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Metal nanostructures in polymeric matrices for optical detection and removal of heavy metal ions, pesticides and dyes from water

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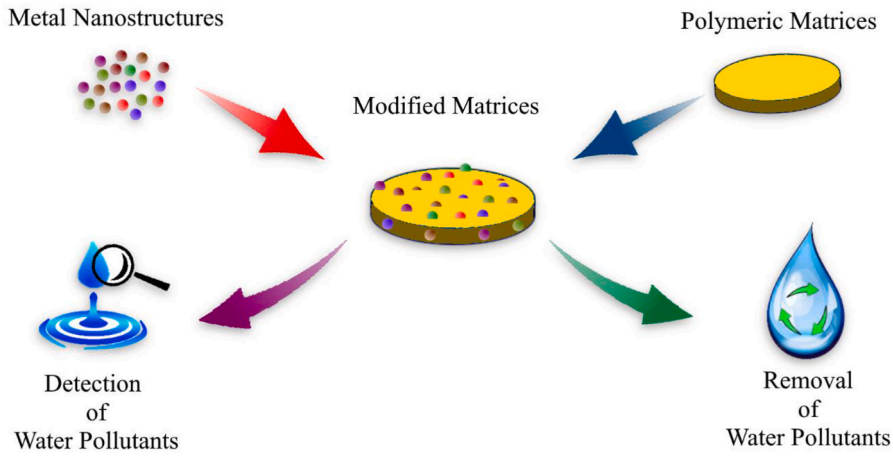
HIGHLIGHTS

- Heavy metals, dyes and pesticides are among the main water pollutants.
- Nanomaterials can work in polymeric matrices for pollutants sensing and remediation.
- Noble nanomaterials show excellent sensing properties towards water contaminants.
- Mixed matrix membranes display unique properties in water purification.
- Metal nanomaterials dramatically improve the properties of membranes and hydrogels.

GRAPHICAL ABSTRACT



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ABSTRACT

Water pollutants such as heavy metal ions, pesticides, and dyes pose a worldwide issue. Their presence in water resources interferes with the normal growth mechanisms of living beings and causes long or short-term diseases. For this reason, research continuously tends to develop innovative, selective, and efficient processes or technologies to detect and remove pollutants from water. This review provides an up-to-date overview on metal nanoparticles loaded in polymeric matrices, such as hydrogels and membranes, and employed as optical sensors and as removing materials for water pollutants. The synthetic pathways of nanomaterials loading into polymeric matrices have been analyzed, particularly focusing on noble metal nanoparticles, noble metal nanoclusters, and metal oxide nanoparticles. Moreover, the sensing properties of modified matrices towards water pollutants have been discussed in addition to the interaction mechanisms between the sensors and the toxic compounds. The last part of the review has been devoted to illustrating the separation mechanism and removal performance of

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membranes loaded with nanomaterials in the treatment and purification of water streams from different contaminants (heavy metals, dyes and pesticides).

1. Introduction

Water is an essential resource for all living organisms. Prudent management and prevention are the best actions for avoiding the contamination of water sources, but poor management can undermine the quality of this essential resource. The water pollution pathways are commonly split in two: natural and anthropogenic. Geological compositions or natural events such as volcanic eruptions or geothermal fluids, which can change the chemical composition of water bodies, are considered as natural sources of water pollutants. Anthropogenic pollution is attributed to human activities such as the widespread use of pesticides and manures on farms, the dumping without or ineffective treatments of industrial wastes directly into the rivers or into the sea (Ghangrekar and Chatterjee, 2018; Madhav et al., 2020; Qasem et al., 2021).

Water contaminants can be discriminated according to their chemical nature such as inorganic pollutants (nitrate, heavy metal ions or halogens) (Abascal et al., 2022; Bijay-Singh and Craswell, 2021; Garba et al., 2020; Hasanpour and Hatami, 2020; Zamora-Ledezma et al., 2021; Zhang and Parker, 2018), organic pollutants (pesticides, dyes or solvents) (Farhan Hanafi and Sapawe, 2020; Garba et al., 2021; Lu and Astruc, 2020; Syafrudin et al., 2021; Xiao et al., 2020), microplastics (Jiménez-Skrzypek et al., 2024; Reimonn et al., 2019), pathogens (Ashbolt, 2015; Tallon et al., 2005), medicines and personal care products (Kallenborn et al., 2018; Kosma et al., 2010). This review focuses on the sensing and removal of heavy metal ions, pesticides, and dyes using polymeric matrices (hydrogels and membranes).

Contamination of water by inorganic heavy metals represents an urgent environmental issue, with serious repercussions on the environment (such as animals, plants, and climate) and human health. The increase of human population along with the rapid development of industrialization have led, during the last decades, to a significant release of heavy metals in wastewater. Surface water seepage and runoff can easily contaminate groundwater with heavy metals posing serious risks for the entire ecosystem and living organisms. Arsenic (As), cadmium (Cd), nickel (Ni), mercury (Hg), chromium (Cr), zinc (Zn), and lead (Pb) are the most common heavy metals encountered in water bodies and their exposure and accumulation in living organisms is responsible of a series of health problems such as neurological diseases, cancer, birth malformations and metabolic abnormalities (Jaishankar et al., 2014; Rehman et al., 2018).

Along with the contamination by inorganic heavy metals, the water contamination by organic pollutants also represents one of the biggest environmental issues that humanity has to cope with. In this framework, the industrial dyes are among the largest group of organic contaminants responsible of water pollution (Farhan Hanafi and Sapawe, 2020). While dyes are used for conferring color in cosmetics, textiles, food, and medicine, part of them can be often released in effluent streams that are discharged in rivers, lakes, and drainage (Maheshwari et al., 2021). Most of the dyes are scarcely biodegradable and their presence in water can pose serious risks to the photosynthetic processes of aquatic life (Galiano et al., 2018a). Moreover, pesticides represent some of the most persistent and recalcitrant water pollutants. The continuous increase in the production of food, in fact, has led to a consistent boost in the production and consumption of pesticides, which are used as chemical agents to prevent and kill pests. Based on the family they belong to and their source, they can be classified in organophosphates, organochlorines, carbamates, and pyrethroids as the most representatives (Rana et al., 2021). It is estimated that just a small fraction of the pesticides employed (about 0.1 %) has a real effect on the target organisms, while the rest is released into the environment, and in particular in water bodies (Bapat et al., 2022). The long exposure of human body to pesticides is responsible of a series of health problems such as cancer, pulmonary and hematological diseases (Bhandari et al., 2020). Therefore, the monitoring and removal of pesticides from water and wastewater is of crucial importance and they represent the two main aspects that have been discussed in this review.

Water monitoring is the first step to understand whether purification of that particular environment is necessary or not. The monitoring phases can be summarized as sampling, sample treatment, and analyte measurement. Several days can pass between the sampling and the quantification of the pollutant, consequently a very rapid approach is highly desirable. For the detection of heavy metal ions, well-established techniques such as atomic absorption spectroscopy, atomic emission spectroscopy or mass spectrometry are exploited to quantify their presence in the water samples (Chen et al., 2021; Hieftje, 2000; Lagalante, 2004). Even in the case of organic pollutants (dyes or pesticides), analytical methods such as gas chromatography and liquid chromatography coupled to the mass spectrometry are employed to determine the concentration of water pollutants (Arabi et al., 2020; Jamil et al., 2020; Qi et al., 2021; Wang et al., 2020; Yadeghari and Farajzadeh, 2021). However, these techniques need an expensive instrumentation, high maintenance costs, pre-treatments of samples, and highly specialized staff. For these reasons, fast and cheap detectors are in high demand. Among non-conventional instrumentation, optical sensors have different advantages such as ease of use, cheap, and if necessary, they can be used for measurements directly on site. Nanomaterials such as quantum dots, noble metal nanostructures, graphene oxide quantum dots and photonic crystals show interesting optical features, which can be modified by the presence of a specific contaminant (Bertelà et al., 2021; Burratti et al., 2018; Gontrani et al., 2021; Kou et al., 2021; M. Liu et al., 2021b; Schiesaro et al., 2020; Velusamy et al., 2021). Among the optical properties, absorption and emission are the most used in the detection of pollutants as will be discussed in the next sections.

Therefore, it is necessary to look for alternatives to investigate an innovative, low-cost and effective method to deal with water contamination. The removal of heavy metals from water can occur through several technologies, which are nowadays available and including oxidation, coagulation flocculation, adsorption, ion exchange and membrane processes (Dabrowski et al., 2004; Lebron et al., 2021; Sadri Moghaddam et al., 2010; Vo et al., 2020; Zou et al., 2014).

In recent decades, a great deal of attention has been paid to techniques based on nanomaterials. Among them, metallic nanoparticles are widely studied as potential nanosorbents due to their physicochemical properties and their versatile, simple and cheap synthesis pathway (Calderón-Jiménez et al., 2017; Sumesh et al., 2011; Thakkar et al., 2010). Interesting features include the possibility of functionalizing their surface with specific capping agents, a factor that plays a key role in defining their physicochemical behavior (hydrophilicity, aggregation, stability) (Hoang et al., 2022; Sharma et al., 2018; Verkhovskii et al., 2019). In addition, the presence of specific functional groups can facilitate interaction with other species, including pollutants, determining their selectivity and affinity towards the target pollutant (Bertelà et al., 2023). Different metal nanoparticles have been applied as nanoadsorbents to successfully treat water with high contaminations of heavy metals (Mensah et al., 2021). Examples of nanoadsorbents system are given by functionalized silver nanoparticles, in which the surface of nanoparticles (NPs) is functionalized with different capping agents (citrate, L-cysteine, glutathione, 3-MPS) in order to stabilize the NPs structure and giving a specific activity, at the same time (Bellingeri et al., 2024; Bertelà et al., 2021; Schiesaro et al., 2020). One of the biggest challenges related to the use of NPs in water remediation is their possible

diffusion into water and their recovery from the wastewater. In this regard, as a possible solution to the problem, several systems have been proposed that involve the incorporation of NPs into matrices or superstructures (such as membranes) that can host them in their structure without altering their chelating activity. These hybrid systems made of membranes and NPs are attracting great interest as they appear to be able to remove toxic metal ions even in low concentrations from contaminated water (Ahmad et al., 2018). In literature, several examples of novel nanomaterials embedded in different host materials were successfully employed to remove the metal ions from water (Ghaemi et al., 2015; Gholami et al., 2014; Riva et al., 2024). Among them, membrane-based operations present a series of important advantages over the other technologies including high removal efficiency, easy operation and scalability and low environmental impact, which make them the preferred choice in several treatment methods for heavy metals removal (Chen et al., 2011; Xiang et al., 2022). Membranes, in fact, are able to retain contaminants because of their pore size dimension (size exclusion) and charge (Donnan repulsion mechanism). Moreover, membranes can integrate into the polymeric matrix specific nanomaterials able to impart to the membrane specific and unique properties (Galiano et al., 2021; Nadig et al., 2021) such as the exclusive recognition and sequestration of heavy metals from water (Moradi et al., 2020). Even in the case of organic pollutants (dyes and pesticides), membrane filtration is considered one of the most effective technique (Deowan et al., 2016). Membranes can remove dyes/pesticides from wastewater by physical filtration and chemical adsorption. The production of polymeric membranes with significant adsorption properties, conferred by the addition of specific adsorbent nanomaterials, is one the most studied strategies for the removal of organic contaminants from water. So far, different nanomaterials have been proposed and embedded into polymeric membranes such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), graphene oxide, MXenes, zeolite and carbon nanotubes (CNTs) (Abdi et al., 2018; Deng et al., 2019; Efome et al., 2018; Gatou et al., 2021; Gu et al., 2018; Long et al., 2023; Shukla et al., 2018; Sulaiman et al., 2020; Wang et al., 2021; Zhang et al., 2021). Their use as fillers can have the double function of tuning the membrane structure and imparting substantial adsorption properties towards organic contaminants (Mokhtari et al., 2022).

This work aims to critically review the recent literature on the use of polymeric matrices (hydrogels and membranes) loaded with metal nanostructures for the optical detection and removal of different types of pollutants from water.

2. Synthesis of hydrogels and membranes

To date, polymers, thanks to their easy processability, high availability and low cost, are the most employed materials for the production of membranes used in water treatment processes. The physical-chemical properties of a membrane, which mainly depend on the material employed and, on the preparation technique, are crucial in determining its performance abilities. The material influences, for instance, the hydrophilicity, the surface charge, and the thermal/mechanical stability of the membrane (Moradi et al., 2020), while the preparation method plays a significant role in affecting the morphology, porosity, and pore size (Tomietto et al., 2022). A current trend in the development of membranes is the integration into the polymeric matrix, of specific nanomaterials able to impart specific and unique properties (Bagnato et al., 2021; Galiano et al., 2021; Msahel et al., 2021; Nadig et al., 2021). The so-called mixed matrix membranes (MMMs), in fact, merge the benefits deriving from polymeric materials, such as low cost, high availability and flexibility with the advantages stemming from inorganic nanomaterials, for example improved selectivity and permeability (Msahel et al., 2021).

However, the preparation of totally defect-free membranes including nanomaterials is still challenging. A poor compatibility, in fact, between the polymer matrix and the nanomaterials can lead to a series of interface defects and inhomogeneities, which can affect the membrane properties and performance. Main defects that can occur in MMMs can be related to: i) the formation of interface voids caused by the detachment of nanoparticles from the polymer matrix; ii) the rigidification of the polymer chains in the proximity of nanoparticles; iii) the obstruction of membrane pores by nanoparticles (Basu et al., 2010; Nik et al., 2012). In order to mitigate these issues, particles with nano-size dimensions are generally preferred since they can be better dispersed into the polymer matrix providing, at the same time, an higher polymer/particle interface area (Perez et al., 2009; Zhang et al., 2012). Surface modification and functionalization approaches are also very useful methods generally used for improving the dispersion of nanomaterials and the particle/polymer interaction and adhesion (Figoli et al., 2022). The preparation of MMMs generally requires the preliminary dispersion of the selected nanomaterial in a suitable solvent followed by the addition of the polymer and possible additives. The membranes are then prepared by phase inversion process, which represents the most employed technique in the preparation of polymeric membranes. The dope solution is cast on a suitable support, for instance a glass plate, and the phase inversion process is induced by adopting different methods: evaporation of the solvent, precipitation in a coagulation bath, temperature variation or precipitation in a saturated vapor environment. According to dope solution composition and preparation conditions, MMMs with different properties and morphologies can be, thus, obtained.

Hydrogels are another class of materials employed for environmental purposes. They have, in fact, a hydrophilic behavior that allows the absorption of high volumes of water, maintaining their structural properties unchanged (Richbourg and Peppas, 2020). Their physicochemical properties are tunable: it's possible to design different hydrogel systems by selecting a particular material composition or concentration and varying the cross-linking method (Cao et al., 2021). Furthermore, in the field of nanotechnological development, hydrogels have been increasingly combined with other materials to form hybrid systems and, in this perspective, hydrogels embedded with nanoparticles gained much attention because the hybrid materials combine the suitable properties of both partners.

Wang and collaborators reported the synthesis of a highly recyclable catalyst Ag-based agarose (HRC-Ag/Agar) hydrogel produced via the *in-situ* reduction of Ag ions. First, agarose powder was dissolved in deionized water and heated to form the agarose hydrosol. Then, the aqueous solution of $AgNO_3$ was added to the agarose hydrosol to form the agarose-Ag^+ hydrosol. After a few minutes of incubation, an aqueous solution of KBH_4 was added to the Ag/Ag + hydrosol. Subsequently, the final solution was allowed to cool to room temperature to form the HRC-Ag/Agar hydrogel (J. Wang et al., 2023b).

In another work (Dutra et al., 2020), PAAm (polyacrylamide)/starch hydrogel discs were synthesized by free-radical polymerization in an aqueous environment. Firstly, the starch was gelatinized in deionized water at 80 °C and then allowed to cool to 30 °C. Next, aqueous solutions of CAN (ammonium cerium nitrate) and AAm (Acrylamide) + MBA (N, N-methylenebisacrylamide) were added and after a few minutes of magnetic stirring, the system was left to stand for 24 h and then purified by immersion in deionized water. Finally, the hydrogel was dried under vacuum, rehydrated and then placed in contact with a solution of $AgNO_3$ for 48 h to promote the penetration of silver ions into the hydrogel. Subsequently, the hydrogel was placed in a flask containing the reducing agent $NaBH_4$ in order to reduce the Ag^+ ions to silver nanoparticles (Ag^0) and after 6 h the AgPNs-PAAm/starch hydrogel was obtained. Fig. 1 depicts the representation of the synthesis of PAAm/starch hydrogels with and without AgNPs.

Vimala and co-workers reported the preparation of semi-interpenetrating (INP) hydrogel–silver nanocomposites based on cross-linked poly (acrylamide) (PAM). They firstly prepared the pristine hydrogel mixing PAM, different carbohydrates, a cross-linker (MBA) and initiating system. After its synthesis, the semi-IPN hydrogels were transferred into a beaker containing $AgNO_3$ aqueous solutions, allowed

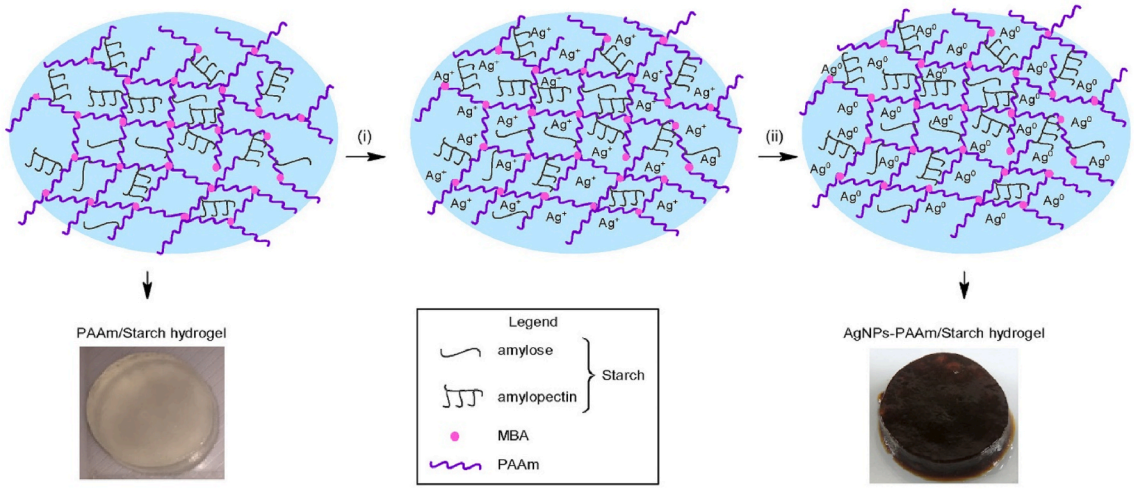

Fig. 1. Schematic representation of the AgNPs-PAAm/starch hydrogel synthesis. Adapted with the permission of Elsevier from (Dutra et al., 2020).

for 1 day with the aim to produce the silver salt loaded semi-IPN hydrogels. Then these systems were transferred into a beaker containing $NaBH_4$ aqueous solution and allowed for 2 h to reduce the silver ions into silver nanoparticles. Fig. 2 shows the scheme of above-mentioned synthesis (Vimala et al., 2009).

Zhang and co-workers described the synthesis of a stimuli-responsive hydrogel (SRhG). Specifically, they synthesized a SRhG composed of agarose embedded with polydopamine-coated gold nanoparticles (Au@PDA NPs), which is reactive to Ag^{+}. They first synthesized the AuNPs via a one-pot protocol using ascorbic acid (AA) as a reducer and cetyltrimethylammonium bromide (CTAB) as a protective agent. After purification of the AuNPs, they added the dopamine (DA) solution to the nanoparticles solution and sonicated the mixture of AuNPs and DA to achieve polymerization of DA on the surface of the AuNPs (Au@PDA NPs). Then, by microwave-assisted heating of the Au@PDA NPs mixture solutions containing agarose, they fabricated the Au@PDA NPs hydrogel (Zhang et al., 2018).

Yu and colleagues worked on the synthesis of polydopamine (PDA)-capped bimetallic AuPt hydrogels (AuPt-PDA hydrogels) as a scaffold for the immobilization of acetylcholinesterase (AChE) and the construction of sensors for the detection of organophosphorus compounds. AuPt-PDA hydrogels were synthesized by adding a $NaBH_4$ solution to the mixture solution containing $HAuCl_4$, H_2PtCl_6 and dopamine. After keeping the solution still for 2 h at 60 °C, the black hydrogels precipitated. The hydrogels thus prepared were washed and then dissolved in ultrapure water by sonication. Then the AChE solution was mixed with the AuPt-PDA hydrogel solution and then sonicated to obtain the final AChE/hydrogel system (Wu et al., 2019).

In their work, Xu and co-workers reported the preparation of nanofibrous membranes containing a thermal plastic elastomer ester (TPEE) nanofibers core and an iron oxides (IOs) shell and investigated their potential application in the removal of Cr(VI) from water. The hybrid system was obtained by combining the electrospinning method with hydrothermal techniques. The synthesis process first required the production of the TPEE/iron alkoxide (IA) composite nanofibrous membrane by electrospinning, using the mix of the TPPE solution and the IA solution as reactant and then the in-situ growth of IOs on TPEE nanofibers (Xu et al., 2012). In another work (Li et al., 2013), polyamide 6 and iron oxide nanocomposites (PA6@FexOy) nanofibrous membranes were prepared by electrospinning and hydrothermal method. Firstly, the PA6 polymer was synthesized by electrospinning. Then a solution of $FeCl_2$–$4H_2O$, glycol (EG) and NH_3–H_2O was prepared to form iron alkoxide (IA). Then, the IA solutions and PA6 nanofibrous membranes were put in contact with the aim of promoting the adhesion of IA to PA6 fibers and forming PA6···IA nanofibrous membranes. The obtained PA6···IA nanofibrous membranes were then placed in a beaker

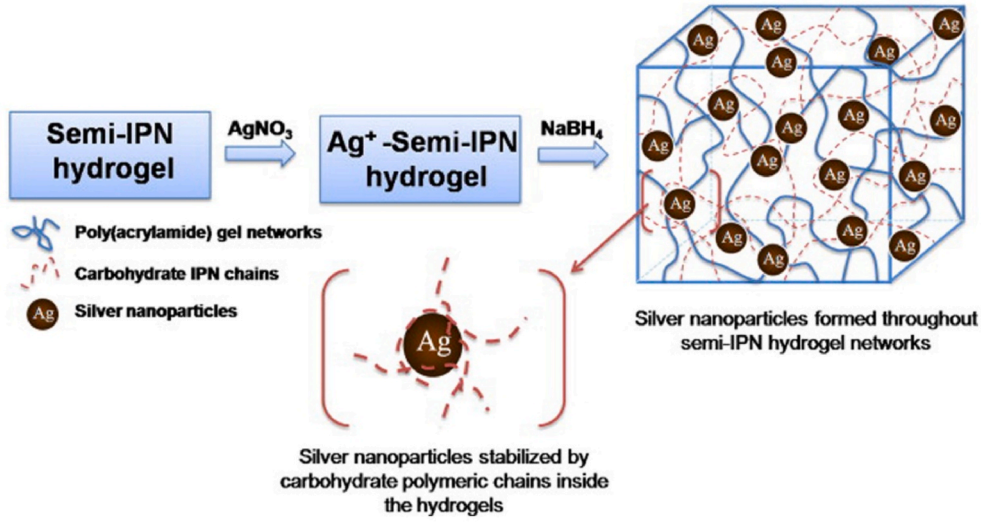

Fig. 2. Representation of the synthesis process of semi-INP hydrogel silver nanocomposite. Reprinted with the permission of Elsevier from (Vimala et al., 2009).

containing deionized water and subjected to hydrothermal reaction to determine the formation of (FexOy) on the fiber template. After the reaction, the composite PA6@FexOy nanofibrous membrane was removed from the water and dried. A schematic diagram of the synthesis of PA6@FexOy is shown in Fig. 3.

Summary of the different types of synthesis of the hybrid systems proposed above, is reported in Table 1.

3. Optical sensors for water pollutants in hydrogels/membranes

In this paragraph, the sensing capabilities of hydrogels/polymeric membranes containing noble metal nanomaterials is discussed. The combination between nanomaterial and hydrogels or polymeric membranes opens up new fields of application. In general, since noble metal nanomaterials are synthesized in aqueous solutions, their employment in real environmental monitoring is difficult and, therefore, their use is often restricted to laboratory activities. Combining the mechanical advantages of polymers as host materials with the optical properties of the nanomaterials, it is possible to obtain portable sensors.

The scientific literature relating to this type of application is in its infancy; in fact, the number of manuscripts dealing with this type of topic is relatively low if compared to the multitude of literature on noble metal nanomaterials in the state of colloidal solution. In the last decade, the number of published peer-reviewed papers about noble metal nanomaterials grew from 13 665 in 2013–22 033 in 2022, highlighting the great interest of the scientific community on this topic. A completely different scenario has been observed by repeating the research of metal nanomaterials in polymeric matrices (hydrogels/membranes). In this case, in fact, the total published articles grew from 587 in 2013 to 1572 in 2022. The number of publications, year by year, was obtained through the website "Web of Science" and these data were used to plot Fig. 4. Only the 4–7 % of the manuscripts deals with the incorporation of noble nanomaterials into polymeric matrices. Finally, a very small part of this 4–7 % refers to the optical sensing of nanomaterials for water pollutants, such as heavy metal ions and pesticides, indicating that this scientific topic has to be explored yet and there is a large margin of improvement. Fig. 4 shows the number peer-reviewed articles sorted for year for the different research keywords.

Among the causes in the paltry scientific production inherent to this topic, we can include:

- The difficulty during the synthesis of materials, namely, the incompatibility between the metal nanomaterials and the host material: this can occur in synthesis techniques in which the nanoparticles/nanoclusters are synthesized first and then inserted into the matrix;
- The release of nanomaterials from the polymeric matrix: if the physical/chemical interactions between the nanomaterial and the polymer are weak, the noble nanomaterials can be released.
- The optical properties can be drastically modified or even lost, by compromising sensor capabilities.
- The homogeneity of nanomaterials dispersion is another issue, in fact, confinement/aggregation of nanomaterials can occur and consequently the non-homogeneity of the system causes differences in the capabilities/properties of the system itself.

3.1. Sensors based on optical absorption

Sensors based on optical absorption exploit the absorbance of the noble nanomaterials and the change of this feature in presence of a specific pollutant. Most of the literature focused on the sensing of heavy metal ions especially mercury cations, Hg(II) (Chen et al., 2017; Jeevika and Shankaran, 2016; Jia et al., 2018; Khalid et al., 2022; Ko et al., 2021; Rithesh Raj et al., 2016; Zhang et al., 2022).

In the work of Martínez-Hernández and co-workers a very interesting optical sensor based on both silver and gold NPs, exploiting the localized surface plasmon resonance (LSPR) phenomenon, was developed. First AuNPs and AgNPs were separately synthesized and stabilized with poly (acrylic acid) (PAA) and poly (allylamine hydrochloride) (PAH), respectively. Subsequently, layer-by-layer deposition, alternating the AuNPs and AgNPs was carried out onto optical fiber core. The two noble metal nanomaterials showed well-located absorption peaks associated to their LSPR in the visible region at 420 nm (AgNPs) and 530 nm (AuNPs) and their bands were considered as references for the detection of Hg(II) ions. The measurements set-up consisted in a light source coupled with the optical fiber where in a section AgNPs and AuNPs were deposited. The light coming from the source passed through the fiber and interacted with the AgNPs/AuNPs layers and the modified light signal arrived to a compact spectrophotometer. For the detecting of Hg (II) ions, the modified fiber was immersed in different concentrations of mercury, obtaining a limit of detection (LOD) of 0.1 mg/L. The authors

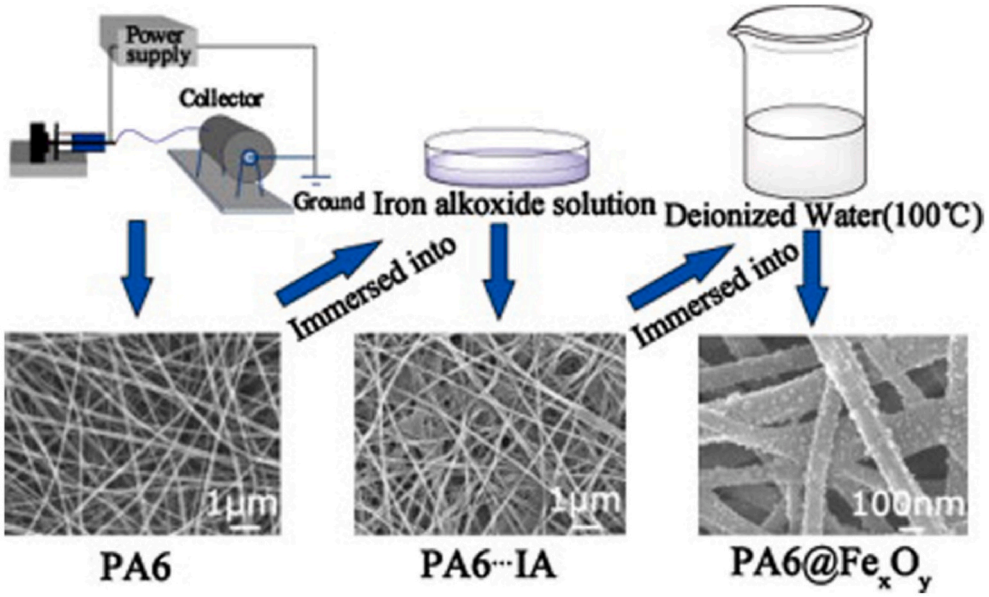

Fig. 3. Schematic representation of the PA6@FexOy composite synthesis. Reprinted with the permission of Elsevier from (Li et al., 2013; Li et al., 2013).

Table 1
Summary of the different types of synthesis of the hybrid systems.

Hybrid system	Synthesis steps	Target	Reference
Au@PDA NPs agarose hydrogel	1. One-pot synthesis of AuNPs; 2. Sonication of the mixture of AuNPs and DA solutions to induce the polymerization of DA on the AuNPs surfaces; 3. microwave-assisted heating of the mixture of Au@PDA NPs and agarose solution to produce the Au@PDA NPs agarose hydrogel.	Silver ions	Zhang et al. (2018)
AuPt-PDA hydrogel	1. One step synthesis of the AuPt-PDA hydrogel: addition of the NaBH4 solution to the mixture containing the $HAuCl_4$, H_2PtCl_6 and dopamine solutions, then heating at 60 °C.	Organophosphorus Pesticide	Wu et al. (2019)
HRC-Ag/Agar hydrogel	1. Sythesys of agarose hydrosol; 2. addition of $AgNO_3$ solution; 3. addition of KBH_4 as a reducing agent for in situ reduction of Ag ions and AgNPs formation.	Aromatic organic pollutants	(J. Wang et al., 2023b)
AgPNs-PAAm/ starch hydrogel	1.Sythesys of PAAm/ starch hydrogel; 2. addition of $AgNO_3$ solution; 3.addition of $NaBH_4$ as a reducing agent for in situ reduction of Ag ions and AgNPs formation.	Phenolic residues	Dutra et al. (2020)
AgNPs-semi-IPN-PAM hydrogel	1.Sythesys of semi- IPN-PAM hydrogel; 2. addition of $AgNO_3$ solution; 3.addition of $NaBH_4$ as a reducing agent for AgNPs formation.	Bacteria	Vimala et al. (2009)
TPEE/IA nanofibrous membrane	1.Preparation of the electrospinning solution by mixing the TPEE solution and the IA solution (consisting of $FeCl_2{\cdot}4H_2O$, EG). 2. Electrospinning of the mixture at room temperature to produce the nanofibrous membrane; 3. hydrothermal treatment to produce the TPEE/IOs nanofibrous membrane.	Hexavalent chromium	Xu et al. (2012)
PA6@Fe_xO_y composite nanofibrous membrane	1.Electrospinning of the PA6 solution at room temperature to produce PA6 nanofibrous membrane; 2. Production of the IA solution mixing $FeCl_2{\cdot}4H_2O$ and EG; 3. Mixing of PA6 nanofibrous membranes and IA solutions; 3. hydrothermal treatment to produce the PA6@Fe_xO_y composite nanofibrous membranes.	Hexavalent chromium	Li et al. (2013)

Gold nanoparticles (AuNPs); dopamine (DA); polydopamine (PDA); highly recyclable catalyst-Ag-based agarose (HRC-Ag/Agar); poly-acrylamide (PAAm); silver nanoparticles (AgNPs); interpenetrating (IPN); poly-acrylamide (PAM); polyamide 6 (PA6); thermal plastic elastomer ester (TPEE); iron oxides (IOs); glycol (EG); iron alkoxide (IA).

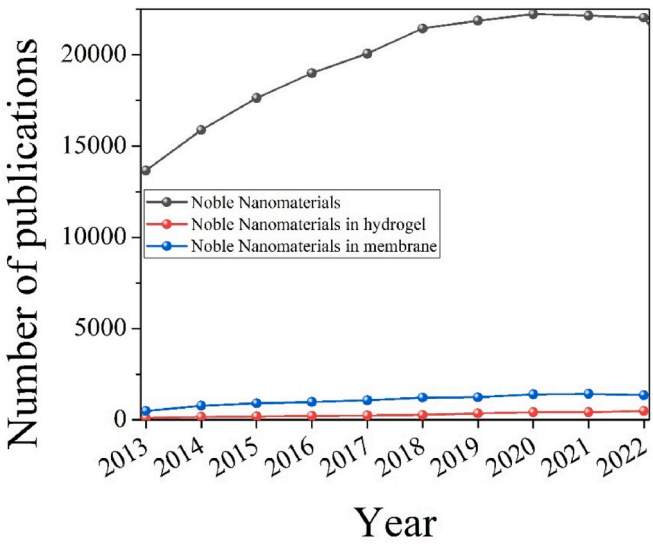

Fig. 4. Number of published papers as a function of years (last decade). Black points refer to the keywords "silver (and gold) nanoparticles" and "silver (and gold) nanocluster"; red dots refer to the keywords "silver (and gold) nanoparticles/nanoclusters in hydrogel"; blue points represent the keywords "silver (and gold) nanoparticles/nanoclusters in membrane". The data have been found in the website Web of Science. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

claimed that only the plasmon peak belonging to the AuNPs underwent a shift towards shorter wavelengths (blue shift), while for the plasmon of the AgNPs there was no significant change (reference signal). A selective amalgamation between Hg and Au occurred during the interaction producing the change of optical features. The authors did not explain the reason why the Hg ions interacted selectively with AuNPs, but probably the cationic polyelectrolyte PAH electrostatically repelled the toxic ions from AgNPs surfaces, avoiding the direct contact among Hg(II) and Ag (Martínez-Hernández et al., 2022).

The amalgam formation (Hg/M, where M = Ag or Au) is exploited to detect the presence of this water pollutant in different cases, as analyzed below. For instance, the workgroup of Saenchoopa synthesized AgNPs via wet chemistry using citrate and γ-aminobutyric acid as stabilizers, then the NPs were dispersed in a gelatin solution that was poured in a Petri dish and kept in refrigerator to give the composite hydrogel. The obtained hydrogels were cut and left in contact (10 min) with different concentrations of Hg(II) aqueous solutions (5–10 000 μM). Fig. 5a shows the picture of the color sensing of the hydrogel doped with AgNPs. The change of color may be due to Hg(II) ions interacting with either amino or carboxylic groups of surface-bound γ-aminobutyric acid. This led to a partial exchange from silver atom to mercury. After that, a redox reaction between Ag (0) and Hg(II) occurred because the standard potential of Hg(II)/Hg (0.85 V) was higher than that of Ag(I)/Ag (0.80 V) (Saenchoopa et al., 2021).

A similar behavior and mechanism were observed in this research (Burratti et al., 2023), where the hydrogel was prepared by mixing the silver nanoparticles stabilized with 3-mercapto-1-propansolfonate (AgNPs-3MPS) and polyethylene glycol diacrylate (PEGDA) and a photo-iniziator (Irgacure 184). The solution was poured in a plastic box and exposed to a UV radiation; the hydrogel was formed by photo-polymerization process. At the end of the synthesis, the doped hydrogel was used for detecting Hg(II) ions by UV–Vis spectroscopy.

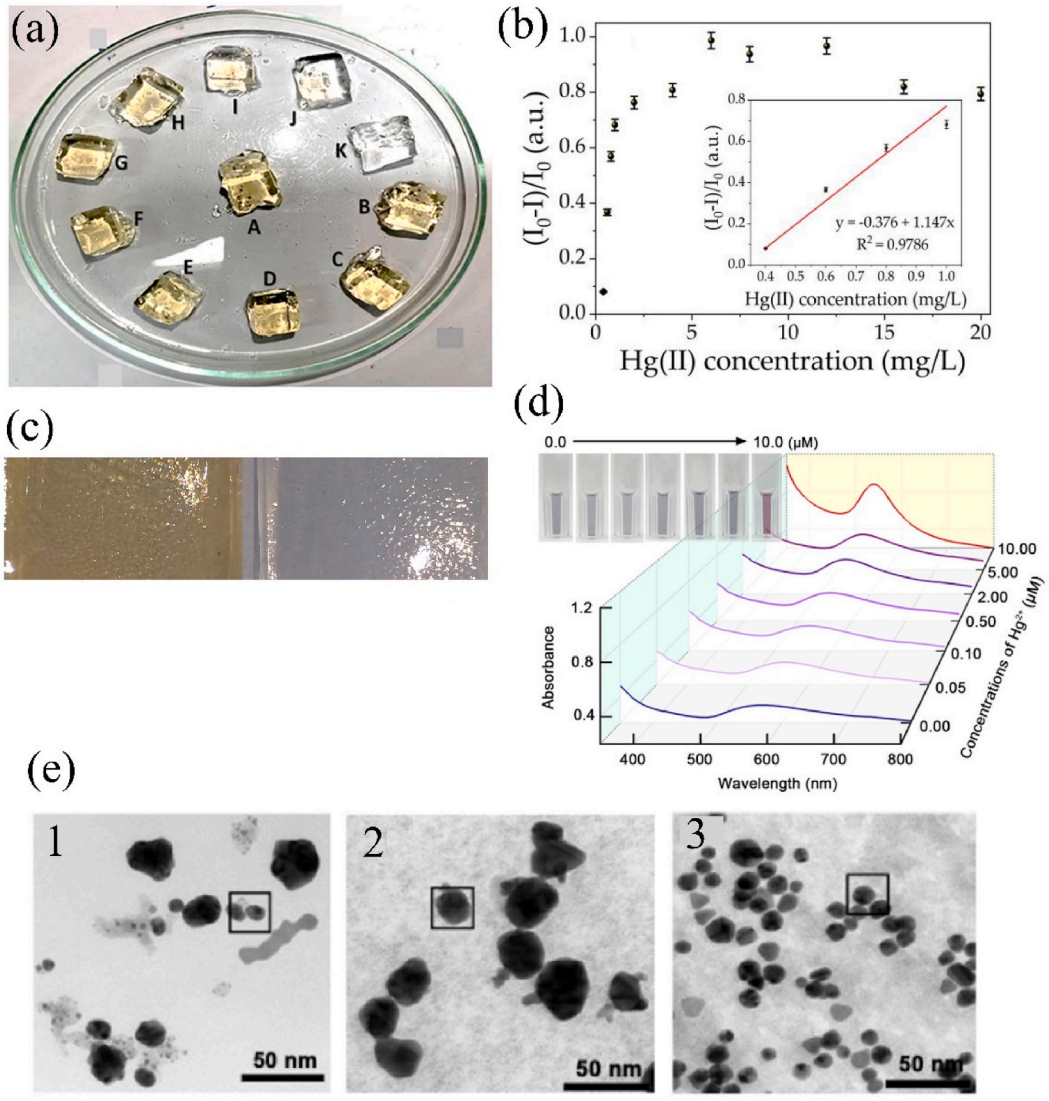

Fig. 5. (a) Photographic image of the AgNPs/Gelatin hydrogel in the presence of different concentrations of Hg(II): (A) pristine AgNPs/Gelatin hydrogel, (B) 5 μM, (C) 20 μM, (D) 40 μM, (E) 100 μM, (F) 400 μM, (G) 600 μM, (H) 1000 μM, (I) 2000 μM, (J) 5000 μM, and (K) 10 000 μM [adapted with the permission of Elsevier from (Saenchoopa et al., 2021); (b) dimensionless ratio $((I_0–I))/I_0$ as a function of Hg(II) concentration (from 0.4 mg/L to 20.0 mg/L), inset: linear range (0.4–1.0 mg/L) with the best fit (red line) of the experimental points (interaction time 24 h); (c) picture of PEGDA-based hydrogels with AgNPs-3MPS: without Hg(II) interaction, left side, and after 24 h of interaction with Hg(II), right side [adapted from (Burratti et al., 2023)]; (d) Real photos and visual absorption spectra of the collected nanostructure aqueous dispersions. TEM images of Au nanostructures collected from hydrogels, which were pretreated in the absence (1) and presence of different concentrations of Hg(II) ions (2): 100 nM and (3): 5 μM [adapted from (Du et al., 2022)]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5b depicts the plot of the ratio $(I_0–I)/I$ as a function of Hg(II) concentration, where I_0 and I represent the maximum value of absorption bands of unpolluted and polluted samples, respectively; by the linear fit it was possible to determine the LOD equal to 0.3 mg/L. Also in this case, the discoloration of the hydrogel occurred once in contact with the Hg (II) solution, as reported in Fig. 5c.

In this work (Du et al., 2022), the researchers synthesized a hydrogel based on L-cysteine and agarose containing gold nanoparticles (AuNPs). The strategy of sensing of these researches included that the hydrogel was pre-incubated in the aqueous solution containing Hg ions and subsequently the Au precursor salt was added. Thank to this process, L-cysteine specifically conjugated with Hg ions via the thiol groups and the optical response from dark blue to red occurred in the solid hydrogel after the incubation of $HAuCl_4$, which was attributed to the formation of regulated Au–Hg nano-amalgams. Based on naked-eye recognition, Hg (II) could be rapidly and simply measured as reported in Fig. 5d. With the increase in Hg(II) concentrations, the colors of the AuNPs bands changed from dark blue to purple and finally to red when the pollution concentration was higher than 10.0 μM. The optical results were analyzed (Fig. 5d), showing that with the increase of Hg(II) ions, the optical absorbance correspondingly increased, and the maximum wavelength of the LSPR band changed from 578 nm to around 540 nm, when the concentrations of Hg(II) ions increased from 0 μM to 10 μM. Referring to Fig. 5e, for the low Hg(II) concentrations, the uniformity of nanostructures increased and consequently, the branched structures and sizes of as-synthesized Au nanostructures slightly decreased (TEM images, panels e1 and e2). Noteworthy that in the presence of high Hg(II) concentrations the produced Au NPs were reduced in size from ≈35 nm to ≈ 15 nm (panel e3), indicating that the presence of Hg(II) ions regulates the sizes of Au nanostructures. In this work, a sensing mechanism was proposed: once the hydrogel was kept in contact with the aqueous solution of Hg(II) ions, the hydrogel pores allowed the diffusion of ions

and subsequently they were fixed by L-cysteine. The Hg(II) ions that interacted with the thiol groups of L-cysteine can involve the growth of Au NPs, resulting in altered size and morphology-dependent LSPR properties. Once the amalgamation has occurred, the aggregative growth of nanostructures from AuNPs to larger-size nanospheres with branched structures was impeded.

A copper ions [Cu(II)] sensor was synthesized by exploiting two DNA strands and gold nanoparticles. To build up the sensor, the two DNA strands were linked to separated polyacrylamide chains, the first one as a substrate (poly-Substrate) and the other one as DNA enzyme (poly-DNAzyme). By mixing the two modified polymers, the Substate and the DNAzyme bond together, forming the hydrogel. If AuNPs were mixed with the two polyacrylamide chains a red hydrogel was obtained and ready to be used as Cu(II) ions sensor. Indeed, adding the ions solution to the hydrogel, the ions diffused inside it and, interacting with the double strand, caused the irreversible dissolution of the Substrate-DNAzyme bond and eventually the dissolution of hydrogel into the liquid form (Lin et al., 2011).

Pesticides are widely used in agriculture and, depending on their aqueous solubility, they either remain in the soil or enter within of ground waters. Compounds resulting from pesticide degradation can persist in animals, vegetables, and water resources and become more concentrated as they move up in the food chain. The easy and fast detection of these water pollutants is, therefore, highly demanded.

In this work (Kestwal et al., 2015), a biosensor based on AuNPs for detecting pesticides in food samples has been fabricated. The sensor consisted in the overlapping of several layers on a plastic substrate. Through double-side adhesive tape, a Whatman filter piece was fastened to one end of the plastic substrate, to act as a test area. Subsequently, acetylcholinesterase enzyme was mixed with fenugreek, agarose and AuNPs and dropped onto the test area. Finally, the solution was allowed to dry at room temperature overnight in a dust free environment, forming the final hydrogel sensor. Carbamates, including carbofuran, oxamyl, methomyl, and carbaryl, were tested to obtain the working dynamic range and LOD of the sensor. This optical biosensor was able to detect carbofuran, oxamyl, methomyl, and carbaryl with limits of detection of 2, 21, 113, and 236 nM, respectively. Furthermore, the fabricated biosensor exhibited good testing capabilities when used to detect carbamates added to various fruit and vegetable samples, demonstrating the practical applicability of the fabricated optical sensor.

The role of noble metal nanoparticles is essential in the determination of dimethoate (insecticide) as reported by Kong and co-workers. In this research, a stimuli-responsive hydrogel (SRHg)-based portable kit, obtained by embedding copper nanoparticles (CuNPs) in agarose hydrogel, was synthesized. The working principle of the sensor was based on two opposite phenomena: the etching of CuNPs from NH_3 that forms highly fluorescent copper nanoclusters (CuNCs) and the inhibition of urease from the presence of dimethoate. For the production of NH_3, the urease and urea were used in the design of the sensor. First the urease and the insecticide were mixed and then the urea was added in the solution, the quantity of NH_3 produced by the enzyme was proportional to the dimethoate concentration. By adding this mixture to the hydrogel with CuNPs, the etching of the particles was proportional to the ammonia produced in the previous step, consequently, the highest the dimethoate quantity the lowest the conversion from CuNPs into CuNCs and thus the photo-emission. In addition, the sensor was employed to detect the dimethoate concentration in real samples, obtaining the recovery values ranging from 99.9% to 110.3% (Kong et al., 2019).

3.2. Sensors based on fluorescence emission

Water pollutant sensors can exploit the fluorescence emission of noble nanomaterials such as gold or silver nanoclusters (AuNCs and AgNCs, respectively), which show bright emission in the visible or IR ranges (Li et al., 2017; Rival et al., 2021).

The nature of the metal nanomaterials and the pollutant species is the key element to determine the type of interaction and the effect on the fluorescent emission band, as described in literature (Burratti et al., 2021a). In this section, several functionalized hydrogels/membranes, as fluorescent sensors for water pollutants, are reported.

A fluorescent gold nanoclusters membrane (FGM) was developed as a fluorescent sensor for Cu(II) ions (Lin et al., 2012). First, the AuNCs were synthesized by chemical reduction method in presence of capping agent (bovine serum albumin, BSA). Then the FGM solution (AuNC suspension) was prepared, by mixing AuNCs solution and phosphoric acid and the pH of the mixed solution was adjusted to the isoelectric point of BSA (pH = 4.7), resulting in the precipitation of Au NCs from the solution. The AuNCs suspension was centrifuged, washed and re-dispersed in deionized water to form a FGM solution. Finally, the FGM solution was casted in a glass mold and dried to denature the FGM solution under vacuum at 90 °C for 2 h. The modified membrane still had the same red emission. The fluorescence of the membrane was quenched by Cu(II) ions; the limit of detection of this system was calculated to be 0.5 μM. A useful property for a sensor is the recyclability, in fact, through the histidine, the emission was totally recovered for at least five times, as shown in Fig. 6a.

A luminescent AuNCs-based hydrogel with three-dimensional (3D) structures was developed as a sensor with high selectivity for Fe(III) ions in water (C. Wang et al., 2023a). The hydrogel was synthesized through the co-assembly of AuNCs stabilized by 4,6-diamino-2-pyrimidinethiol (DPT) with citric acid (CA) and Al(III). Once synthesized the hydrogel,

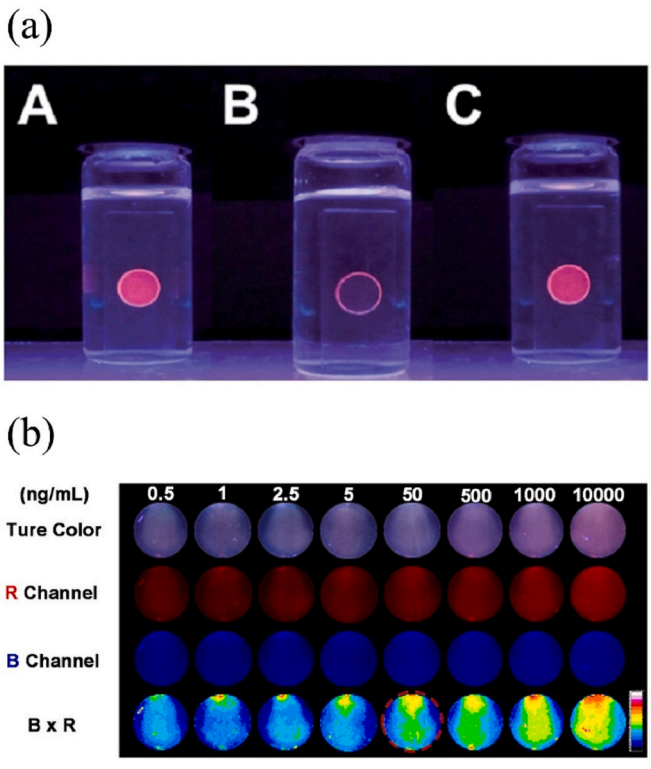

Fig. 6. (a) Reversible quenching of FGM fluorescence by Cu^{2+}. The fluorescence of FGM under UV light excitation (365 nm) in water (A); the fluorescence of FGM under UV light excitation (365 nm) in the presence of 1 mM Cu^{2+} ion; (C) the recovery of the FGM fluorescence by immersing into 10 mM histidine [adapted with the permission of Royal Society of Chemistry from (Lin et al., 2012)]; (b) true-color images are slit into RGB channels and the B x R response is calculated from pixel arrays of B and R channels (adapted with permission from (Yan et al., 2022). Copyright (2024) American Chemical Society. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the photoemission of the system was tested with different concentrations of Fe(III) 0–100 μM (LOD = 10.2 μM), revealing a quenching of the fluorescence as a function of the Fe(III) concentration increasing. The mechanism underlying the decrease in luminescence was the dynamic quenching. The hydrogel can be recovered by using ascorbic acid, which is able to strongly bind Fe(III), reducing it from Fe(III) into Fe(II) and turning on the fluorescence again. Finally, the system was employed in tests inside complex environments (river water, mineral water, fresh apple juice and oxidized apple juice). The PL intensity in mineral water and fresh apple juice was only slightly reduced. On the contrary, the photoemission intensity of AuNCs-based hydrogel in river water and oxidized apple juice decreased significantly, and the addition of river water and oxidized apple juice under 365 nm UV light was in sharp contrast with the hydrogel strong luminescence. These phenomena and results are positively correlated with the actual iron contents of samples: oxidized apple juice > river water > mineral water > fresh apple juice. This result indicates that low Fe(III) content can be detected in complex samples and proves that hydrogel sensing system has a great potential in monitoring Fe(III) in environmental and biological media.

A wood-derived nanocellulose hydrogel (WNH) with gold nanoclusters (AuNCs) was prepared by Luo et al. In the research, the detection performance of WNH with AuNCs was investigated, reporting a good selectivity for Hg ions through the quenching of the photoemission. The decrease of the photoemission intensity was attributed to the partially reversible Au(I)–Hg(II) metallophilic bond on the nanoparticles surface, indeed, adding a strong reducing agent (sodium borohydride) the photoemission was partially recovered. In addition, a second application was studied, namely, the adsorption properties towards Hg (II) ions in water, revealing a very high maximum adsorption capacity (234.4 mg/g) (Luo et al., 2021).

Fluorescent silver nanoclusters (AgNCs) were embedded in a hydrogel based on PEGDA (Burratti et al., 2021b). The hydrogel was photopolymerized by a UV source directly in a disposable cuvette for the easiness of use and portability of the sensing material. The photoluminescence emission of AgNCs was increased in presence of Pb(II) ions, this behavior was ascribed to the combination of two phenomena: Photoinduced Electron Transfer (PET) that occurs in the absence of Pb (II), and Chelation-Enhanced Fluorescence (CHEF), which happens in presence of the toxic ions. The carboxyl groups of the polyelectrolyte that stabilize the AgNPs (polymethacrylic acid) act as chelating agents producing the CHEF process.

Benefiting from the stimuli-responsive property and powerful loading capacity, functionalized hydrogels are favorable for the fabrication of sensing devices. In this work (Yan et al., 2022), fluorescent AuNCs were synthetized using glutathione as reducing and capping agent. Through the coordination action between Zn(II) and the carboxyl group of glutathione or N atom of 2-methylimidazole, AuNCs@ZIF composites were successfully obtained and possessed a typical rhombic dodecahedral shape. The aggregation-induced emission (AIE) active hydrogel was synthetized by incorporating the AuNCs@ZIF composites into the hydrogel system through the diffusion hybridization method. In the co-assembly process, a double-network structure was obtained from the self-sorting association of glutaraldehyde-cross-linked bovine serum albumin (BSA) and alginate crosslinks mediated by Ca(II) ions (SA). The assembled AuNCs@ZIF collapsed as the enzymatic product thiocholine (TCh) was introduced, which was obtained by acetylcholinesterase (AChE)-catalyzed hydrolysis of acetylthiocholine (ATCh). Compared to the initial AuNCs@ZIF, the typical rhombic dodecahedral shape started to decompose and the AuNCs expelled from the framework. In presence of chlorpyrifos (pesticide), AChE was irreversibly inhibited and the decomposition of ZIF was blocked, consequently the PL emission color shifted from blue to red. Thus, chlorpyrifos indirectly regulates the AIE effect of the AuNCs, which can be quantified on the basis of the fluorescence emission of the probe system. The increase of the chlorpyrifos concentration (0.5–10 000 ng/mL) shifted the fluorescence emission from blue to red as reported in Fig. 6b. The fluorescence color is spitted into the three primary colors (RGB: red, green, blue) through an algorithm (the green line is not showed in the picture). The blue and red signals of the hydrogel discs were enhanced with an increasing chlorpyrifos concentration under optimal conditions, obtaining a dual-signal fluorescence change. Signals were standardized (B × R) by multiplying the blue intensity values with the red channel to obtain pseudo colors, which enhanced the accuracy and sensitivity of the corresponding color via amplifying the response signal. Notably, the detection limit (LOD) of the B × R response was calculated to be 0.2 ng/mL.

The comparison in sensing features of different materials is reported in Table 2.

4. Mixed matrix membranes (MMMs) for heavy metals removal from water

The performance of polymeric membranes can be extraordinarily enhanced through the addition of nanomaterials into the membrane matrix producing the so-called MMMs. Nanomaterials can offer, in fact, a series of unique advantages such as increasing the surface area, providing higher reactivity, improving the mechanical strength of the final membrane. These nanomaterials can be included on the surface of the membrane trough post-modification strategies, for instance surface coating, interfacial polymerization, grafting or located inside the membrane structure through immobilization approaches, such as blending, physical entrapment (Huang et al., 2023).

For instance, ZnO nanoparticles has been incorporated into cellulose acetate membranes with the aim of improving their antimicrobial activity, water permeability and metal ions removal (Khan et al., 2015). In particular, the uptake capacity of produced MMMs was studied towards different metal ions including Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Fe^{2+}, Al^{3+}, Fe^{3+}, Sb^{3+} and Sr^{3+}. Among all the metals evaluated, it was found that the nanocomposite membranes were more selective in the removal of Fe^{2+} ions which was related to an electrostatic attraction or a chelating mechanism of ZnO NPs. Moreover, the nanocomposite having 2 wt% of ZnO showed the highest uptake capacity of Fe^{2+} due to the fact that, at higher concentrations, the agglomeration of nanoparticles caused a reduction of the active surface area. Besides their ability in removing Fe^{2+}, all the membranes loaded with ZnO displayed also anti-bacterial activity against *E. coli*.

Zinc doped aluminium oxide (Zn:Al_2O_3) nanoparticles were incorporated into polysulfone (PSf) membranes for the selective removal of Pb(II) and As(V) from water (Sherugar et al., 2021). The selection of these nanomaterials was related to the fact that alumina (Al_2O_3) is already known to act as an adsorbent for heavy metals thanks to its high porosity and surface area, while the presence of Zn can prevent the agglomeration of NPs increasing the selectivity towards the target metals. The PSf MMMs were prepared by dispersing the NPs in N-methyl pyrrolidone (NMP) followed by the addition and solubilization of the polymer. The polymer solution was then cast on glass plate and coagulated in water. From the filtration experiments carried out it was found that the increase in NPs concentration led to an increase of water flux (up to 160 L/m^2 h due to a porosity and hydrophilicity improvement) and of rejection efficiency of metals with a maximum of >87% for As and >98% for Pb measured at neutral pH. The MMMs displayed also superior anti-fouling properties respect to pristine PSf membranes as a consequence of the improved surface hydrophilicity and weaker electrostatic interaction between the foulants and the membrane surface.

MMMs were developed incorporating wet and dry zirconium based UiO-66-NH_2 into PVDF membranes for the removal of Mo(VI) ions from aqueous solutions (Wu et al., 2023). UiO-66 metal organic frameworks (MOFs) have already demonstrated adsorption properties towards dyes and heavy metals form water due to their great number of active sites (Ahmadijokani et al., 2020). Moreover, the presence of the amino group in UiO-66-NH_2 can provide superior performance in coordination and electrostatic attraction (Yao et al., 2016). From the results it was found that pristine PVDF membranes had a moderate Mo(VI) removal (about

Table 2
Comparison table of materials for the optical sensing of water pollutants.

Material	Sensor based on	Water pollutant	Investigated range	LOD	Reference
AgNPs@PAA/AuNPs@PAH	Optical absorption	Hg(II)	0.1–50 mg/L	0.1 mg/L	Martínez-Hernández et al. (2022)
AgNPs@gelatin	Optical absorption	Hg(II)	5–10 000 μM	n.a.	Saenchoopa et al. (2021)
AgNPs@PEGDA	Optical absorption	Hg(II)	0–20 mg/L	0.3 mg/L	Burratti et al. (2023)
AuNPs@l-cysteine	Optical absorption	Hg(II)	0–10 μM	3.7 nM	Du et al. (2022)
AuNPS@PAM/DNA	Optical absorption	Cu(II)	0–1000 μM	n.a.	Lin et al. (2011)
AuNPs@fenugreek/agarose	Optical absorption	Carbofuran	2–10 nM	2 nM	Kestwal et al. (2015)
		Oxamyl	10–100 nM	21 nM	
		Methomyl	100–500 nM	113 nM	
		Carbaryl	200–1000 nM	236 nM	
CuNPs@agarose	Optical absorption	Dimethoate	0.001–10 mg/L	0.002 mg/L	Kong et al. (2019)
AuNCs@BSA	Fluorescence emission	Cu(II)	30–500 μM	0.5 μM	Lin et al. (2012)
AuNCs@DTP/CA/Al(III)	Fluorescence emission	Fe(III)	0–100 μM	10.2 μM	(C. Wang et al., 2023a)
AuNCs@WNH	Fluorescence emission	Hg(II)	$1*10^{-5}$ – 300 mg/L	0.09 μg/L	Luo et al. (2021)
AgNCs@PEGDA	Fluorescence emission	Pb(II)	0–200 μM	8 μM	Burratti et al. (2021b)
AuNCs@ZIF	Fluorescence emission	chlorpyrifos	0.5–10 000 ng/mL	0.2 ng/mL	Yan et al. (2022)

n.a. = not available.

70%) and that the addition of UiO-66-NH_2 significantly improved their separation performance. The membrane loaded with the highest concentration of wet MOF (10 wt%) showed the highest rejection rate (90.3%) with a high permeation flux (171.3 L/m^2 h). This was related to the highest number of adsorption sites and water transport channels of this membrane which improved the interaction between the filler and Mo(VI). The rejection efficiency of the PVDF pristine membrane was about 70% Furthermore, the addition of MOF resulted in a remarkable enhancement in the anti-fouling properties of the membrane as a consequence of the improvement of surface hydrophilicity (water contact angle of 45°) which hindered the adhesion of BSA that was used as model foulant.

Iron based nanoparticles have been also explored for the removal of heavy metals from water. In particular, materials displaying magnetic properties, are generally easily dispersible, less toxic, chemically inert and easily functionable. Moreover, magnetic NPs can be functionalized with other inorganic materials with the aim of improving their stability in solution and providing new sites for covalent binding with specific ligands to the NP surface (Tahoon et al., 2020).

$NiFe_2O_4$ NPs were embedded into PSf hollow fiber membranes, for the selective removal of different heavy metal ions from water (Mondal et al., 2017). $NiFe_2O_4$ NPs were selected on the basis of several reasons: i) they are negatively charged at normal or slightly acidic pH values facilitating the electrostatic interaction with positively charged heavy metals; ii) their hydrophilicity improves the formation of a membrane with a porous architecture; iii) they offer high surface area ideal for maximizing the adsorption of heavy metals. The addition of NPs conferred to the membrane an improved negative surface potential, increasing, at the same time, water permeability and pore size. The pore radius, in fact, increased from 38 to 56 Å by adding 3 wt% of NPs respect to pure PSf membrane. From the filtration tests carried out, it resulted that, among the heavy metals investigated, Pb(II) and Cu(II) showed the highest rejection rate (up to 99.3%) when treated with the membrane loaded with 3 wt% of $NiFe_2O_4$ NPs against the negligible adsorption capacity displayed by the pristine PSf membrane. The authors also performed experiments using real samples of battery industry having an initial Pb(II) concentration of 8.6 mg/L. In this case, the membrane loaded with $NiFe_2O_4$ NPs was able to reach the industrial effluent discharge limit in about 10 h of filtration with a reduction of flux from 38 L/m^2 h to 18 L/m^2 h in 15 h.

Iron based NPs were also explored by (Mishra et al., 2020) for the removal of Pb(II), Cd(II) and Cr(VI) from water. In particular, ferrous

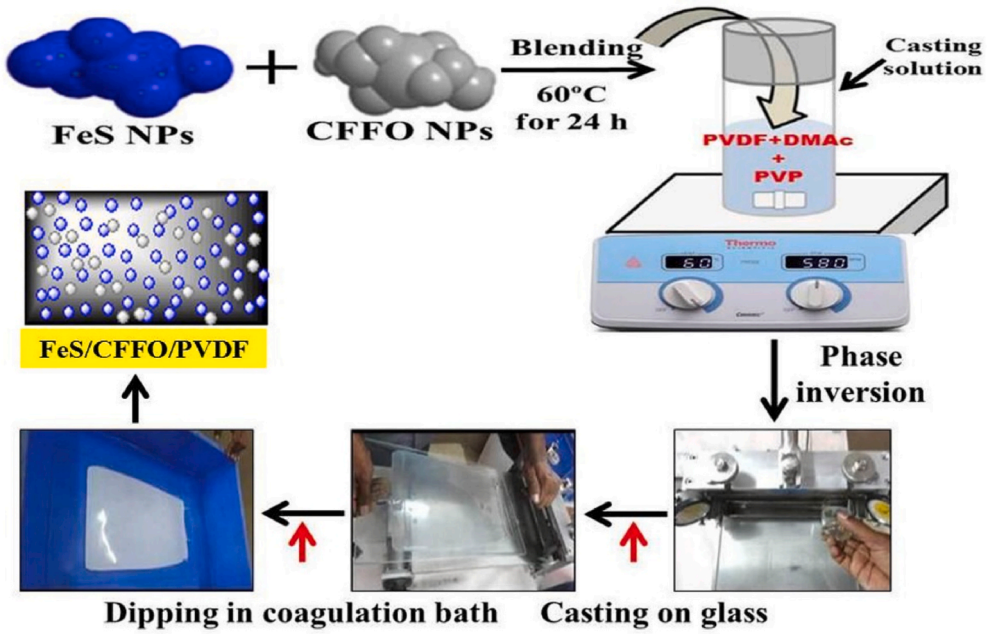

Fig. 7. Schematic illustration of the preparation of FeS/CFFO/PVDF membrane [reprinted from (Mishra et al., 2020) with the permission of Elsevier].

sulfide (FeS) and carboxyl-functionalized ferroferric oxide (CFFO) NPs were incorporated (individually and in combination) into PVDF membranes prepared by phase inversion technique (Fig. 7). Membranes were prepared by dispersing the proper quantity of NPs (1 wt%) in the solvent dimethylacetamide (DMAc) followed by polymer addition and solubilization. The obtained dope solution was then cast on a glass plate and immersed in an aqueous coagulation bath until precipitation and formation of the final membrane. The membranes prepared using both nanomaterials displayed the highest flux (about 1200 L/m^2 h), respect to the membranes prepared with the individual nanomaterials, as a consequence of their higher hydrophilicity, porosity and pore size. From the heavy metals removal tests, it resulted that the combination of both nanomaterials in the same membrane was beneficial for improving their removal efficiency. In particular, the FeS/CFFO/PVDF membrane displayed a rejection rate up to 99.78% for Pb, 99% for Cd and 88.4% for Cr. The higher removal rate observed for Pb, was related to the hydrated radii of Pb(II) respect to other metal ions which could have led to a complex which underwent to an enhanced rejection through size exclusion mechanism. The membrane displayed also very interesting results when tested for the simultaneous removal of multiple heavy metal ions from real contaminated water. Also in this case, the FeS/-CFFO/PVDF membrane showed rejection values higher than 90% for all the heavy metals investigated (Cr, Pb, Cd and As).

A list of modified membranes with different NPs and their removal performances is summarized in Table 3.

5. MMMs for dyes removal from water

Among the nanomaterials employed in membranes for dyes removal, MOFs which consist of inorganic metal ions or clusters coordinated to organic linkers, are very well appreciated for the preparation of adsorptive membranes due to their high porosity degree, great surface area, tunable pore size, chemical stability and excellent compatibility (C. Zhang et al., 2019a).

In the work of Wu and colleagues (Wu et al., 2023), for instance, the UiO-66-NH_2 MOFs were used as fillers in PVDF membranes for the removal of the cationic dye Rhodamine B (RhB) and the anionic dye Congo red (CR). From the filtration experiments carried out, it resulted that the pristine PVDF membranes presented low flux and low dyes rejection (Fig. 8a). However, the addition of UiO-66-NH_2 greatly enhanced both the flux and the dye removal up to 96.4% for RhB and 98.3% for CR when the concentration of filler in the membrane was 10 wt% (Fig. 8a). The improvement in the dyes rejection was attributed to three different factors: i) the electrostatic adsorption or Donnan exclusion between the membrane and the dye; ii) the high number of adsorption sites exhibited by UiO-66-NH_2 fillers; iii) the formation of a cake layer with retentive properties formed during the filtration process. Moreover, from the kinetic experiments carried out, it resulted that the adsorption behavior was fitted better by a pseudo second-order kinetics model, implying that chemisorption was the main adsorption mechanism involved. The visual effect of the two dyes filtration is shown in Fig. 8b.

The immobilization of nanomaterials with catalytic properties in a membrane structure can guarantee a series of benefits. The ordered and predefined structure of a membrane, in fact, allows an efficient flow-through reaction avoiding, at the same time, the catalysts dispersion during reaction and the on-site separation at the end of the reaction (Xin and Hao, 2014). Moreover, the porous architecture of the membrane improves the contact probability between the pollutant and the embedded catalyst greatly increasing the reaction rate (Huang et al., 2023). On this regard, Fe/Cu bimetallic Fenton catalysts were incorporated into PES membranes for the degradation of CR dye (Huang et al.,

Table 3
Literature data on heavy metals removal using membranes loaded with various NPs.

Membrane material	Membrane preparation conditions	Nanoparticles	Heavy metal	Initial heavy metal concentration (mg/L)	Removal operative conditions	Removal efficiency (%)	Reference
PVDF	Solvent: DMF Additive: PVP T = 50 °C	UiO-66-NH_2 (2–10 wt%)	Mo(VI)	200	T = 25 °C	75–90	Wu et al. (2023)
PSf (20 wt%)	Solvent: NMP (80 wt%) T = RT	Zn:Al_2O_3 (0.1–0.3 g)	As(V), Pb(II)	10	Room temperature, Pressure: up to 5 bars	As: 5- 87 Pb: 30- 98	Sherugar et al. (2021)
PSf (18 wt%)	Solvent: DMF (82 wt%) T = 60 °C	$NiFe_2O_4$ (1–3 wt%)	Pb(II), Cu(II), Zn (II), Cd(II), Ni(II), Cr(III)	50	pH = 4.3–10	Pb: 89.4–98.7 Cu: 94.2–99.3 Zn: 60.9–89.4 Cd: 55.4–71.4 Ni: 56.9–72.8 Cr: 42.7–53.7	Mondal et al. (2017)
PVDF (16 wt%)	Solvent: DMAc (81 wt%) Additive: PVP (2 wt%) T = 60 °C	FeS/CFFO (1 wt%)	Pb(II), Cd(II), Cr (VI)	5	pH = 4.5, 6.5 Pressure: 1 bar Room temperature	pH:4.5 Pb: 99.8–99.0 Cd: 89.1–90.1 Cr: 82.9–88.4 pH: 6.5 Pb: 99.78–99.1 Cd: 95.3–99.0 Cr: 76.5–86.18	Mishra et al. (2020)
PES (15 wt%)	Solvent: NMP	PANI-TiO_2 (3–7 wt%)	Cu(II)	20	pH = 7	94	Pakdel Mojdehi et al. (2019)
PAN (7 wt%)	Solvent: DMF T = RT	Carbon nanofibers (CNF)/TiO_2 (0.5–6 wt %)	Pb(II), Cu(II), Cd (II)	50	pH = 3-7	Pb: 87 Cu: 73 Cd: 66	Kumar et al. (2018)
PSf (15 wt%)	Solvent: NMP (80 wt%) T = 60 °C	ZnO-GO-NiO (0.1–0.5 wt%)	Pb(II), Cd(II)	50	pH = 5.5 Pressure: 2 kg/cm^2	Pb: 99.02 Cu: 98.64	Maqbool et al. (2023)
PEI (0.5 wt %)/PSf (support)	Water, TMC/n-hexane (0.1 wt-v%	ZnO (0–0.02 wt%)	Cu(II), Zn(II), Ni (II)	1000	Pressure: 4 bar	Cu: 95.6 Zn: 96.6 Ni: 96.9	Yan et al. (2024)

*DMF: dimethylformamide; PVP: polyvinylpyrrolidone; PANI: Polyaniline; PAN: polyacrylonitrile; GO: graphene oxide; PEI: polyethyleneimine; TMC: trimethylene carbonate.

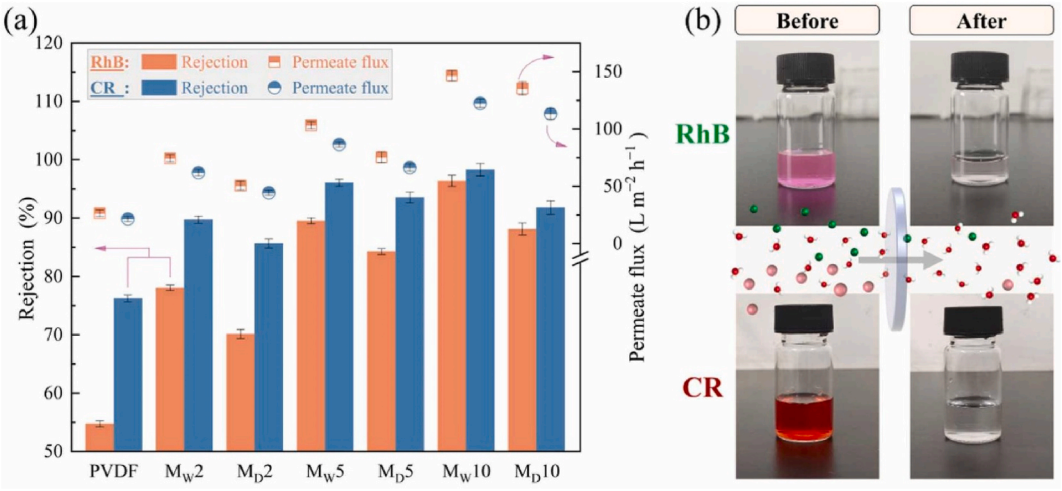

Fig. 8. (a) Dye rejections of membranes (50 mg/L RhB or CR, 1.5 bar, 25 °C); (b) RhB or CR solution before and after filtration [adapted from (Wu et al., 2023) with the permission of Elsevier].

2023). From the tests carried out, it resulted that the membrane loaded with 18 wt% of NPs exhibited the best performance in terms of dye degradation reaching a removal rate of 98.8% in 5 h. Higher concentrations of Fe/Cu catalysts, however, led to a decrease in the degradation performance of the membrane probably due to an agglomeration phenomenon of the particles and in a consequent reduction of the available catalytic sites. The highly porous structure of the membrane resulted to be very beneficial for the exposure of the catalyst. Moreover, it promoted the flow through the membrane structure accelerating the contact between the dye and catalysts in the membrane, which fostered the degradation process.

The catalytic activity of TiO_2 nanoparticles for the removal of dyes from water was investigated by Galiano and colleagues (Galiano et al., 2018b). In particular, in order to improve their dispersion into the solvent and their stability into the polymer matrix, the TiO_2 nanoparticles were previously chemically functionalized with the surfactant sodium dodecyl sulphate (SDS). The membranes were thus produced in hollow fiber configuration using PVDF as a polymer with a concentration of TiO_2 of 0.5 wt% (Fig. 9). The prepared hollow fibers were tested for the degradation and removal of methylene blue (MB) dye from water under

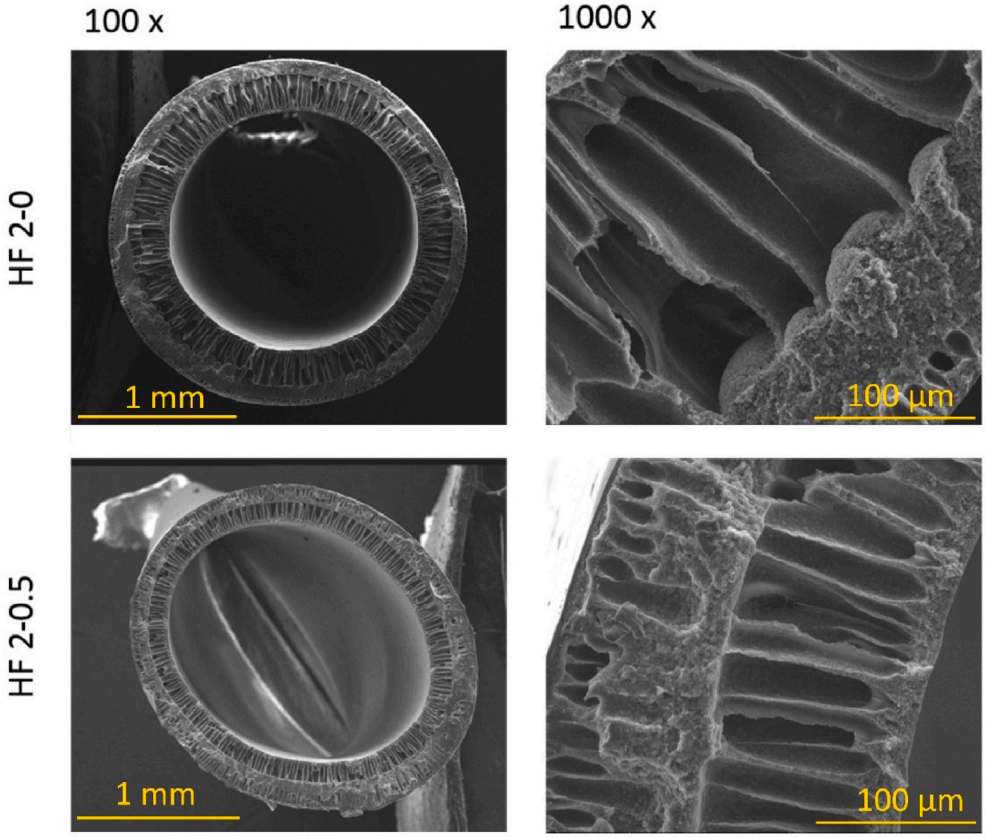

Fig. 9. Cross section of PVDF hollow fibers pristine (HF 2-0) and with TiO2 (HF 2-0.5) membranes at different magnification. Rearranged from (Galiano et al., 2018b).

UV irradiation. While no degradation of MB was observed for the pristine PVDF membranes, the hollow fibers loaded with TiO_2 displayed a clear degradation of the dye under UV irradiation (97% after 300 min). The kinetics of MB degradation showed good fit to pseudo first order reaction which was in agreement with the Langmuir-Hinshelwood model.

Another approach that has been investigated for the removal of dyes from water using membranes relied on the use of an electrical field. A conductive Ni/NiO layer, for instance, was deposited on the surface of a PVDF membrane for the removal of different dyes from water (Y. Zhang et al., 2019b). While the removal efficiency of the dyes RhB and MB was not satisfying (below 60%), the rejection for CR dye increased from 49.83% to 97.93% when the voltage was increased from 0 V to 20 V with a measured permeability of 202.51 ± 9.63 L/m^2 h bar. The rejection of CR was attributed to the fact that, being a negatively charged molecule, the voltage favored the repulsion forces between the dye and the conductive membrane.

Table 4 summarizes literature works related to the removal of different dyes from water using membranes loaded with various metal oxides NPs.

6. MMMs for pesticides removal from water

Among the several approaches available, membrane processes represent one of the most appreciated technologies in pesticides remediation from water. As for the contaminants described in the previous paragraphs, also for the pesticides, the integration of nanomaterials into the polymeric matrix can lead to an important improvement of the physicochemical characteristic of the membrane (such as chemical and mechanical resistance, thermal stability) as well as conferring unique and tailored properties.

Chitosan-based membranes loaded with Ag nanoparticles for the removal of Imidacloprid pesticide from contaminated water were prepared by Moustafa and co-workers (Moustafa et al., 2021). The membranes were prepared by blending a dispersion of Ag NPs (0.2 %) into a chitosan solution (3 %) followed by casting of the dope solution in a Petri dish until complete evaporation of the solvent. From the adsorption tests carried out, it was found that the removal of the pesticides was strictly dependent on the pH. The highest adsorption of Imidacloprid was found at pH = 6 (85 % removal) respect to the pristine chitosan membrane which displayed an adsorption of just 40 %. The authors explained that the adsorption mechanism of the pesticide was mainly based on electrostatic interactions.

In another work, thin film nanocomposite (TFN) membranes by

Table 4
Literature data on dyes removal using membranes loaded with various metal nanoparticles.

Removal mechanism	Membrane material	Membrane preparation conditions	Nanoparticles	Dye	Initial dye concentration	Removal operative conditions	Removal efficiency (%)	Reference
Adsorption	PVDF	Solvent: DMF Additive: PVP T = 50 °C	UiO-66-NH_2 (2–10 wt%)	RhB, CR	50 mg/L	Pressure = 1.8 bar	RhB: 96.4 CR: 98.3	Wu et al. (2023)
	PAN (10 wt %)/PVDF (14 wt%)	Solvent: DMF T = RT	SiO_2 (1.5–2.5 wt%)	Basic Red 18	30 mg/L	pH = 7 Volume = 250 ml	97.25	Mahmoodi et al. (2021)
	PVDF	Solvent: DMF Additive: PEG T = RT	Cu/Al	Erythrosin B	6 mg/L	Volume = 25 ml	72	Abbasi et al. (2021)
	PVDF (17 wt%)	Solvent: NMP T = 60 °C	Fe/Co (0.05–0.2 wt%)	Malachite green	50 ppm	Pressure = 0.05 bar	97	Iqbal et al. (2022)
Catalysis	PES (12–16 wt%)	Solvent: DMAc (64-60 wt %) Additive: PEG (24 wt%) T = 70 °C	Fe/Cu	CR	50 mg/L	Volume = 150 ml pH = 8	98.8	Huang et al. (2023)
	PVDF (19 wt%)	Solvent: NMP (54.5 wt%) Additive: PVP (16 wt%); PEG (10 wt%)	TiO_2 (0.5 wt%)	MB	10 μmol/L	Volume = 250 ml Pressure = 0.5 bar	97	Galiano et al. (2018b)
	PVDF	Solvent: DMAc T = 60 °C	Zif-67 (0.025–0.1 wt%)	Orange II MB RhB	20 mg/L	Time = 30 min	Orange II: 97.3 MB: 98.2 RhB: 90.5	(D. Liu et al., 2021a)
	PVDF	PVDF functionalized membrane with polydopamine (PDA)	MOF-74 (8, 12, 16, 20 mg)	RhB	20 mg/L	Volume = 100 ml	97.1	Zheng et al. (2022)
Filtration	PVDF	Dispersion of nanoparticles filtered through a PVDF commercial membrane	Mg–Al layered double hydroxides-graphene oxide (0.5–2 wt%)	MB	50 ppm		~100	Zeng et al. (2019)
	PVDF (20 wt%)	Solvent: DMAc (78.2–78.9 wt%) Additive: PVP (1 wt%) T = 70 °C	Fe_3O_4-halloysite nanotubes (0.1–0.8 wt%)	CR, MB	100 mg/L		CR: 92.1 MB: 84.7	Liu et al. (2020)
Electric/ filtration	PVDF	PVDF membrane coated with PDA layer	Ni/NiO	RhB, MB, CR	RhB: 20 mg/L MB: 20 mg/L CR: 50 mg/L	Volume = 50 ml Pressure = 0.1 MPa Voltage = 20 V	RhB: 11 MB: 40 CR: 98	(Y. Zhang et al., 2019b)
	PVDF	Commercial PVDF membrane soaked in a Ag and Ni solution	Graphene oxide-silver (Ag)- nickel (Ni)	CR	50 mg/L	Voltage = 30 V	98.02	Zhao et al. (2019)

PEG: polyethylene glycol; PDA: polydopamine.

adding modified SiO_2 nanoparticles were embedded into a polyamide (PA) layer that was deposited via interfacial polymerization on a PSf asymmetric membrane (Rakhshan and Pakizeh, 2015). The addition of SiO_2 NPs (from 0 to 0.3 w/v%) led to a decrease of membranes contact angle (from 66° to 47°) as a consequence of the hydrophilic nature of the NPs and to a slight decrease of membrane pore size (from 0.35 to 0.32 nm). When tested for the removal of three different pesticides (atrazine, propazine and prometryn), the incorporation of SiO_2 (0.17 w/v%) led to an increase in the rejection of propazine and atrazine of 7% and 4%, respect to the pristine membrane. This was explained by considering that the addition of SiO_2 resulted in membranes with a more compact and dense structure which were able to limit the permeation of the small solutes. However, the molecular sieving effect was not the only mechanism involved in the separation of the pesticides. Electrostatic interactions between the pesticide and the membrane surface played also a crucial role. The lowest rejection observed for propazine, in fact, was related to its larger dipole moment.

Another class of visible-light-driven nanocomposite membrane was proposed in this work (Xu et al., 2021), by embedding TiO_2 and graphitic carbon nitride (g-C_3-N_4) into chitosan membranes for the removal of the pesticides 2,4-dichlorophenol (2,4-DCP) and atrazine. The prepared membranes showed a pore size of about 10 nm and a very hydrophilic surface exhibiting a contact angle value of about 17°. The photocatalytic studies proved that the MMM was able to remove more than 90% of both pesticides and the kinetics data of the photocatalytic tests well fitted with a pseudo-first-order correlation. The reusability of the system was also demonstrated by washing the membrane with water after each photocatalytic test where no decrease in photoactivity after the first 10 cycles was observed.

The removal of four different pesticides (2,4-dichlorophenoxyacetic acid (2,4-D), glyphosate, trifluralin and butachlor) was studied (Hosseini and Toosi, 2019), by using ultrafiltration PSf membranes loaded with GO/TiO_2 NPs. The blended membranes showed higher values of porosity (from 39 to 67%), enhanced pure water flux (from 7 to 326 kg/m^2 h) and surface charge respect to the pristine PSf membrane. These results can be explained by considering the hydrophilic nature of the GO/TiO_2 NPs, which enhanced the permeation of water molecules trough the membrane. Moreover, the addition of the fillers also improved the pore size of the membrane (from 8 to 45 nm), which was also responsible of the water permeability improvement. The dynamic filtration experiments revealed that the herbicides with larger size and lower solubility (such as trifularin and butachlor) presented the highest rejection, thus suggesting that the size exclusion was the main mechanism involved in their removal. From adsorption tests, it resulted that the data fitted a Langmuir isotherm. Maximum adsorption capacity for glyphosate, 2,4-D, butachlor, and trifluralin were found to be 26.59, 19.08, 9.44, and 7.69 mg/g, respectively.

PAN nanofiber-based membranes embedding Fe_2O_3 NPs were synthetized, by electrospinning technique, for the selective removal of diazinon from water (Pordel et al., 2019). The mean diameter of nanofibers containing NPs was 180.16 nm, slightly lower than the unloaded PAN nanofibers (206 nm). The addition of Fe_2O_3 NPs also led to a decrease of membranes contact angle (from 60° to 46°) because of the presence of a significant amount of hydroxyl groups, which made the membrane more hydrophilic. As shown in Fig. 10a, the addition of NPs led to an improvement of diazinon removal, reaching its maximum value (about 84 %) when the concentration of Fe_2O_3 was 0.1 wt%. Fig. 10b shows the influence of pH on the diazinon removal efficiency. The highest rate of removal efficiency was observed at neutral pH. However, under acidic and alkaline conditions, the efficiency was reduced. This can be due to a possible corrosion effect of Fe_2O_3 NPs and nanofibrous membrane under these conditions.

Table 5 summarizes literature works related to the removal of different pesticides from water using membranes loaded with various metal NPs.

7. Conclusions and future outlook

Metal nanostructures, thanks to the rapid development of technologies for their versatile chemical synthesis and their characteristics such as stability, functional flexibility and low cost, represent promising new materials for water pollutants monitoring and treatment. Furthermore, their combination with polymer matrices opens up new opportunities for applicability in these fields. So far, different synthetic approaches have been developed for obtaining hybrid materials able to detect and/or remove water pollutants such as heavy metal ions, pesticides and dyes.

In this context, this review summarizes the recent literature about the synthesis and applications of metal nanostructures combined with polymeric matrices (membranes and hydrogels) used both as sensing and removing materials for some of the main water pollutants, such as heavy metals, pesticides and dyes in order to provide readers with a clear and updated guide to the subject. Combination of nanomaterials with polymeric matrices, in fact, is often a perfect match which allow to combine the benefits stemming both from polymer materials and inorganic clusters.

The aim of the review is, therefore, to fill the gap in literature on this subject by comprehensively synthesizing existing research, identifying emerging topics, and suggesting areas for future investigation. As described in this review, a plethora of nanomaterials have been already investigated and successfully used for the production of combined systems, which exhibit noteworthy properties in the sensing and removal of

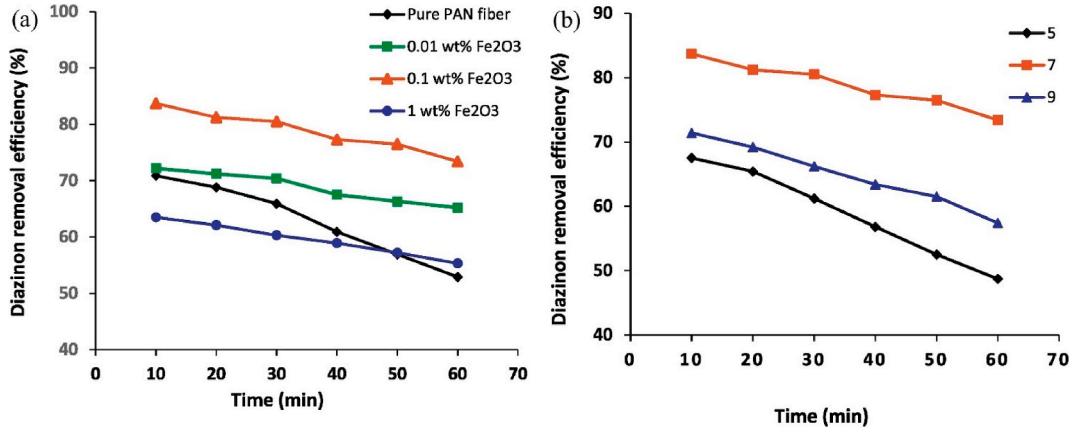

Fig. 10. a) Effect of Fe_2O_3 nanoparticles concentration of the removal of diazinon (pH = 7); b) the effect of pH on diazinon removal efficiency (0.1 wt% Fe_2O_3). Adapted from (Pordel et al., 2019) with permission of Elsevier.

Table 5
Literature data on pesticides removal using membranes loaded with various metal NPs.

Removal mechanism	Membrane material	Membrane preparation conditions	Nanoparticles	Pesticide	Initial pesticide concentration	Removal operative conditions	Removal efficiency (%)	Reference
Adsorption	Chitosan (3 wt%)	Solvent: aqueous acetic solution	Ag (0.2 wt%)	Imidacloprid	0.2–2 g/L	pH = 6	85	Moustafa et al. (2021)
	Cellulose acetate	Solvent: acetone	Zn (0.1 mg)	Metolachlor Acetochlor	0.5 g/L	Adsorption time: 20, 30 min	Metolachlor: 99.8 Acetochlor: 61.4	Shad et al. (2021)
Filtration	PA/PSf	Solvent: NMP	SiO_2 (0.03–0.3 w/v)	Atrazine, Propazine, Prometryn	100 μg/L	Pressure = 10 bar	Atrazine: 97 Propazine: 91 Prometryn: 98	Rakhshan and Pakizeh (2015)
	PSf	Solvent: NMP T = 60 °C	GO/TiO_2 (0.25–1 wt%)	2,4-D, Glyphosate, Trifluralin, Butachlor	20 mg/L	Pressure = 1 bar	2,4-D: 61 glyphosate: 53 trifluralin: 73 butachlor: 69	Hosseini and Toosi (2019)
	PAN	Solvent: DMF T = 40–50 °C	Fe_2O_3 (0.01–1 wt%)	Diazinon	10 mg/L	pH = 7 Filtration time = 10 min	84	Pordel et al. (2019)
Catalysis	Chitosan	Solvent: aqueous acetic solution	TiO_2 + g-C_3-N_4 (25 mg)	2,4-DCP Atrazine	2,4-DCP: 20 mg/L Atrazine: 2 mg/L	Lamp irradiation = 100 mW/cm^2	>90%	Xu et al. (2021)
	PVDF (12 wt %)/PAN (2 wt %)	Solvent: DMF	TiO_2	Diuron	10 mg/L	Sun simulator	96	Nthumbi and Ngila (2016)

various contaminants from water. In water monitoring, gold and silver nanoparticles were found to be the most diffused pollutant sensors embedded into polymer matrices, thanks to their excellent optical absorption and fluorescence emission properties. On this matter, noble-based nanoparticles still represent the election choice.

On the other hand, in water remediation, the types of nanomaterials employed for the removal of the investigated contaminants are much diversified and heterogenous. Different nanomaterials based on Fe, Zn, TiO_2, Si, Co, Cu and Ni are, in fact, efficiently used through their entrapment into polymer matrices and the exploitation of their peculiar properties for the removal of the pollutants. These structures function using different removal approaches which can be based on: adsorption, catalysis, filtration or electric repulsion.

Despite significant advancements, challenges such as the potential toxicity, the long-term stability, and the scalability production of these nanomaterials remain. Future research should focus on addressing these issues by exploring biocompatible materials, long-term performance studies, and scalable fabrication techniques. Additionally, integrating smart sensing technologies and real-time monitoring systems with these materials can further enhance their practical applications. Furthermore, when dealing with nanomaterials, it is crucial to consider the existing regulations and standards governing their use in water treatment. These regulations address the safe production, handling, application, and disposal of nanomaterials to ensure they do not pose risks to human health or the environment. While significant strides have been made in regulating nanomaterials, ongoing research and development necessitate continual updates to these regulations. International collaboration and the harmonization of standards are crucial for effectively managing the risks associated with nanomaterials in water-related fields, ensuring both environmental safety and public health protection. This is the reason why stabilizing nanomaterials in polymeric matrices (like hydrogels and membranes herein discussed) is extremely important for their effective application in various fields, including water treatment and monitoring, and material science in general. The stability of nanomaterials within these matrices ensures their proper dispersion, prevents agglomeration, and maintains their functional properties. This approach not only enhances the performance of the nanomaterials but also expands their potential uses across different fields.

CRediT authorship contribution statement

Luca Burratti: Writing – review & editing, Writing – original draft, Methodology, Data curation, Conceptualization. **Emanuela Sgreccia:** Writing – review & editing, Writing – original draft, Validation, Methodology. **Federica Bertelà:** Writing – review & editing, Writing – original draft, Methodology. **Francesco Galiano:** Writing – review & editing, Writing – original draft, Validation, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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