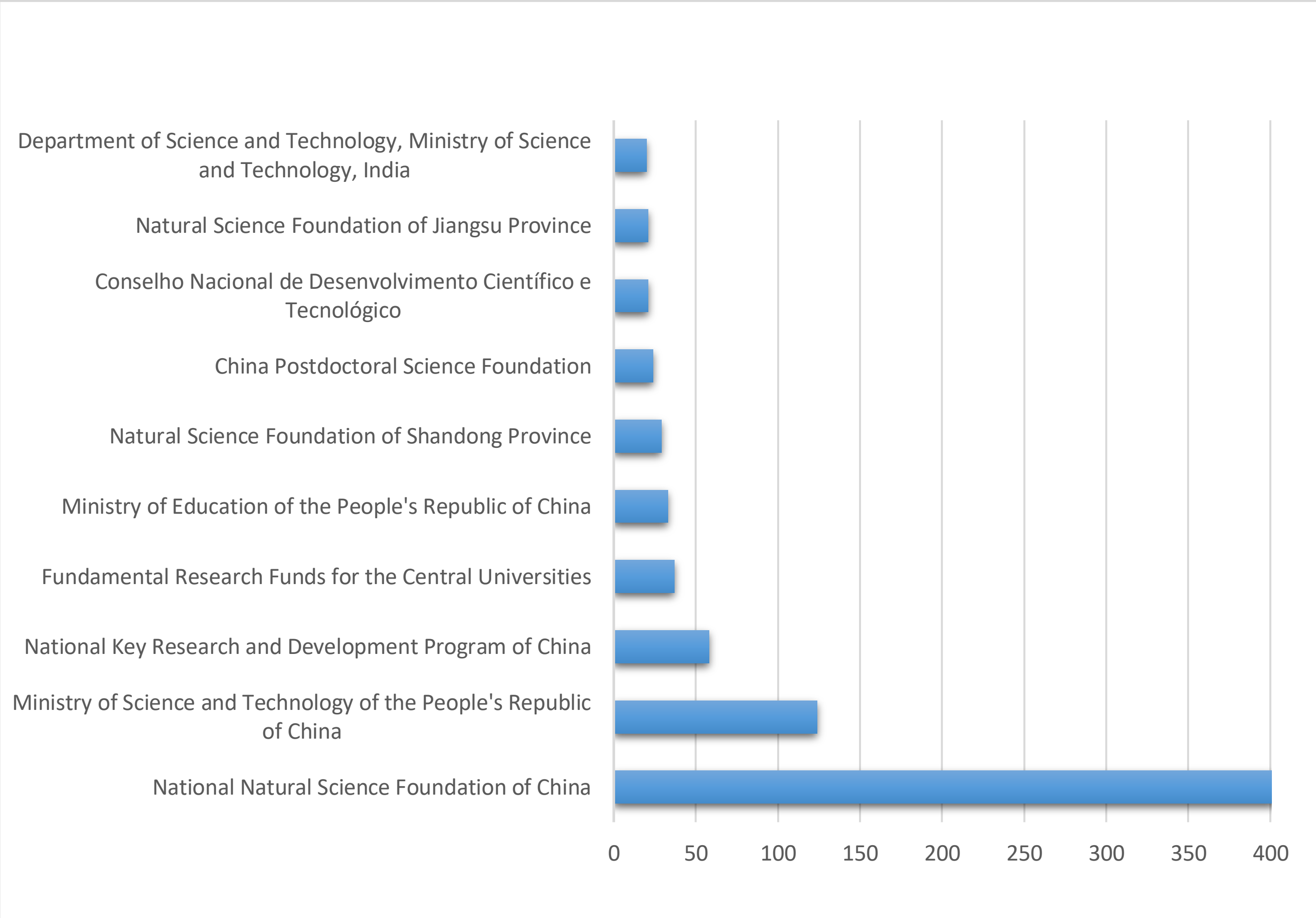


Fig.III. 8: presents a compilation of the ten most productive institutions based on their productivity.

III.1.8 Documents per year by source

Table III.2 presents the Documents per year by source concerning the adsorption of heavy metals from aqueous medium via chitosan adsorbent.

International Journal of Biological Macromolecules has the highest number of documents, with 245 documents. Journal of Hazardous Materials and Chemical Engineering Journal occupying the second and third positions have published (86 and 65 documents). Carbohydrate Polymers (63 Documents) and Chemosphere (44 documents). Journal of Environmental Chemical engineering (39 documents). Desalination And Water Treatment (37 documents).

Colloids And Surfaces a Physicochemical and Engineering Aspects and Journal of Colloid and Interface Science and Polymers they have (34 documents).

Table III.2: presents the Documents per year by source

Source	Documents
International Journal Of Biological Macromolecules	245
Journal Of Hazardous Materials	86
Chemical Engineering Journal	65
Carbohydrate Polymers	63
Chemosphere	44
Journal Of Environmental Chemical Engineering	39
Desalination And Water Treatment	37
Colloids And Surfaces A Physicochemical And Engineering Aspects	34
Journal Of Colloid And Interface Science	34
Polymers	34

III.2. Scientific mapping analysis

III.2.1 Highly cited publication

A document is acknowledged when it is often referenced by others. Consequently, the quantity of citations serves as a significant metric for assessing the impact of a work. **Table III.3** enumerates the ten most referenced articles in decreasing order based on citation count. **Table III.3** presents comprehensive data, including source, type, year, and number of citations (NC), average citations per year (AC), number of authors (AN), number of institutions (IN), and number of countries/regions (CN). The evaluation of these articles is only based on compliance with the Scopus database standards.

The following data presents a summary of the three most referenced works, as identified by a search performed on the Scopus database: Low-cost adsorbents for heavy metals uptake from contaminated water: The study on health and prospective applications is the most cited, with 3095 references in the literature. The Journal of Journal of Hazardous Materials published this study in 2003. Reviews the effectiveness of various low-cost materials in removing heavy metals from contaminated water. Instead of commercial activated carbon, the study focuses on inexpensive, locally available adsorbents such as chitosan, zeolites, and lignin. The review analyzes data from approximately 100 studies to compare the adsorption capacities of these materials with activated carbon. Notably, chitosan demonstrated high adsorption capacities for Hg^{2+}, Cr^{6+}, and Cd^{2+}, while lignin showed exceptional capacity for Pb^{2+}. Zeolites also exhibited significant removal efficiencies for Pb^{2+} and Cd^{2+}. The study highlights that the effectiveness of these adsorbents varies based on their chemical modifications and the concentration of the metal ions.

The authors suggest that these low-cost materials offer promising alternatives for treating inorganic effluents contaminated with heavy metals. The findings are significant for developing sustainable water treatment solutions in regions with limited resources. **[42]**

The second most-cited publication has garnered 2967 citations. A review of potentially low-cost sorbents for heavy metals, was published in the Journal of Water Research published Bailey et al. (1999) reviewed various low-cost sorbents for removing heavy metals from water. They identified materials like chitosan, lignin, peat moss, and seaweed as effective alternatives to commercial adsorbents. The study highlighted impressive adsorption capacities, such as 1587 mg Pb/g for lignin and 1123 mg Hg/g for chitosan. These sorbents are cost-effective and often derived from natural or waste sources. Chemical modifications can further enhance their adsorption properties. The review emphasizes the potential of these materials for sustainable water treatment solutions. The findings are significant for developing countries seeking affordable methods to address heavy metal contamination in water. **[43]**

The third most referenced study, authored by Close, D et al., is in the Journal of Progress in Polymer Science (Oxford) and is titled "Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment" It has received 1993 citations. The review discusses recent advancements in polysaccharide-based materials as adsorbents for wastewater treatment. It highlights the use of natural polymers like chitin, chitosan, starch, and cyclodextrin, which are modified to enhance their adsorption capacities. These materials are effective in removing pollutants such as heavy metals, dyes, and aromatic compounds from contaminated water.

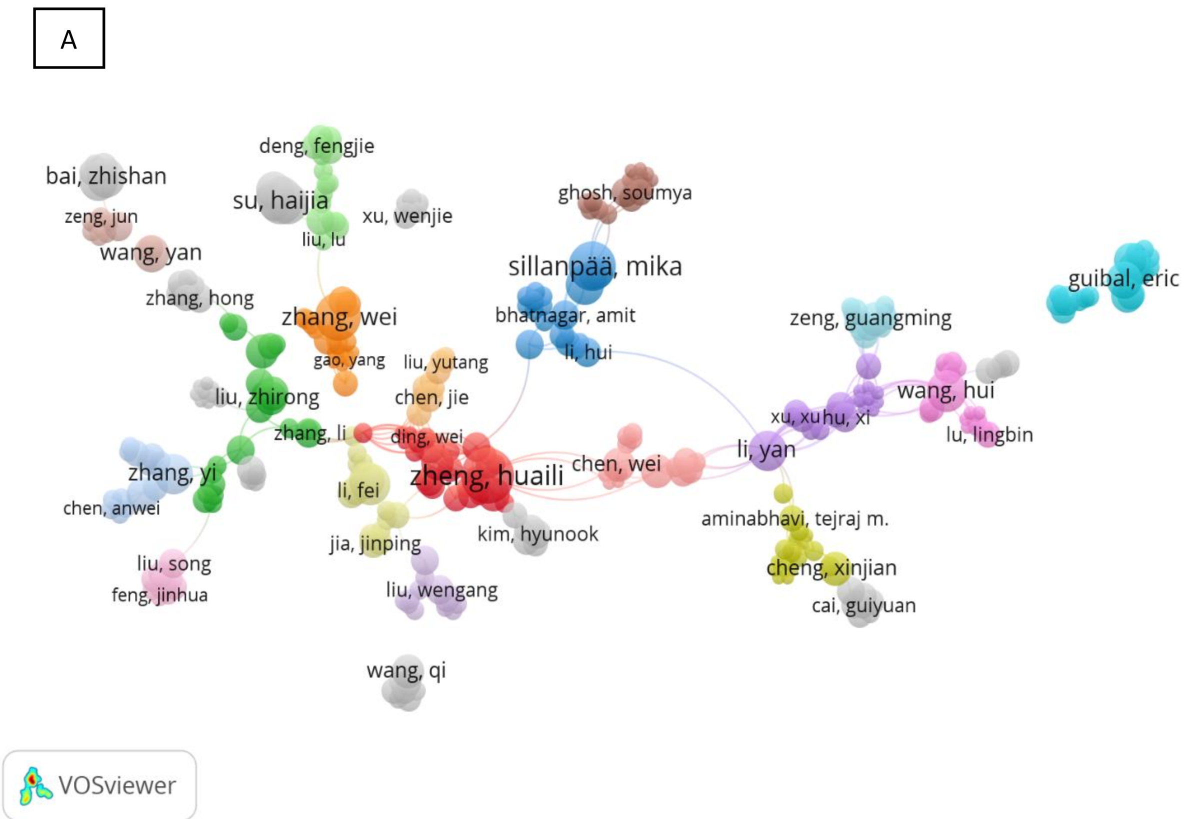
The article emphasizes the benefits of using biopolymers, including their biodegradability, low cost, and environmental friendliness. It also addresses the challenges in optimizing these materials for large-scale applications. The review provides insights into the synthesis, properties, and performance of these adsorbents. It concludes by suggesting future directions for research to improve the efficiency and applicability of polysaccharide-based adsorbents in wastewater treatment. [**44]**

Table III.3: The top 10 highly cited publications.

Rank	Title	Source	Type	Year	NC	AC	AN	IN	CN
1	Low-cost adsorbents for heavy metals uptake from contaminated water	Journal of Hazardous Materials	Review	2003	**3095**	140.68	2	1	1
2	A review of potentially low-cost sorbents for heavy metals	Water Research	Review	1999	**2967**	114.11	2	2	1
3	Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment	Progress in Polymer Science (Oxford)	Review	2005	**1993**	99.95	1	1	1
4	Adsorption of dyes and heavy metal ions by chitosan composites	Carbohydrate Polymers	Review	2011	**1860**	132.85	2	2	1
5	Low cost adsorbents for the removal of organic pollutants from wastewater	Journal of Environmental Management	Review	2012	**1199**	92.23	3	1	1
6	Metal complexation by chitosan and its derivatives	Carbohydrate Polymers	review	2004	**1106**	52.66	3	3	1
7	Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads	Reactive and Functional Polymers	Article	2002	**958**	41,65	3	1	1
8	Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: Isotherms, kinetics and thermodynamics	Journal of Hazardous Materials	Article	2011	**819**	58,5	3	3	1
9	Preparation and adsorption properties of monodisperse chitosan-bound Fe_3O_4 magnetic nanoparticles for removal of Cu(II) ions	Journal of Colloid and Interface Science	Article	2005	**745**	37,25	2	1	1
10	Application of chitosan for the removal of metals from wastewaters by adsorption - Mechanisms and models review	Critical Reviews in Environmental Science and Technology	Article	2007	**730**	40,55	4	2	2

III.2.2 The cooperation analysis of the authors

The authors' cooperation network visually depicts the links among researchers in the domain of chitosan and heavy metals. VOS viewer indicates that 8245 authors have published pertinent documents. Establish the minimum count of papers and citations for an author at one. A total of 2267 writers attained the criterion. 57 of these authors form the biggest interconnected network, as seen in **Fig. III.9 (A)** node signifies an author, with the node's size indicating the author's total strength of cooperation (TLS) with other writers. A relationship between two nodes signifies that the authors have co-authored articles. In **Fig. III.9 (A)**, the 57 writers are categorized into six groups, each represented by distinct colors. Red and green nodes indicate clusters 1 and 2, respectively, while blue and yellow nodes represent clusters 3 and 4. Sundha, P.N has the highest TLS, followed by Gomathi, T and Zheng, Huaili. Furthermore, Zheng, Huaili has the most collaborators, with close working ties with li.hong and Chen, Wei and Luo, honbing. **Fig. III.9 (B)** depicts the chronological distribution of publications by different authors. The shade of the node correlates to the author's average year of publication. The darker coloration, the older the average year of the related author's writings. Authors in cluster 6 collaborated quite early, with most authors in clusters 1 and 2 publishing in 2022 on average. Furthermore, major partners engaged more closely in 2018.



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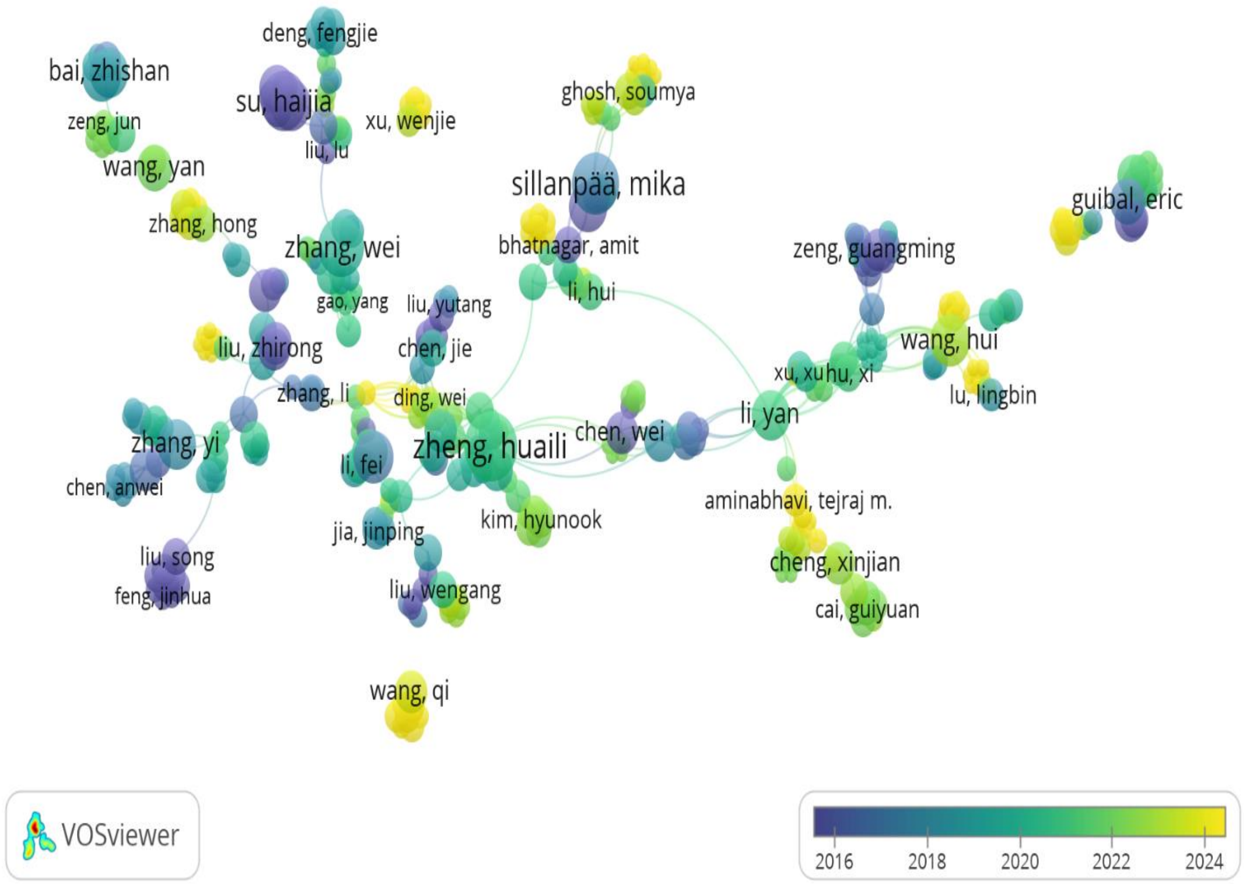

Fig.III.9: The collaboration network of authors**. (A)**The largest connected network with 56 authors. **(B)** The collaboration network of authors with timeline.

III.2.3 Keywords analysis

Keywords are significant in research papers because they communicate the study's major ideas and concepts. Researchers may acquire insights into the shifting patterns and orientations of research in a certain topic by undertaking a longitudinal study of term frequency and occurrence. The SCOPUS database divides keywords into two categories: author keywords and Plus keywords. This research focuses on assessing writers' keywords. In a bibliometric study, the titles and authors' keywords are very important since they act as the readers' initial exposure to the piece. These features give insights into the important themes highlighted by the authors in their study.

An inquiry was done to assess current trends in research on adsorption chitosan and heavy metals. The goal was to assess the frequency of terms used in this research. **Fig.III.10** shows the co-occurrence keyword map created by the VOSviewer program, which efficiently detects active study topics. "

A total of 6103 author keywords were found, with 22 meeting the requirement of having at least six instances of the term. This led to the discovery of three clusters, each representing a separate study approach. Cluster 1 includes a variety of chitosan, heavy metals, and adsorption capacities. Cluster 2 contains terms linked to article, chemistry, water pollutants, chemical, and kinetics. Cluster 3 contains terms linked to waste water management, cadmium, and bioremediation, respectively. In **Fig.III.10**, the size of each circle in the network visualization diagram represents the frequency of keyword occurrences. Keywords such as chitosan, heavy metals and article, chemistry, suggesting that they appear more often.

Keywords may also signify the progression of a discipline. This section does a timeline analysis of terms from 2000 to 2025 with Cite Space. The time slice is set to one, and the timeline analysis of keywords is shown in **Fig. III.10 (a)** the keywords are categorized into four clusters each designated with a log-likelihood ratio. The chronological arrangement of the keywords in each cluster was dictated by their first appearance timings on the timeline. The interconnected arcs in **Fig. III.10 (b)** illustrate the symbiotic interaction among keywords. **Fig III.10 (C)** illustrates that "functional dyspepsia" is the first cluster, designated as cluster #0, with publications spanning from 2000 to 2025. The remaining clusters are designated as «adsorption ","chitosan", "heavy metals ","article ", and "pH" sequentially. The prolonged period of cluster #1 indicates that adsorption have consistently been a focal point of study and a prevailing trend. The temporal scope of cluster #1 (adsorption) and cluster 2 (chitosan) extends until 2025. These clusters have increasingly emerged as a focal point of study in the discipline and are likely to remain prominent for the foreseeable future.

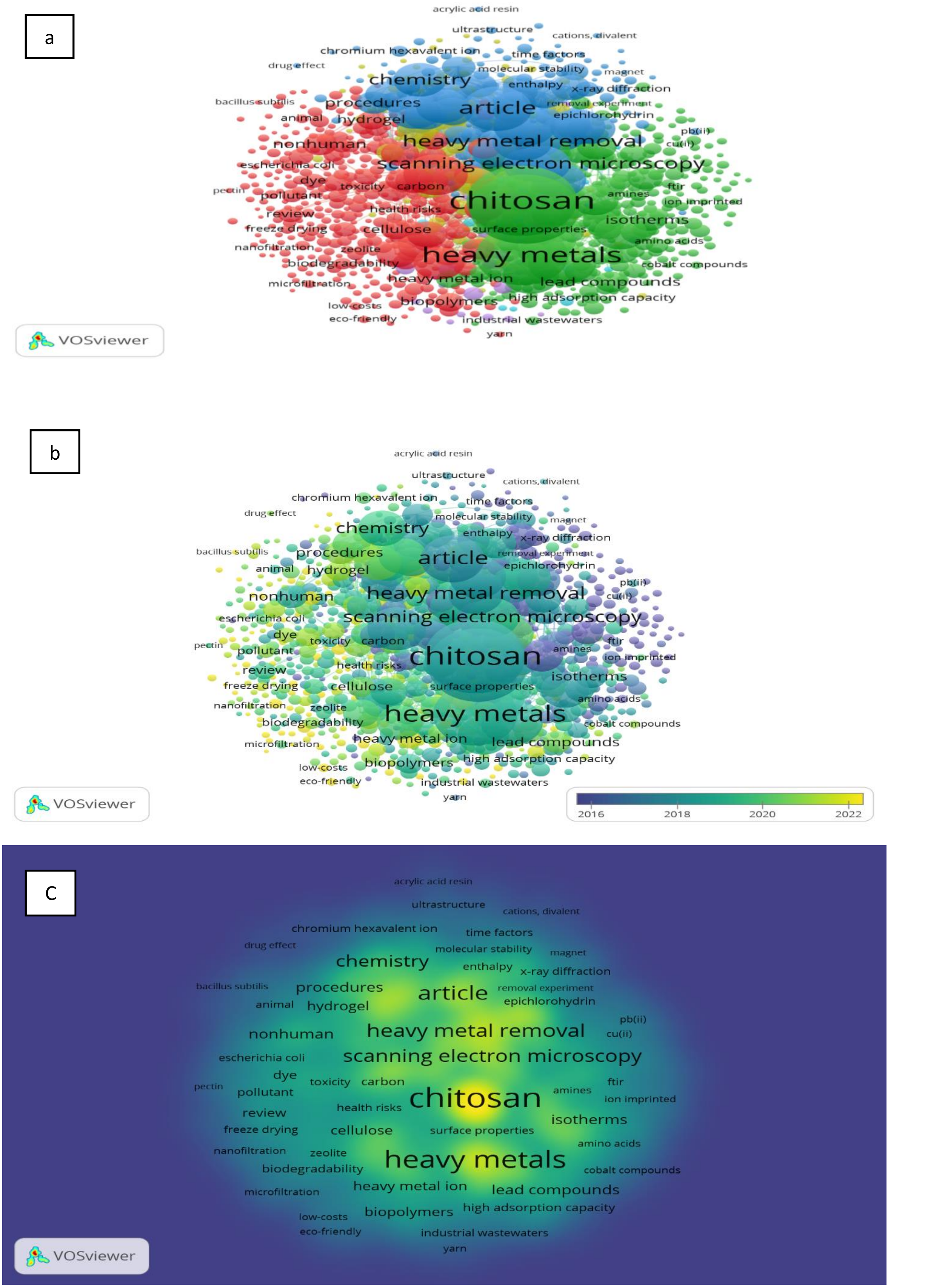

Fig III.10 (a) visualization of the Keywords co-occurrence network, **(b)** visualization of the Keywords co-occurrence network with timeline, **(c)** density of network

III.2.4 Reference analysis

Co-cited references are defined as two texts that are mentioned concurrently within a certain context. From 2000 to 2025, 103646 references were mentioned in 2267 articles. A network map was generated to illustrate the co-cited references, particularly those having a minimum co-citation count of two **(Fig.III.11)** Of the 103646 mentioned references, 15 fulfilled the criteria. Three clusters were created. Each cluster is denoted by a unique color, while the size of each node reflects its citation frequency.

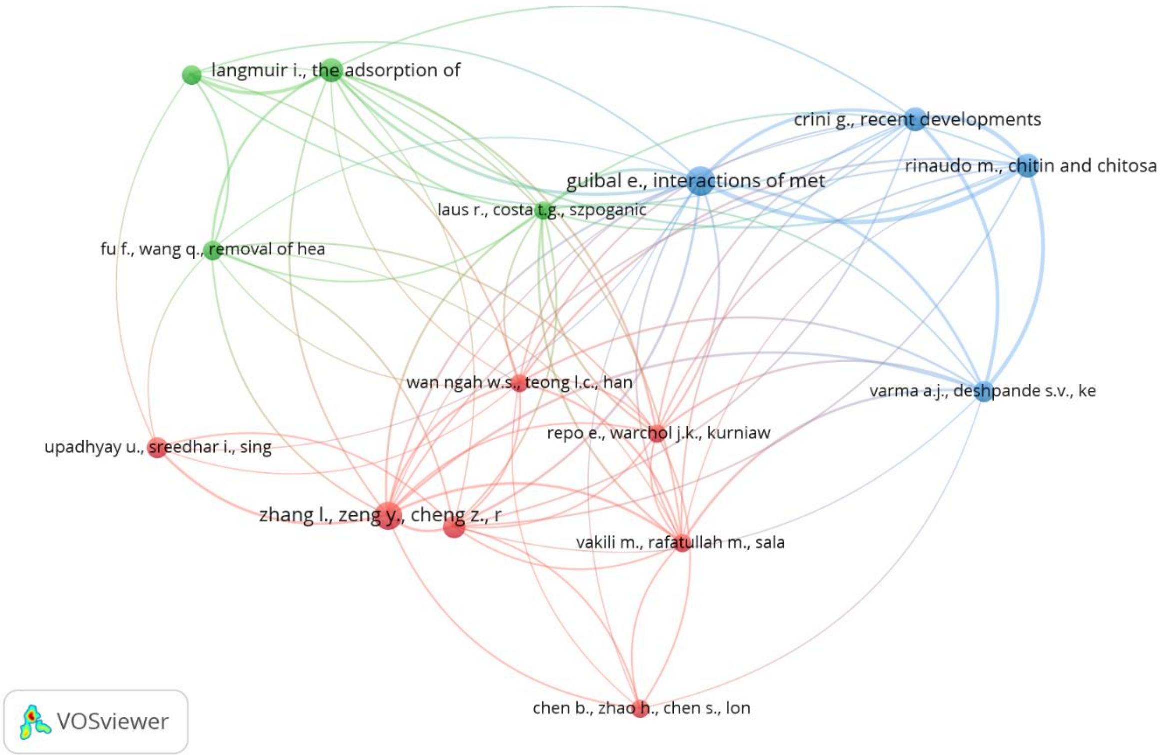

Fig.III.11 Network map visualization of co-cited references.

III.3 Literature-based screening

The performance of several biosorbents, mostly derived from agricultural, forestry, and industrial waste, is addressed. A description of the typical approaches proposed for improving the adsorption capacity, selectivity, and mechanical strength of the biosorbent is examined, followed by a discussion of variables influencing Biosorption, isotherm models, and kinetic models. **Table III.4** provides a comprehensive summary of all recent research in which biosorbents were produced for metal removal, with succeeding subsections highlighting the significant discoveries and trends identified during the table's compilation.

III.4 Classification of biosorbents biosorbents are divided into two types

live biosorbents, which include algae, fungus, yeast, and bacteria, and non-living biosorbents (such as rice husk, coal fly ash, neem leaves, neem bark, clay, and so on), which are mostly produced from agricultural, forestry, and industrial waste. However, compared to non-living biosorbents, live biosorbents have several disadvantages. For example, because of their intrinsic friability, they often have poor mechanical strength, necessitating immobilization to boost stability, which raises the cost of the biosorbents. Furthermore, living biosorbents are difficult to store because live cells need certain conditions to be maintained, but nonliving biosorbents are easy to store since there are no metabolic energy requirements. Furthermore, although nonliving biosorbents may be regenerated and reused several times, living biosorbents have a limited reuse owing to the buildup of harmful substances inside live cells. Therefore, nonliving biosorbents have a modest advantage over living biosorbents **[45]**. Converting trash from industry, agriculture, and forestry into biosorbents, (nonliving) has helped to manage waste more effectively. It has also resulted in the creation of value from economically useless items. Biosorption studies have been conducted using rice husk, nutshell, fruit and vegetable peel, leaves, bark, wheat bran, and other agricultural wastes. Plant-based biomaterials have shown to be effective biosorbents owing to their static binding capacity to metals present in wastewater. This binding happens by cell-surface sorption, intracellular, and extracellular accumulation. According to research on plant-based Carnauba fruit biomass, the presence of lignocellulose on the surface aids in the sorption process **[46]**, while the presence of a carboxylic group in the rubber leaf aids in metal sorption from aqueous solution. Industrial waste has a wide spectrum of physiochemical qualities that may be exploited to successfully remove metal. Byproducts from industries, such as coal fly ash, sawdust blast furnace slag, industrial sludge, and so on **[47]**, may be utilized to prepare biosorbents. Biorefinery, pulp, and paper sector byproducts mostly include a propyl-phenolic group, while metal and mining industrial slag contains silicon and metal oxides. Red mud generated by the alumina industry contains metal oxides that improve biosorption effectiveness. A research on sawdust found that functional groups such as phenolic, carbonyl, amino, amide, and alcoholic groups in sawdust, a waste product from the wood industry, are favourable in the sorption process. **[48]**

Table III.4 present the Literature-based screening

Sl.	Metal Removed	Source/ Effluent	Bio sorbent Composition	Modification	Synthesis	Process Parameter %	removal or Removal capacity mg/g)	Desorption	Merits	Demerits	Kinetics	Isotherm	Ref
1	Pb (II)	aqueous solutions	$MgFe_2O_4$/ Schiff base/Chitosan	Schiff base formation via condensation of terephthalaldehyde and amino pyrazine	Crosslinking of $MgFe_2O_4$ nanoparticles with modified chitosan	pH 5.5, 100 min contact time, 328 K temperature	290.7 mg/g	Over 94.8% retention after five cycles	High adsorption capacity, excellent recyclability, eco-friendly	Potential interference from competing ions like Zn(II) and Cu(II)	Pseudo-second-order	Langmuir (R^2 = 0.9997)	**[49]**
2	Cu(II) Cr(VI)	Aqueous solution	Chitosan Schiff base	MoS_2 and C_3N_4 incorporation	Crosslinking with vanillin, incorporation of MoS_2 and C_3N_4	Cu(II): pH 7, 100 mg/L initial concentration Cr(VI): pH 3, 100 mg/L initial concentration	Cu(II): 132.83 mg/g Cr(VI): 137.25 mg/g	Not specified	High adsorption capacity, magnetic separation, recyclability	Not specified	Pseudo-second-order	Langmuir models	**[50]**
3	Pb^{2+}, Zn^{2+}	Water	Magnetic chitosan/reduced graphene oxide	Reduced graphene oxide	Not specified	pH : Not specified	Pb^{2+}: 169.58 mg/g, Zn^{2+}: 421.78 mg/g	Not specified	High Adsorption capacity	Not specified	Pseudo-second-order	Freundlich models	**[51]**
4	Cd^{2+} Pb^{2+} Cr(VI) and Cr(III)	Water	Almond shell biochar (nBC)	Modified with FeS and chitosan	Pyrolysis of almond shells	Not specified	Cd^{2+}= 85.6 mg/g Pb^{2+}= 89.63 mg/g Cr(VI): 94.2 mg/g, Cr(III): 75.62 mg/g	Not specified	High adsorption capacity	Not specified	Pseudo-second-order	Langmuir models	**[52]**
5	U(VI)	Tailings waste water	Calcium phytate cross-linked polysaccharide hydrogel	Cross-linking with calcium phytate	Not specified	Not specified	Not specified	Not specified	High selectivity for U(VI) removal	Not specified	Pseudo-second-order	Langmuir models	**[53]**

Sl.	Metal Removed	Source/ Effluent	Bio sorbent Composition	Modification	Synthesis	Process Parameter %	removal or Removal capacity mg/g)	Desorption	Merits	Demerits	Kinetics	Isotherm	ref
6	Cr(VI)	Aqueous solution	Chitosan-coated almond shell biochars (Ch-ASC400, Ch-ASC500)	Coating with chitosan	Pyrolysis of almond shells at 400°C and 500°C, followed by chitosan coating	Adsorbent dosage: 1.5 g/L; Contact time: 120 min; pH: 1.5; Temperature: 25°C	Ch-ASC400: 37.48 mg/g; Ch-ASC500: 36.65 mg/g	Not specified	High adsorption capacity; Effective at low pH; Biocompatible	Reduced efficiency in the presence of Cl^- ions; Adsorption capacity decreases with increasing Cl^- concentration	Pseudo-second-order model ; Intra-particle diffusion model	Langmuir and Freundlich models	**[54]**
7	Pb(II) Zn(II)	Aqueous solution	Chitosan	Cross-linked with formaldehyde	Shrimp -derived chitosan	Dosage: 0.4 g, Temperature: 25°C, pH: Not specified	Zn(II)=20.34% removal Pb(II)= 13.54% removal	Reversible	Environmentally friendly, cost-effective	Limited removal capacity	Pseudo-second-order	Langmuir (R^2 = 0.9934)	**[55]**
8	Ni(II)	Aqueous solution	Chitosan / magnetite composite beads	Coating chitosan on Fe_3O_4 nanoparticles	Coprecipitation method	pH: 6; Contact time: 150 min; Temperature: Room temperature	52.55 mg/g	Not specified	High adsorption capacity; Magnetic separation; Simple synthesis	Limited information on regeneration; Specific to Ni(II)	Pseudo-second-order model	Langmuir models	**[56]**
9	Pb(I)	Aqueous solution	Electrospun PAN/α-Fe_2O_3 nanofibers	Incorporation of α-Fe_2O_3 nanoparticles into PAN matrix	Electrospinning technique	pH: 5.5; Contact time: 120 min; Temperature: 25°C	81 mg/g	Not specified	High adsorption capacity; Magnetic separation; Recyclable	Limited information on regeneration; Specific to Pb(II)	Pseudo-second-order model	Langmuir models	**[57]**
10	Pb(II)	Aqueous solution	Chitosan-coated Fe/MOF-5 composite film	Coating chitosan on Fe/MOF-5 composite	Solution casting method	pH: 3; Contact time: 120 min; Temperature: 25°C	219.78 mg/g	Desorption efficiency : >94.8% after 10 cycles	High adsorption capacity; Recyclable; Eco-friendly	Reduced efficiency in the presence of Cl^- ions; Adsorption capacity decreases with increasing Cl^- concentration	Pseudo-second-order model ; Intra-particle diffusion model	Langmuir and Freundlich models	**[58]**

GENERAL CONCLUSION

General Conclusion

For the first time, progress and hotspots in the field adsorption of heavy metals from aqueous medium via chitosan adsorbent were explored by the bibliometric method. The data was retrieved from the Scopus® database covering the period in 2000-2025 years. The analysis collected 2267 scientific publications. The number of papers published on this research topic has increased dramatically in 2024, and China, the India, and Iran are the three countries whose authors are responsible for the largest numbers of published papers. Countries with large numbers of papers have close cooperation's. The top 10 authors we mention among them, Sundha, P.N. emerges as the preeminent author with the highest number of publications, indicating a significant interest and promotion of research in this field. Likewise, the writers Gomathi, T and Zheng, H, ranked second and third, respectively. The 10 core journals cover the fields of the most popular research areas are engineering science, chemistry, chemical engineering, Materials Science.

The bibliometric evaluation of the Scopus database on the use of chitosan and its derivatives for the adsorption of heavy metals from wastewater reveals a rapidly growing interest in this field, highlighting its relevance and importance in environmental remediation. Over recent years, there has been an increasing number of publications, reflecting the rising recognition of chitosan as an effective, eco-friendly, and cost-efficient material for wastewater treatment.

Key trends identified in the analysis include a growing focus on the modification of chitosan to enhance its adsorption capacity, stability, and selectivity for various heavy metals such as lead, cadmium, copper, and arsenic. Research also emphasizes the role of chitosan composites and cross-linked derivatives, which improve the adsorbent's performance and regeneration potential. Furthermore, advancements in understanding the underlying mechanisms of adsorption and the influence of environmental factors like pH, temperature, and contact time are evident.

Despite these advances, challenges remain regarding the scalability and practical implementation of chitosan-based adsorbents in industrial wastewater treatment. There is also a need for more studies on the regeneration and reuse of chitosan materials, as well as a comprehensive evaluation of their long-term environmental impact.

In conclusion, chitosan and its derivatives show great promise in the field of heavy metal removal from wastewater. The bibliometric analysis underscores the continued expansion of research, which will likely lead to further innovations in the development of more efficient and sustainable water treatment solutions. Future studies should focus on overcoming the remaining challenges, especially regarding large-scale applications and environmental sustainability

Annex

Analyze search results

Back to results

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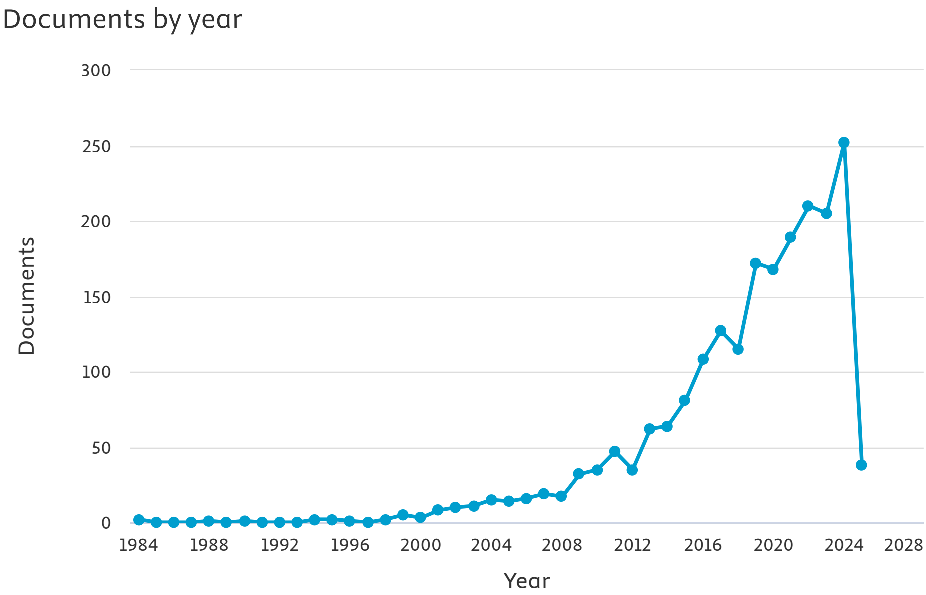
TITLE-ABS-KEY (adsorption AND chitosan AND heavy AND metals) AND (LIMIT-TO (EXACTKEYWORD , "Chitosan") OR LIMIT-TO (EXACTKEYWORD , "Adsorption") OR LIMIT-TO (EXACTKEYWORD , "Heavy Metals") OR LIMIT-TO (EXACTKEYWORD , "Metal Ions") OR LIMIT-TO (EXACTKEYWORD , "Heavy Metal"))

2,069 document results

Select year range to analyze: 1984 to 2025 Analyze

Year	Documents
2025	38
2024	252
2023	205
2022	210
2021	189
2020	168
2019	172
2018	115
2017	127



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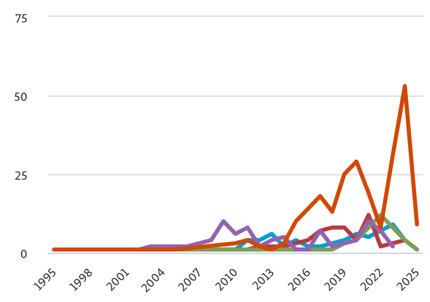
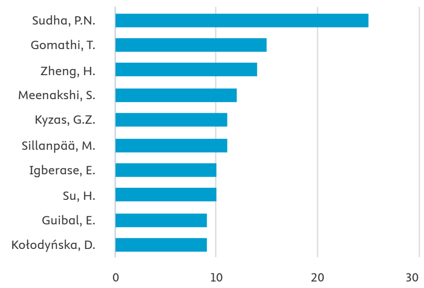
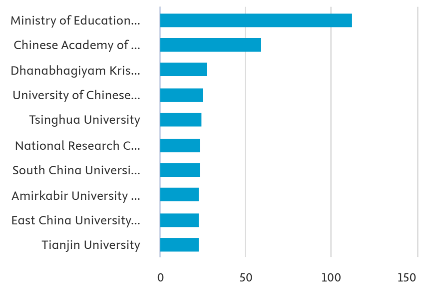
Documents per year by source



Documents by author



Documents by affiliation



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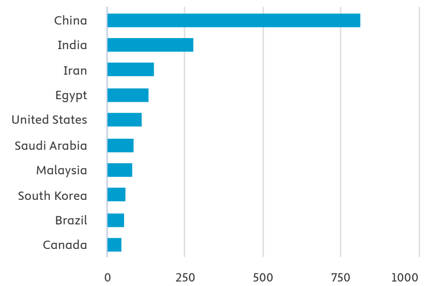

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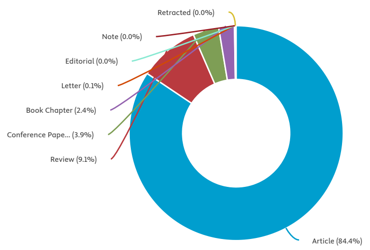
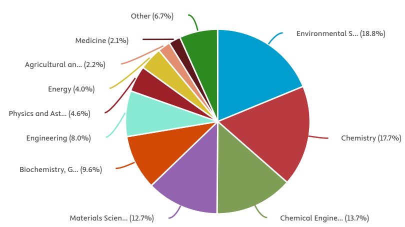
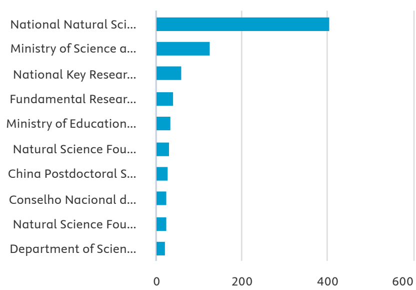


Documents by subject area



Documents by funding sponsor



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المذكرة: الكيتوزان ومشتقاته لامتصاص المعادن الثقيلة من مياه الصرف الصحي: التقييم الببليومتري لقاعدة بيانات سكوبس

اللقب: براهمي الاسم: عائشة المؤطر: نواصر ايمان

ملخص

في السنوات الأخيرة، استُخدم الكيتوزان ومشتقاته على نطاق واسع لحل المشكلات المتعلقة بتكنولوجيا الامتزاز لمعالجة المياه ومياه الصرف الصحي، وذلك بفضل وظائفه ومرونته وقابليته للتحلل البيولوجي وقوته النوعية العالية، وذلك من خلال استغلال بنيته الهرمية. في هذه الورقة البحثية، نقدم تحليلا ببليومتريا شام الا لفهم أفضل لتقييم السليلوز في أبحاث امتزاز المعادن الثقيلة القائمة على السليلوز (Chito&HM-ads) خلال الفترة من 2000 إلى 2025. اخترنا الأدبيات من المجموعة الأساسية لقاعدة بيانات سكوبس كهدف بحثي، واستخدمنا برنامج ببليومتريا للتصور لتحليل 2276 دراسة مُجمعة. تستخدم هذه الورقة البحثية عارض vos viewer و Cite Spaceو Bibliometrix لإجراء تحليل ببليومتري ورسم خرائط علمية. وقد وجدنا أن الأبحاث المتعلقة بامتصاص المعادن الثقيلة القائمة على الكيتوزان من مياه الصرف الصحي قد حظيت باهتمام واسع في مختلف دول العالم، وخاصة الدول النامية، حيث قدمت الصين مساهمات كبيرة.

Memory title: Chitosan and its derivatives for adsorption of heavy metals from wastewater: Bibliometric evaluation of Scopus database.

Name: Brahmi First name: Aicha Directed by: Nouacer Imane

Abstract:

In recent years, chitosan and its derivatives have been widely applied to solve issues related to adsorption technology for water and wastewater treatment because of their functionality, flexibility, biodegradability and high specific strength by exploiting hierarchical structure. In this paper, we provide a comprehensive bibliometric analysis to better understand the evaluation of cellulose in cellulose-based adsorption of heavy metals (Chito&HM-ads) research from 2000-2025. We selected literature from the core collection of the Scopus database as the research object and used visualization bibliometric software to analyze the 2276 collected studies. This paper uses VOS viewer, Cite Space, and Bibliometrix to perform bibliometric analysis and science mapping. We found that the research on the chitosan-based adsorption of heavy metals from wastewater has received widespread attention in various countries around the world, especially developing country, Chinese have made significant contributions.

Keywords: adsorption, chitosan, bibliometric analysis, heavy metals.

Titre du mémoire : Chitosane et ses dérivés pour l'adsorption des métaux lourds des eaux usées : évaluation bibliométrique de la base de données Scopus.

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Résumé:

Ces dernières années, le chitosane et ses dérivés ont été largement utilisés pour résoudre les problèmes liés aux technologies d'adsorption pour le traitement de l'eau et des eaux usées en raison de leur fonctionnalité, de leur flexibilité, de leur biodégradabilité et de leur résistance spécifique élevée grâce à l'exploitation de leur structure hiérarchique. Dans cet article, nous proposons une analyse bibliométrique complète afin de mieux comprendre l'évaluation de la cellulose dans les recherches sur l'adsorption des métaux lourds à base de cellulose (Chito&HM-ads) de 2000 à 2025. Nous avons sélectionné la littérature issue de la collection principale de la base de données Scopus comme objet de recherche et utilisé un logiciel de visualisation bibliométrique pour analyser les 2 276 études collectées. Cet article utilise VOS Viewer, Cite Space et Bibliometrix pour réaliser l'analyse bibliométrique et la cartographie scientifique. Nous avons constaté que la recherche sur l'adsorption des métaux lourds des eaux usées à base de chitosane a reçu une large attention dans divers pays du monde, en particulier dans les pays en développement, et que les Chinois ont apporté des contributions significatives.

Mots clés : adsorption, chitosane, analyse bibliométrique, métaux lourds.