Natural and synthetic hydrogels for dye removal

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Hidrogeles naturales y sintéticos para eliminar tintes.

Hidrogels naturals i sintètics per a l'eliminació de colorants

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SUMMARY

In recent years, dyes have been classified as recalcitrant contaminants in wastewater, exhibiting significant toxicological characteristics for flora, fauna, and humans. Various techniques are currently being studied for the remediation of water contaminated with dyes. Among the most relevant alternative technologies are bioadsorption, biocoagulation, the use of composite materials, advanced oxidation processes, etc. However, these methods have some disadvantages. Similarly, the use of hydrogels specifically designed for the treatment of contaminated water is a viable and effective alternative. This is due to their ability to adsorb large amounts of water, high porosity, and multiple active sites. This research describes dyes, their classification, toxicity, and ecotoxicity. Additionally, it presents some alternative treatments for water remediation, emphasizing the design of hydrogels based on synthetic and natural macromolecules. These hydrogels are proposed as promising materials for the removal of dyes from contaminated water. The aim of this research is to highlight synthetic and natural hydrogels as promising materials for the decontamination of water from dyes.

Keywords: Hydrogels, Colorants, Dyes, Natural and Synthetic.

RESUMEN

En los últimos años, los colorantes han sido clasificados como contaminantes recalcitrantes en aguas residuales, exhibiendo características toxicológicas significativas para la flora, la fauna y los humanos. Actualmente se están estudiando diversas técnicas para la remediación de aguas contaminadas con colorantes. Entre las tecnologías alternativas más relevantes se encuentran la bioadsorción, la biocoagulación, el uso de materiales compuestos, procesos de oxidación avanzados, etc. Sin embargo, estos métodos presentan algunas desventajas. Asimismo, el uso de hidrogeles diseñados específicamente para el tratamiento de aguas contaminadas es una alternativa viable y eficaz. Esto se debe a su capacidad para absorber grandes cantidades de agua, alta porosidad y múltiples sitios activos. Esta investigación describe los tintes, su clasificación, toxicidad y ecotoxicidad. Además, presenta algunos tratamientos alternativos para la remediación de aguas, destacando el diseño de hidrogeles a base de macromoléculas sintéticas y naturales. Estos hidrogeles se proponen como materiales prometedores para la eliminación de colorantes del agua contaminada. El objetivo de esta investigación es destacar los hidrogeles sintéticos y naturales como materiales prometedores para la descontaminación del agua de colorantes.

Palabras clave*:* Hidrogeles, Colorantes, Tintes, Naturales y Sintéticos.

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RESUM

En els últims anys, els colorants s'han classificat com a contaminants recalcitrants a les aigües residuals, que presenten característiques toxicològiques importants per a la flora, la fauna i els humans. Actualment s'estan estudiant diverses tècniques per a la remediació d'aigües contaminades amb colorants. Entre les tecnologies alternatives més rellevants es troben la bioadsorció, la biocoagulació, l'ús de materials compostos, processos avançats d'oxidació, etc. No obstant això, aquests mètodes presenten alguns inconvenients. De la mateixa manera, l'ús d'hidrogels dissenyats específicament per al tractament d'aigües contaminades és una alternativa viable i eficaç. Això es deu a la seva capacitat d'adsorbir grans quantitats d'aigua, alta porositat i múltiples llocs actius. Aquesta investigació descriu els colorants, la seva classificació, toxicitat i ecotoxicitat. A més, presenta alguns tractaments alternatius per a la remediació de l'aigua, destacant el disseny d'hidrogels basats en macromolècules sintètiques i naturals. Aquests hidrogels es proposen com a materials prometedors per a l'eliminació de colorants de l'aigua contaminada. L'objectiu d'aquesta investigació és destacar els hidrogels sintètics i naturals com a materials prometedors per a la descontaminació de l'aigua dels colorants.

Paraules clau*:* Hidrogels, Colorants, Colorants, Naturals i Sintètics.

INTRODUCTION

Water is a vital resource for all forms of life on the planet. However, its quality is threatened by the increasing presence of various contaminants such as bacteria [1], viruses, parasites [2], fertilizers, pesticides, pharmaceuticals, nitrates, phosphates, plastics, and even radioactive substances [3,4,5,6,7]. According to the World Health Organization (WHO), more than 1.8 billion people use contaminated drinking water, leading to diseases such as cholera, dysentery, typhoid fever, polio, and preventable deaths. Understanding the various sources of contamination and their consequences is crucial for implementing effective measures for sanitation, prevention, and control of these contaminants [8,9].

Humans require water for various daily activities and consumption. Approximately 1,386 million km^2 of water exists on the planet, with the majority (96.5 %) in oceans. Only 2.05 % of the total water is freshwater, and about 0.26 % of this freshwater is available in lakes and rivers for human consumption [10]. It is essential to be aware of the importance of protecting the limited water supply. In recent years, water scarcity has become a global issue, affecting around half of the world's population [11]. The problem of water availability is increasing due to contamination from various industrial and anthropogenic sources. These contaminants end up in lakes, rivers, streams, groundwater, and ultimately, the oceans. Water pollution, coupled with drought, poor sanitation, and population growth, has contributed to a freshwater crisis threatening the sources we depend on for drinking water and other fundamental needs [12].

Water contaminants encompass a range of compounds that can alter the quality and safety of water. These include inorganic, organic, microbiological, emerging, and solid materials [13]. Water pollution can originate from various sources, entering water directly or through legal and illegal discharges from industries such as pharmaceuticals, textiles, food, plastics, paints, water treatment plants, hospital waste, etc. Oil pipeline leaks and hydraulic fracturing (fracking) operations can also degrade water supplies. Wind, storms, and improper disposal of waste, especially plastic waste, can contribute to waste entering waterways [14,15].

Concept of Dyes

One of the primary sources of water pollution is dyes, which are used to add color to various substrates such as textiles, food, cosmetics, and plastics [16]. Dyes are complex, unsaturated organic chemicals with the ability to selectively absorb certain wavelengths of visible light and reflect others, resulting in the perception of color. The chemical structures of dyes contain a delocalized system with conjugated double bonds called chromophores and color-aiding groups called auxochromes. The chromophore exhibits electron resonance, allowing it to absorb light in the electromagnetic spectrum, while auxochromes control the wavelength and solubility of the compound [17]. The table 1 presents some chromophores and auxochromes groups. Chromophores can be conjugated systems (π bonds), aromatic groups, groups with non-bonding electrons (π electrons), or transition metal complexes [18]. Dyes have different forms and chemical structures, and their selection depends on the substrate to which coloration is desired, as well as desired properties such as solubility, stability, and resistance to fading [19]. Colorants include both dyestuffs and pigments. Dyestuffs are colored chemicals that have an affinity for the substrate where they are applied through various physicochemical interactions. On the other hand, pigments do not have affinity or any interaction with the substrate, so they are applied through binders. Both dyestuffs and pigments have a chromophore [17]. Until the 19th century, the primary source of dyes was natural resources. However, after the discovery of mauve aniline in 1856 by William Perkin, there was a global production boom of synthetic dyes. These synthetic dyes stood out for their low cost, variety of colors, and extensive production. Synthetic dyes are chemically synthesized and designed to provide bright and durable colors. They are applied through various methods such as immersion dyeing, pad dyeing, and printing methods [20,21].

Table 1. *Main chromophore and auxochrome groups.*

Chromophore groups	Auxochrome groups
Azo (-N=N-)	Amino (NH_2)
Carbonyl (C=O)	Alkoxyl (-OR)
Nitroso (-NO, -N-OH)	Dimethylamine ($-N(CH_3)_2$)
Nitro ($-NO_2$, =N-OH)	Electron donating groups
Sulfur (-C=S)	Methylamino ($-NHCH_3$)
Vinyl (-C=C-)	

Classification of Dyes

The classification of dyes is done in different ways depending on their physicochemical characteristics or their origin. One primary classification is based on their origin, where dyes are categorized into natural and synthetic. Natural dyes are obtained from natural sources such as plants, animals, minerals, and microorganisms [22]. Many plants contain natural pigments in their flowers, leaves, fruits, or roots. For example, red beets can be used to obtain an intense red dye [23], while curcumin is used to achieve a bright yellow shade [24]. Additionally, some natural dyes are derived from insects and minerals. Carmine acid or carmine (*Coccus cacti* L.) is an intense red dye extracted from cochineal insects, which feed on the sap of certain plants. It is widely used in the food industry to impart a reddish tone to various products such as sodas, juices, ice creams, and jams [24,25]. Malachite, a green mineral, has historically been used as a pigment. Other minerals used include hematite (red), zinc oxide (white), and titanium dioxide (white) [26]. Fig 1 presents the chemical structure of carminic acid, a chemical substance used as a natural dye extracted from cochineal.

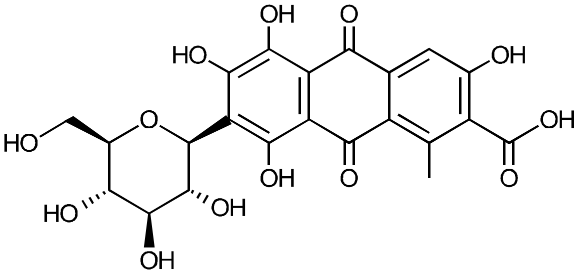

Fig 1 *Chemical structure of carminic acid dye.*

Synthetic Dyes

Synthetic dyes are used in various industries, including food, textiles, cosmetics, printing inks, and pharmaceuticals. They are popular due to their availability, ability to consistently reproduce colors, and relative cost-effectiveness compared to natural dyes. Azo dyes are a class of synthetic dyes containing the azo functional group (-N=N-). Some azo dyes, such as Tartrazine, Allura Red (E129), and Sunset Yellow (E110), have been associated with potential health effects, including allergies, asthma, and behavioral disorders. Moreover, some of these dyes can release toxic compounds when breaking down in the environment [27]. Phthalocyanines are another class of synthetic dyes widely used in the textile and printing ink industries, such as phthalocyanine blue or phthalocyanine green. Some of these dyes contain heavy metals like Copper, Zinc, or Nickel, which can be toxic and have negative effects on the environment if released during production or product use. Synthetic dyes, like Aniline and its derivatives, are used in the textile and ink industries. These compounds are toxic and can persist in the environment. Some have been reported as potential carcinogens with negative effects on human health, in Fig 2 The chemical structure of phthalocyanine blue is presented [28].

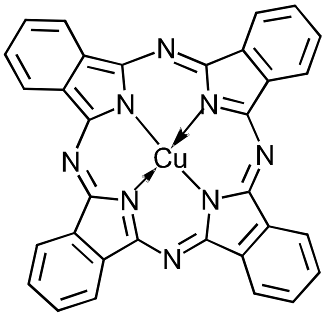

Fig 2 *Chemical structure of synthetic phthalocyanine blue dye.*

Another common classification of dyes is based on their solubility in Fig. 3. Dyes can be water-soluble or fat-soluble. Water-soluble dyes dissolve easily in water (anionic and cationic) and are commonly found as food colorants. In contrast, water-insoluble dyes (Azoic, dispersed dyes, sulfur dyes) do not dissolve in water, usually requiring organic solvents for solubilization. They are often used in textile dyeing. Liposoluble dyes available in the market include azoic dyes like Sudan I, Sudan II, Sudan III, and Sudan IV, classified by the International Agency for Research on Cancer (IARC) as class three carcinogens [29].

Finally, dyes can be classified according to their chemical structure into acid dyes and basic dyes. Acid dyes contain acidic groups (anionic) and are primarily used to dye silk, wool, and nylon fibers. An example is carmine acid. Basic dyes have basic groups (cationic) and are employed to dye acrylic fibers, with methylene blue being an example. In the textile industry, acid dyes are often preferred due to their high solubility in water and affinity with various textiles. It is important to note that some dyes may possess toxic properties or negative environmental impacts. Therefore, their use must be regulated and controlled to ensure the safety of individuals and minimize their environmental impact. Additionally, dyes persist in water and are challenging to biologically degrade, making them a subject of extensive research, Fig 3 presents a general classification of the dyes [30].

Toxicity and Ecotoxicity

Certain dyes are considered toxic due to their chemical properties or the presence of harmful compounds. Some dyes associated with potential toxic effects include Azo dyes. Some of these have been linked to negative health effects such as allergies, or even carcinogenicity. An example is Disperse Blue 373 and Disperse Violet 93 [31]. Reductive azoic dyes, used in textiles and plastics, can release aromatic amines like aniline, o-toluidine, and o-dianisidine, raising concerns about their potential carcinogenicity. Other azoic dyes causing worry include benzidines and p-phenylenediamine (PPD), capable of causing allergic reactions and dermatitis in some individuals, and widely used in hair dyes. Some types of dyes containing heavy metals like lead have been used as pigments in dyes and paints. However, lead is highly toxic and can cause neurological, renal, and

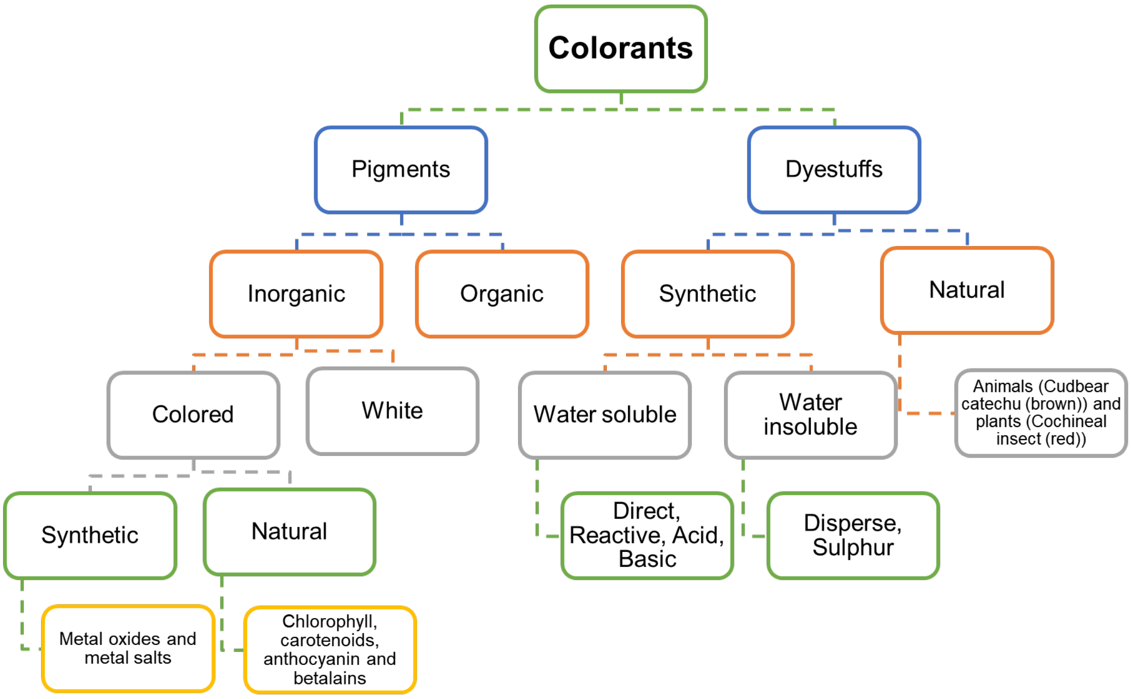

Fig 3 *Classification of dyes.*

other adverse health effects. Its use has been restricted in many countries due to its harmful effects [16].

The presence of such dyes in water bodies can lead to a variety of negative effects and disturbances in the ecological balance. These include alterations in dissolved oxygen reduction due to the blocking of sunlight, hindering some photochemical reactions. Moreover, dyes contribute to eutrophication by releasing components like nitrates (NO^{3-}), nitrites (NO^{2-}), and phosphates (PO_4^{3-}) into aquatic environments. These compounds can also bring about changes in aquatic conditions such as temperature, turbidity, and pH, negatively affecting flora and fauna. Due to these reasons, there has been an increased focus on the study of materials that can function as adsorbents for dyes [32].

Methods for the Treatment of Contaminated Water

The deterioration of water quality is primarily due to anthropogenic activities and inadequate sanitation. The chemical industry utilizes approximately one million tons of dyes each year, and an estimated 10 % of these are discharged into wastewater without any prior treatment [33]. The main industries contributing to dye pollution are (Fig 4), the dyeing industries (21 %), paper and pulp industries (10 %), tannery and paint industries (8 %), dye manufacturing industries (7 %), and the textile industry (54 %), accounting for over half of the total contamination. Wastewater includes all water from human or industrial activities. Due to significant pollution and the indiscriminate use of this

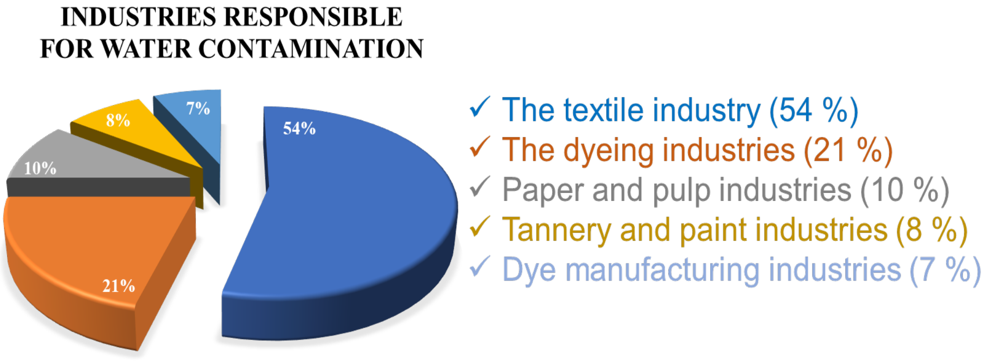

Fig 4 *Main industries responsible for water contamination by dyes.*

vital liquid, authorities demand that such water must be treated before being discharged or reused [34,35].

Wastewater from the chemical, pharmaceutical, and textile industries often contains substantial amounts of non-biodegradable organic compounds. The persistence of these compounds requires pretreatment before biological treatment. Wastewater characteristics such as pH, conductivity, or the presence of inhibitory compounds play a crucial role in contaminant biodegradation. The goal of any effluent treatment is to eliminate contaminants, ensuring that the effluent meets specifications for discharge set by competent authorities [36].

Industrial effluents generally contain different types of pollutants, which can be divided into two categories: inorganic pollutants and organic pollutants. Inorganic pollutants can be transformed into less hazardous substances through oxidation-reduction processes or separated from effluents through precipitation, sludge formation, or concentrated contaminant solutions. Meanwhile, organic compounds are typically treated through biological, chemical, or thermal oxidation, converting them into CO_2 and H_2O, and other oxidation-derived compounds, usually classified as biodegradable, persistent, or refractory [37].

Various physical and chemical processes are employed for the removal of contaminants from industrial effluents, including chemical coagulation, flocculation, simple sedimentation, activated sludge, biological filters, and reverse osmosis. The table 2 outlines the advantages and disadvantages of these processes. They are classified into primary, secondary, and tertiary methods. Primary methods involve physical operations for the removal of settleable and floating solids. Secondary treatment employs biological and chemical processes to eliminate organic material and some metals from the water. Tertiary processes use more sophisticated methodologies for the removal of contaminants that cannot be conventionally separated [38]. However, they exhibit several deficiencies, such as autotoxicity, durability, and, most notably, the manufacturing and operational cost of methods, which is a barrier to universal adoption. Some alternative methods aim to be less aggressive to the environment [39,40].

Alternative Treatments

Multiple approaches exist for treating water contaminated with various compounds, and the choice of the appropriate technique depends on the type of contaminant to be removed [41]. Currently, various alternative methodologies are employed for the sanitation of this vital liquid, focusing on environmentally friendly techniques that do not entail secondary pollution. Among these methodologies, the production of composite materials stands out. This involves combining adsorbent materials by incorporating different compounds or nanocompounds such as zeolites, biochar, and metallic nanoparticles [42,43]. Biocoagulation-flocculation is another alternative method, based on the use of natural coagulants extracted from plants. It is currently employed in Latin American and African countries to improve water quality. Compounds used include *Moringa oleifera* L. flour, guarango extract, and Arabic gum. Similarly, advanced oxidation processes are alternative methodologies for the sanitation of contaminated water. These processes are based on the production of reactive and oxidizing species that attack organic compounds until reaching mineralization, transforming them into H_2O and CO_2 [44]. Finally, another of the materials most used today for the removal of contaminants are hydrogels.

Hydrogels

Hydrogels are soft materials implemented in various sectors such as water treatment, food technology, and biomedicine [45]. They exhibit a hydrophilic nature due to the functional groups present in their polymeric chains (OH, COOH, SO_3H), giving them the ability to absorb and retain large amounts of water. Hydrogels are usually classified based on their origin as synthetic or natural [6,46], their ionic charge: neutral, cationic, and anionic, pore size, and swelling capacity. Moreover, they can be synthesized through various routes, including free radical synthesis, physical crosslinking, chemical crosslinking, irradiation, and graft polymerization. These materials can also take on different geometries such as spheres, rings, films, amorphous structures, and cylinders. A crucial aspect of these materials is their crosslinking, as it significantly impacts their porosity,

Table 2. *Advantages and disadvantages of dye removal methodologies.*

Method	Advantages	Disadvantages
Chemical coagulation	Reduction of precipitation time, elimination of fine particles.	Additive process, Complex dosage, High volume of hazardous waste.
Flocculation	Ability to remove suspended solids.	Increase waste levels.
Simple sedimentation	Economical process and easy operation.	Limited removal efficiency.
Activated muds	Useful in various types of wastewaters.	High operation, construction, and maintenance costs.
Biological filters	It does not require the addition of chemicals, it can be complemented with another technique, temperature resistance.	Long process, high maintenance, and operation costs, in addition to presenting low removal efficiencies.
Reverse osmosis	Elimination of bacteria and pathogens, elimination of impurities.	Removal of salts, high costs, maintenance, acidification of water.

swelling, elasticity, and mechanical strength. Literature reports the study of various parameters such as the type of crosslinking agent, crosslinking time, degree of crosslinking, and crosslinking conditions; however, an excessive increase in polymer chain crosslinking may reduce the efficiency of removing environmental contaminants [47].

Hydrogel Synthesis

The design of such materials is of great importance because, through design, various polymeric matrices and reinforcements can be proposed to provide specific qualities and overcome the disadvantages of other alternative methods for removing dyes from contaminated water [48].

Hydrogels can be synthesized from monomers, polymers, or a combination of both [49]. These polymers can be synthetic, such as polyacrylamide (PAM), poly (methyl methacrylate) (PMMA), poly (ethylene glycol) (PEG), poly (vinyl alcohol) (PVA) [50], etc., or natural based on polysaccharides or proteins like chitosan, hyaluronic acid, xanthan gum, gelatin, collagen, Arabic gum, guar gum, and alginate, in addition to monomers or polymers [51]. It is essential to use an initiator that triggers the formation of active species for polymerization. The addition of crosslinking agents is indispensable to achieve the crosslinked structure, carrying out either physical or chemical bonding depending on the required stability and the polymer used. Various bonding types may include hydrogen bonding, ionic and electrostatic interactions, as well as π-π* stacking. Chemical crosslinking methods involve in situ radical polymerization, Diels-Alder cycloaddition reactions, condensation reactions, and Michael addition. Different reinforcements can be added to obtain composite hydrogels and enhance the desired hydrogel properties, such as antimicrobial effects, biodegradation, or increasing the number of active functional groups within the hydrogels to enhance interaction with dye molecules, facilitating contaminant removal [52,53]. Various physicochemical and biological methods have been implemented for water sanitation, sometimes synergizing these methods for better results. Consequently, hydrogels have been widely used primarily based on the adsorption method [54].

Adsorption of Contaminants

Freshwater is the primary essential substance for human life; however, this resource is limited. Rapid population growth, agricultural activities, and anthropogenic actions have led to increasing water pollution by heavy metals (Cu^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Fe^{3+}, As^{5+}, and $Cr^{3/6+}$), dyes (methylene blue, indigo carmine, rhodamine, and sunset yellow, etc.), microplastics, and organic substances (pharmaceuticals, fertilizers, oil, and pesticides). As a result, there is a growing interest in the sanitation of this liquid, as many of these contaminants are toxic to the human body. Due to their swelling capacity, hydrogels are considered promising materials for water treatment [55].

Adsorption in hydrogels is based on the physical or chemical interaction between contaminants and the functional groups present in their structure. These functional groups may exhibit affinity for certain contaminants, favoring their selective adsorption on the hydrogel surface. The removal of contaminants can occur through π-π* interactions, n-π* interactions, surface adsorption, hydrogen bonding, van der Waals interactions, Yoshida hydrogen bond, electrostatic attraction, and ion exchange (Fig 5). The diffusion and deposition of the contaminant mainly depend on the

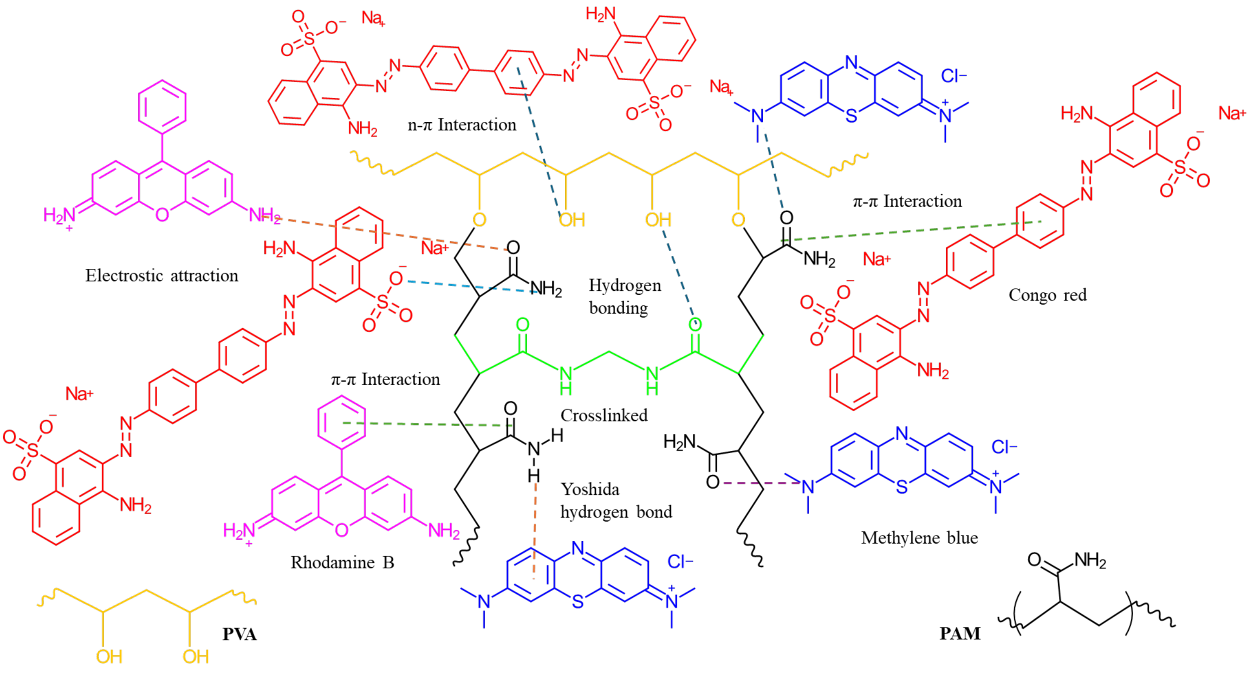

Fig 5 *Schematic illustration of Methylene blue, Rhodamine B and Congo red adsorption mechanism by the PAM/PVA hydrogel.*

pore size. In general, the more pores within the adsorbent, the greater the specific area and contaminant retention [56,57]. However, the interaction mechanism depends entirely on the type of contaminant to be removed. Nevertheless, the efficiency of adsorption is limited by several factors: temperature, pH, and the hydrogel's surface area [55].

Important factors for considering a hydrogel as a good adsorbent include high adsorption performance, reusability, easy operation, and cost-effectiveness. Hydrogels possess ideal characteristics such as simplicity, high selectivity, good mechanical strength, high performance, biocompatibility, and recyclability compared to other types of adsorbents (e.g., activated carbon, zeolites, biomass, micro and nanoparticles, inorganic minerals) [58].

Synthetic Hydrogels for Dye Removal

The search for new materials with improved properties is a relevant task for researchers today. The incorporation of various components into synthetic hydrogels (natural macromolecules, nanoparticles, biopolymers, metallic ions) has increased due to the enhanced properties they present. For instance, Maijan *et al.* studied the synthesis of a hydrogel based on polyacrylamide (PAM) with the integration of a biodegradable synthetic polymer such as poly (vinyl alcohol) (PVA) and the inclusion of SiO_2-functionalized ZnO nanoparticles. The synthesized hydrogel exhibited a swelling capacity of around 8000 %, and it removed 96 % of methylene blue within just 24 hours. The adsorption studies were fitted to a Langmuir isotherm and a pseudo-second-order model, showing a maximum adsorption capacity of 757 mg/g, making it a promising and cost-effective material that could eliminate secondary pollution from water treatment processes [59].

In another study, Abdul *et al.* in Saudi Arabia reported the preparation of a hydrogel composed of natural clay, poly (acrylic acid) (PAAac), and tannic acid (TA) for the adsorption of crystal violet dye (CV). The authors varied the TA concentration (2.5, 5, 7.5, and 10 %) and found that the pure hydrogel had a swelling capacity of 7061 %, and dynamic swelling decreased to less than 500 % once TA was added. Adsorption studies revealed that the hydrogel containing 5 % TA showed the highest dye removal capacity, with a maximum adsorption capacity of 444.5 mg/g and an efficiency of over 50 % after 5 cycles. Despite its low swelling capacity, the synthesized hydrogel exhibited better removal capacity compared to pure hydrogel, making it a promising material for cationic dye removal [60].

Within the realm of synthetic hydrogel synthesis, a notable study by Mota *et al.* in 2023 reported the creation of a self-healing hydrogel for the removal of organic contaminants from water. The hydrogel was synthesized based on poly (acrylic acid) (PAAac) and poly (vinyl alcohol) (PVA) with the incorporation of Fe^{3+} ions as a crosslinking agent. The designed hydrogel showed a significant improvement upon adding Fe^{3+}, exhibiting an efficiency of over 60 % in removing methylene blue even after 10 cycles. Additionally, the authors reported that the hydrogel's self-healing capability was attributed to electrostatic interactions formed by the addition of Fe^{3+}, achieving a healing efficiency of 88 % over an 8-hour period at room temperature. The self-healing capacity is a promising property for such materials, as some conventional hydrogels are very fragile, posing challenges to their implementation in various applications [61]. Although the study and synthesis of hydrogels based on synthetic polymers have decreased, the incorporation of biopolymers and/or natural macromolecules has increased as they enhance their applications and provide new properties such as antimicrobial effects and biodegradability.

Natural Hydrogels for Dye Removal

The use of hydrogels based on natural macromolecules for dye removal in water has recently increased. Currently, there is a focus on ensuring that materials used for water sanitation and quality improvement do not pose risks during and after their use. One alternative is the implementation of hydrogels based on natural macromolecules for the decontamination of this natural resource. In 2023, Jung *et al.* described the development of a pH-sensitive smart hydrogel based on carboxymethyl cellulose nanofibrils and chitin nanofibrils, using citric acid as a green crosslinking agent. This hydrogel demonstrated the ability to remove cationic and anionic dyes such as methylene blue and acid orange 7, achieving a dye removal percentage of 95.1 % after reuse for 5 cycles. Additionally, the hydrogel showed an excellent adsorption capacity of 372 mg/g for the anionic dye and 140.5 for the cationic dye, attributed to the hydrogel's selective capacity concerning pH [62].

In China, Ma *et al.* developed a promising hydrogel based on chitosan with the incorporation of natural rectorite nano-clay (REC) and poly (2-acrylamido-2-methyl-propane-sulfonic acid). The maximum adsorption capacity of methylene blue by the synthesized hydrogels was 1303.49 mg/g, representing 3 to 6 times higher adsorption than reported for activated carbon. The hydrogel with the highest REC concentration exhibited a dye removal rate of 99.6 % in various types of waters, including seawater, the Yangtze River water, Yellow River water, and tap water producing completely colorless water. The synthesized material was viable in a pH range of 2-11, making it a promising material for methylene blue removal in water [63].

In India, Zia *et al.* reported the development of a ternary hydrogel based on carboxymethyl cellulose, chitosan, and L-glutamic acid crosslinked with $ZnCl_2$ for the removal of methyl orange and Amido Black-10B dyes. They found that after immersing the hydrogel in a buffer solution for 72 hours, there was a break in the hydrogel matrix, resulting in the absence of adsorption for methyl orange dye. However, in a basic medium (pH 9.2), the hydrogel's adsorption behavior was efficient, achieving a dye removal efficiency of 67.82 % and a maximum adsorption capacity of 84.77 mg/g. They described that the incorporation of Zn provided more contact sites for better adsorption, improved stability, and increased mechanical strength, proposing this hydrogel as a promising material for large-scale effluent treatment plants [64].

The study of hydrogels based on natural macromolecules has gained significant momentum due to their swelling and adsorption capacities. However, it is crucial to continue research due to the low chemical resistance and mechanical properties of these materials. The optimal conditions for the removal of anionic and cationic dyes using hydrogels based on natural macromolecules are presented in Table 3.

Alginate/CA-sawdust/UiO-66-NH2, alginate of calcium with sawdust modificated with citric acid and Zr-based metal-organic framework; Alg/XG/AgNPs/Dex/Ca, alginate/xantham gum cross-linked with $CaCl_2$ and silver nanoparticles; Alg-Ch, alginate-chitosan; LN-NH-SA@3, aminated lignin and sodium alginate; $AgTiO_2$@AG-g-P(AM-co-AN), arabic gum grafted polyacrylamide-polyacrylonitrile and nanoparticles

Table 3 *Natural hydrogels for dye removal*

Hydrogel	Dye used	% Dye removal	q_e (mg/g)	pH	Ref.
FG-g-poly(AAm)	malachite green (MG)	99.1	585	pH 7	65
MMTNS composite hydrogel beads (MMTNS, AA, AM, PVA and SA)	methylene blue	90	564.97	pH 8 and 10.	66
2-amino terephthalic acid crosslinked chitosan-bentonite composites	Congo red, brilliant blue	(> 90 for CR and > 75 for BB)	4950 and 2053	pH 6	67
ChNFs/CMCNFs	Acid orange 7, and Methylene blue	95.1	372.0 for Acid orange and 140.5 for ethylene blue	The pH of the Acid orange was 2, and Methylene blue was 10	62
CS/XG.SiO_2	methyl orange	75	294	pH 5.30	68
XG-HNC	crystal violet (CV)	99	1566.97	pH 7	69
β-CD/MGO/PAA	methylene blue, and malachite green	99.1, and 95.0	2802.67 for the methylene blue and 1470.33 for malachite green	The pH of the methylene blue was 11 and malachite green was 10	70
Pectin hydrogel with hyperbranched polyethylene imine having graphene oxide	Crystal violet	--------	192	Acidic media	71
CS-g-GEL/BNC	Congo red	93.85	453.87	pH 9	72
CMCht/OCAA	Methylene blue	94	564.64	pH 8.0-12.0	73
LE–acrylic	Methylene blue	83	2445	pH 7	74
A/CS	Acid blue 93	90	1839	pH 7	75
CAG-NaAlg-cl-polyAA/Fe_3O_4	Auramine O, crystal violet and malachite green	99.26, 99.16 and 99.66	---------	pH 7	76
β-CD into AA, AM	methylene blue	94.9	122.27	pH 7	77
Alg-Ch	Rhodamine B, fluorescein	---------	328.9 and 80.13	Neutral pH	78
MCNCs/starch-g-(AMPS-co-AA)	Crystal violet and methylene blue	96.2 and 95.6	2500 and 1428.6	pH 6	79
Alg/XG/AgNPs/Dex/Ca	Methylene blue	98	---------	pH 10-12	80
Gltn/AAc	Methyl Orange and methylene blue	98.77 and 97.01	---------	The pH of the methylene orange was 4 and methylene blue was 9	81
LBG-cl-Poly(DMAAm)	Brilliant green	97.7	142.85	pH 5.8	82
Pn-g-poly(AAm)	malachite green	97	120.772	pH 7	83
CMC-CHT-GLU	Amido Black-10B	67.82	84.77	pH 9.2	64
TG-*cl*-GA/CC HNC	Methylene blue	80	2145	pH 11	84
AgTiO2@AG-g-P(AM-co-AN)	Methylene blue	---------	104.50±3.02	pH 8	85
Gellan gum/bacterial cellulose	Safranin and crystal violet	---------	17.57 and 13.49	pH 7	86
PAA/CS-PVAm composite	Methylene blue	97.74	596.14	pH 7	87
CS/CMC-PEG	Congo red, Methylene blue	86.8 and 96.62	1053.88 and 331.72	The pH of the Congo red was 4 and methylene blue was 11	88
LN-NH-SA@3	Methylene blue	87.64	388.81	pH 7	89
CANFe	Methylene blue	92.4	860	pH 8	90
SA@6DP	Crystal violet	99.873	83.565	---------	91
CSAA-HG_2	Methylene blue	99.88	19.92	pH 2	92
chitosan-g-poly (2-acrylamido-2-methyl-propane-sulfonic acid)	Methylene blue	99.6	1303.49	pH 2–11	63
Alginate/CA-sawdust/UiO-66-NH_2	Methylene blue	99	25.52	pH 6	93
LP/AA/DC/PVA-2	Methylene blue and Congo red	99.6 and 81.67	222.65 and 316.46	The pH of the methylene blue was 10 and Congo red was 4	94
CS/PHPA/GO	Methylene blue	99.26	476.19	pH 3-5	95
BP@SA/H	Rhodamine B	>80	745	pH 6	96
Cassava starch and poly(vinyl alcohol)	methylene blue	~99	1170	---------	97
Pectin-crosslinked gum ghatti	malachite green	98.65	658.1	pH 2-9	98
Polydopamine and 1–6-Hexanediol diglycidyl ether	Crystal violet	---------	107	pH 7	99

q_e: Maximum adsorption capacity

$AgTiO_2$; β-CD/MGO/PAA, b-cyclodextrin/magnetic graphene oxide functionalized polyacrylic acid; LBG-cl-Poly(DMAAm), bean gum and N, N-dimethyl acrylamide; BP@SA/H, biomass polymer into sodium alginate biopolymer; CMC-CHT-GLU, carboxymethyl cellulose with chitosan crosslinked $ZnCl_2$ and L-Glutamic acid; CMCht/OCAA, carboxymethyl chitosan and oxidized acetoacetate cellulose; BP50, cassava starch and poly(vinyl alcohol); ChNFs/CMCNFs, chitin nanofibrillar and carboxymethyl cellulose nanofibrils; CSAA-HG2, chitosan and aspartic acid; A/CS , chitosan crosslinking acrolein; CANFe, chitosan grafted acrylamide and N-vinylimidazole with Fe_3O_4 magnetic nanoparticles; CS/CMC-PEG, chitosan/carboxymethyl cellulose and polyethylene glycol; CS/PHPA/GO, chitosan/partially hydrolyzed polyacrylamide and graphene oxide nanosheets; CS/XG.SiO_2, chitosan/silica nanoparticles-modified xanthan gum; CS-g-GEL/BNC, chitosan-grafted-gelatin with bentonite nanoclay; CAR0.1, chitosan-grafted-poly (2-acrylamido-2-methyl-propane-sulfonicacid) and natural rectorite; Gltn/AAc, Copolymerization of acrylic acid and gelatin; SA@6DP, pits powder and sodium alginate; FG-g-poly(AAm), fenugreek gum-grafted-polyacrylamide; gellan gum/bacterial cellulose, gellan gum/bacterial cellulose; LE–acrylic acid hydrogels, lignin esters and acrylic acid; MMTNS composite hydrogel beads (MMTNS, AA, AM, PVA and SA), montmorillonite nanosheets with different amounts of MMTNS, acrylic acid, acrylamide, sodium alginate and polyvinyl alcohol; 2-amino terephthalic acid crosslinked CH-B composites, NH_2-terephthalic acid crosslinked-chitosan-bentonite; PG, pectin with hyperbranched polyethylene imine having graphene oxide; LP/AA/DC/PVA-2, pectin, acrylic acid, dimethyldiallyl ammonium chloride, and polyvinyl alcohol; PGH, pectin-crosslinked and gum ghatti; Pn-g-poly(AAm), pine gum and polyacrylamide; PAA/CS-PVAm composite, polyacrylic acid and chitosan with polyvinylamine; PPH, pullulan/polydopamine and 1–6-Hexanediol diglycidyl ether; MCNCs/starch-g-(AMPS-co-AA), starch grafted copolymers of 2-acrylamido-2methyl propane sulfonate and acrylic acid with magnetite-functionalized cellulose nanocrystals; TG-cl-GA/CC HNC, tragacanth gum crosslinked with glutaraldehyde and nanoparticles $CaCO_3$; XG-HNC, xanthan gum with 2-acrylamido-2-methyl-1-propanesulfonic acid and acrylic acid-graphene oxide functionalized with vinyltriethoxysilane; β-CD into AA, AM, β-cyclodextrin copolymerized with acrylamide and acrylic acid; CAG-NaAlg-cl-polyAA/Fe_3O_4, κ-carrageenan and sodium alginate crosslinked acrylic acid and nanoparticles Fe_3O_4.

CONCLUSIONS

The effective treatment of wastewater is one of the current primary objectives due to the scarcity of water resources. The study, development, and application of various highly effective, green, and economical technologies for wastewater treatment are essential. Various technologies, including biological processes, filtration, coagulation, advanced oxidation processes, and ion exchange, have been used for treating water with organic contaminants such as dyes. Among them, the adsorption process has emerged as one of the most viable methods for water sanitation. Various adsorbents have been studied and applied for the removal of contaminants in wastewater. However, the implementation of hydrogels in water has significantly increased in recent years. This technology offers several advantages, including low cost, high efficiency, reuse of the adsorbent, and operational ease. Research in this area is ongoing; however, it is crucial to design hydrogels based on materials that do not pose a risk to human health or the environment, with specific properties such as biodegradability and non-toxicity. This work highlighted some of the key studies conducted in recent years involving natural macromolecules and biopolymers for the synthesis of hydrogels with applications in dye removal from water.

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