Future Challenges and Perspectives in Water Purification by Hybrid Materials

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Abstract One of the main emerged trends in the water purification sector is hybrid materials adoption. Due to their peculiarity of combining several components into one formulation, hybrid materials are effective in removing a panoply of pollutants from contaminated water. Thereby, they provide a conceivable alternate to conventional water purification. Nevertheless, considerable challenges are remaining in the industrial process scale-up, including, stability, lifecycle, sustainability, and cost-effectiveness. The main objective of this book chapter is to allow scrutiny and gain an appropriate understanding of future perspectives and challenges faced by hybrid materials, for the simple reason that a proper understanding of the challenges will add to the understanding of measures to be taken.

1 Introduction

Despite the great number of existed materials families, it was found that it cannot fulfill all the technological and scientific required functions, which underlines the need for a new class of materials with improved properties. Hybrid materials are one of the most successful examples. In a broader sense and as their name suggests, hybrid materials are built by combining two or more materials in a single polymeric matrix to give rise to super properties compared with their individual counterparts [1].

There are various other definitions of hybrid materials from different viewpoints currently in use in the literature that are all perfectly satisfactory; going from describing hybrid materials formation as a consequence of electron orbitals

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arrangement of two or more materials [2], to their description based on different chemical bonds development between two or more materials [3]. There is no defined classification exist for hybrid materials since they could be classified according to countless different criteria. Hybrid materials could be a mixture of inorganic materials, organic materials, or their combination where all components are called on to render their contribution.

For organic–inorganic hybrid materials, two types of organic components could be used; small organic molecules or organic macromolecules as polymers/biopolymers. These latter along with inorganic particles such as metals are the most used components for organic–inorganic hybrid materials production. Each material has its own emphasis and role. For example, polymers/biopolymers matrices are often responsible for the hybrid material structural properties, components cohesion, and shape flexibility, while inorganic reinforcements are responsible for rigidity, thermal and mechanical stability, electric and magnetic properties [4].

Generally speaking, two types of hybrid organic–inorganic materials may be distinguished based on their strength interactions and synthesis approaches as seen in Fig. 1;

(1) hybrid materials with chemical bonds between their components synthesized throughthe chemical process giving rise to covalent cross-linking polymers.
(2) hybrid materials with weak bonds synthesized through the inorganic component's incorporation into the polymeric matrix giving rise to blends and interpenetrating networks [4].

To obtain stable and homogeneous hybrid materials over long periods, it is recommended and preferable to properly implement chemical interactions as crosslinking, and covalent bonds between the different hybrid materials components. Otherwise, potential shortcomings may exist as phase separation, loss of material integrity, or leaching out of the material's constituents. To tackle this issue, in situ preparation

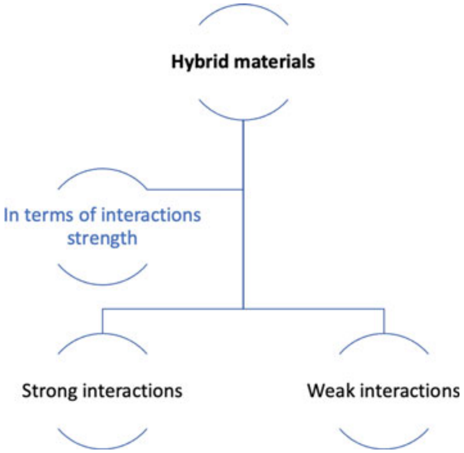

Fig. 1 Classification of organic–inorganic hybrid materials

in presence of both organic and inorganic components is the most used method to enable greater compatibility among the hybrid material's components.

Since the hybrid materials, applications are controlled by their features including physical, chemical, thermal, structural, and morphological properties. It is noteworthy that these properties can be tuned in a controlled way by adequately changing their structure, components, and their preparation approaches. It lies therein all the interest of elaborating hybrid materials as materials that are fit for their purposes.

There exist different routes for hybrid materials elaboration as briefly described below [1];

- In situ approach based on the chemical transformation of the used precursors leading to
- *The sol–gel* method is based on wet chemical methods to give rise to highly homogeneous hybrid materials by encapsulating the organic components within the derived inorganic components.
- *Building block* approach based on maintaining the molecular integrity of starting components.
- *The hydrothermal* method is based on crystallizing techniques at high temperatures and pression to engender hybrid materials with better nucleation control.

2 Hybrid Materials for Water Decontamination

Hybrid materials would have served many purposes, but mainly in treating contaminated water to eliminate its pollutants. According to the literature, hybrid materials have several outstanding properties that make them excellent tools for water decontamination, including high surface area, remarkable stability, high porosity, tunable properties, and a greater affinity towards a panoply of water pollutants. On that account, hybrid materials provide an unusually efficient option for meeting the growing needs for sustainable water treatment [5].

Broadly speaking, the most emergent water pollutants could be divided into three major categories: inorganic pollutants (heavy metals, nitrates, nitrites, phosphate…), organic pollutants (phenols, phenols, COD, BOD…), and microbiological pollutants (*E. Coli, S.Aureus*…) [6]. This section provides a summary of the recent hybrid material's achievement in water depollution.

2.1 Elimination of Inorganic Pollutants

Efficient sequestering action on heavy metals using hybrid materials was reported by several studies. As an illustration, Ni (II) and Pb (II) were effectively removed using a hybrid Xanthan gum- Glutathione/Zeolite with a high uptake of the order of 85% and 93% respectively [7]. Another hybrid material based on bentonite and guar gum was elaborated for lead removal from real wastewaters obtained from electroplating and battery manufacturing. The study has revealed an uptake removal of 83.5% using ion exchange and electrostatic interactions between the hybrid and the heavy metal [8]. Hybrid materials based on copolymers were also investigated for heavy metals removal. Hybrid copolymer chitosan-g- PMMA silica gel was elaborated via an emulsifier free emulsion polymerization to remove toxic Cr(VI) from waters with a removal efficiency of 98% at an optimum pH of 4 [9].

Besides heavy metals, nitrogen and phosphate compounds are also among the most frequently encountered inorganic contaminants. For removing both phosphate and nitrate, a hybrid composite based on Fe_3O_4/ZrO_2/chitosan was elaborated at mild conditions leading to a maximum adsorption amount of the order of 26.5 mg P/g and 89.3 mg/g, respectively [10]. Another study has reported that a fast and efficient removal of nitrate (74% in 5 min) was achieved using a hybrid material based on chitosan incorporated with Al_2O_3 and Ag-doped TiO_2 nanoparticles.

2.2 Elimination of Organic Pollutants

Since organic pollutants are countless, the researchers tend to assess the effectiveness of their hybrid materials using the three parameters' indicators of organic pollution namely; TOC (Total organic carbon), COD (chemical oxygen demand), and BOD (biochemical oxygen demand). Elaborating hybrid materials capable of removing these three parameters at once would be ideal. The best illustration is magnetic Gluten/Pectin/Fe_3O_4 hybrid material that has demonstrated its ability to remove simultaneously 80% of BOD, 60% of COD, and 50% of TOC [11].

Another hybrid material based on zinc oxide nanoparticles and chitosan was prepared to remove organic dissolved matter from milky wastewater. The study carried out has yielded great results; COD removal around 97% [12].

Phenol compounds are among the most toxic and recalcitrant organic contaminants. Many studies have already demonstrated the hybrid material's capability of removing recalcitrant phenols from water. The hybrid material based on trimethyl chitosan-loaded cerium oxide CeO_2 particles is a case on point. It shows an effective removal of three phenolic compounds of the order of 78%, 90%, and 60% for 2-chlorophenol, 4-chlorophenol, and phenol, respectively.

Loads of studies have underlined the removal of dyes using hybrid materials. Photocatalytic hybrid material based on TiO_2, clay, and alginate biopolymer was elaborated in order not only to adsorb the dye chromophore groups but to destruct them using UV irradiations. In other words, the prepared hybrid material has shown an ability to effectively removing color with 98% uptake along with dissolved organic matter COD with 93% uptake [13]. Similarly, a hybrid material based on alginate and iron modified TiO_2 was elaborated with the ability to remove methylene blue under both UV and Visible irradiations depending on the treatment conditions [14].

2.3 Elimination of Microbiological Pollutants

Water microbiological contamination is defined as the presence and prevalence of pathogenic microorganisms. Fortunately, enough, hybrid materials have made it possible to cope with microbiological pollution and benefit from their tuned antibacterial and antifungal activities. As many studies have proven, hybrid materials based on chitosan have been shown due to their natural prominent antibacterial activity against a broad spectrum of bacteria and fungi [15]. Likewise, hybrid materials based on silver nanoparticles have also shown potent antibacterial activity due to the strong reaction of silver nanoparticles with the bacteria proteins and DNA besides generating free radicals which would surely lead to bacterial membrane damage [16].

A chitosan hybrid material based on cellulose, titania, and silver nanoparticles was elaborated via a one-pot synthesis method and shown a maintaining great antibacterial activity up to 12 h [17]. Two different fungal strains; *Rhizoctonia solani* and *Alternaria alternate* were used to assess the antibacterial and antifungal activity of a novel hybrid material based on cellulose, Nickel metallic nanoparticles, and polyaniline. Considerable inhibitions of the fungal growth were recorded of the order of 42% and 50% for R. solani and A. Alternate, respectively [18].

Combining antibacterial activity with magnetic properties would guarantee a strong recoverable hybrid material for water treatment. The hybrid material based on Poly (aniline-co-pyrrole), alginic acid, and magnetic nanoparticles is a case on point. After being synthesized via an in situ co-precipitation, the magnetic hybrid material was tested against five bacteria; *Bacillus subtilis*, *Staphylococcus aureus*, *Candida albicans*, *Pseudomonas aeruginosa*, and*Escherichia coli* where it has shown good antifungal and antibacterial activities [19].

The following table summarizes the various applications of hybrid materials in water decontamination (Table 1).

3 Challenging Aspects of Hybrid Materials in Water Purification

The employment of hybrid materials in water purification has pursued a quite long development path. In fact, an abundant number of research studies at bench-scale testing have been conducted on the issue. Nevertheless, it may seem a paradoxical finding that only a very modest number of systems based on hybrid materials have been practically used in water purification.

The major constraint lays in the gap between the laboratory-scale and industrial-scale in terms of hybrid materials efficiencies. Actually, in academic research, there is a tendency to idealize, overvalue, and overestimate the performances of the hybrid materials as well as making a lot of good promises concerning their industrial scaling-up that would fall by the wayside if no real consideration is taken of their potential

Table 1 The summary of the applications of hybrid materials in water decontamination

Hybridmaterials	Pollutant	Removal	References
Inorganicpollutants			
Chitosangrafted- PMMA/Silica	Cr(VI)	98%	[9]
Xanthangum-Glutathione/ Zeolite	Ni (II) Pb(II)	85% 93%	[7]
Guargum/bentonite	Pb(II)	83.5%	[8]
Fe_3O_4/ZrO_2/chitosan	Nitrate Phosphate	89.3 mg/g 26.5 mgP/g	[10]
Organicpollutants			
Chitosan-zinc oxide	COD	97%	[12]
Alginate/Bentonite impregnated TiO_2 beads	Methylene Blue COD	98% 93%	[13]
Chitosan-Guar gum blend silver nanoparticle	TOC	82–84%	[20]
Trimethyl chitosan-loaded cerium oxide particles	2-chlorophenol 4-chlorophenol phenol	78% 90% 60%	[21]
Magnetic Gluten/Pectin/Fe_3O_4 hydrogel	COD BOD TOC	60% 80% 50%	[11]
Microbiologicalpollutants			
Hybridmaterials	Bacteria	Inactivation/inhibition	References
Nanometer-thick titania/chitosan/Ag-NP film	Escherichia coli Staphylococcus aureus	$\cong$ 100% $\cong$ 100%	[17]
Poly(aniline-copyrrole)@ Fe_3O_4@alginic acid	Candida albicans Staphylococcus aureus Escherichia coli Pseudomonas aeruginosa Bacillus subtilis	Good antibacterial and antifungal activities	[19]
Hybrid nickel doped polyaniline/cellulose	Alternariaalternate Rhizoctoniasolani	50% 42%	[18]
Chitosan-manganese dioxide	Escherichia coli Staphylococcus aureus	50%	[22]

limitations, as technical practicability and feasibility. Therefore, there is an overriding need to prevent the research and industrial community from being misled attributable to the shift to industrial large scale. And this by identifying the most frequent challenges and roadblocks that may be found.

Herein, we shall emphasize the main future challenges regarding hybrid material's future applications in the water purification sector.

3.1 Scaling Up

Currently, nearly all the research studies based on hybrid materials for water treatment are conducted on a batch scale. Scaling up is referring to moving from the laboratory to industrial applications which is a major part of research and development (R&D). Scaling up is not only a matter of quantitative concept by increasing in the batch size, but also a matter of feasibility of the process (scalable or not), its productiveness, and its effectiveness that need to be fully checked and explored. These batch experiments play a pivotal role in allowing a prior statement and initial understanding of the depollution process using hybrid materials but don't reflect fully the real yields at larger scale. The slow-going shift from lab scale to large practice is due to the intricacy of the large system proceedings.

In fact, the design and preparation of hybrid materials for certain pollutants removal from simulated contaminated water at lab scale requires limited quantities of materials and chemicals besides reduced energy consumptions. That is not the case for larger scale, where a lot of variables may interfere and demand additional processing, besides involving considerable process modifications. On top of that, other sciences may get in line as engineering, economics, and materials science to ensure the maintaining of the effectiveness and meet the growing demands and expectations of industrial applications.

For better profitability of hybrid materials performances and smoother sustainable implantation in the water depollution sector, several actions can be undertaken:

- Examination of synthesis methods for a better outcome.
- Structuring of scalable models for engineering suitability studies and economic analysis.
- Effective quality control and relevant analytical methodology during all the process steps for quality guarantee.
- Evaluation of purity profiles of the starting materials and the final materials.
- Production of large sufficient and homogeneous quantities of hybrid materials well characterized for the critical prototyping phase testing, thus industrial assessment.
- Good documentation of technology transfer methodologies.

3.2 Stability

Good sorption or catalytic efficiencies of hybrid materials are not enough to meet the expected demand at larger scale. Good structural stability and high fatigue resistance of hybrid materials even in extreme water conditions are the key factor that is driving the progress and the perception of water purification quality.

Since hybrid materials are made up of two or more parts, their stability reflects first and foremost a maintained assembly of all their components and their active parts over a long life without any sort of leaching in the reaction medium. The second priority is ensuring identical reliability and effectiveness over long periods.

Recognizing and understanding the factors that may lead to the non-stability of hybrid materials are pivotal to prevent their occurrence and bring stability to the materials even after multiple reuses.

According to most of the literature, the performance and stability evaluation of hybrid materials is usually done under simulated conditions closely resembling the real ones but inshort-term experimental studies. In fact, the sufficient ins and outs of long-term effect on hybrid materials decontamination mechanism, and their stability are missing and need to be fully explored. All this is intended to serve as the basis for future larger-scale implantation.

Checking out the stability of the hybrid materials is usually done by these means:

- Exploring the leaching behavior of hybrid materials into the water medium using analytical tools as atomic absorption spectroscopy (SAA) and inductive coupled plasma emission (ICP) [13].
- Examining the hybrid materials changes before and after treating polluted water through X-ray photoelectron spectroscopy (XPS) to assess the binding energies, chemical composition, and atomic percentages of hybrid materials components [23, 24].
- Determining the saturation magnetization in the case of magnetic hybrid materials [24, 25].

The good stability of hybrid materials opens a double-wide window of attractive opportunities for their practical applications at an industrial scale. Reusability and regeneration for longtime cycling are the perfect examples.

3.3 *Reusability and Regeneration*

The reusability and regeneration abilities of hybrid materials are the very sine qua non not just for their economic feasibility but even for their straightforward application on larger scale. Indeed, these two criteria are a major source of value addition to hybrid materials that it is advisable to fully take into account when developing these materials as this assists in making the most of the significant time and money necessary to manufacture them.

Materials reusability or recycling depicts their ability to be reused several times in a row until their saturation and overload with water pollutants, translating into a decline in their effectiveness and depollution performances. One solution comes to mind immediately: restoring the material's primary depollution features and this by their regeneration. This latter helps benefit from the hybrid materials for subsequent reuses which serve as the basis for potential cost-reduction opportunities.

Aside from the economic benefits of materials regeneration, recovering the adsorbate pollutants is indispensable especially in the case of toxic heavy metals that need to be desorbed and concentrated for further industrial purposes instead of their leaching in the environment. For materials reusability assessment at lab scale, hybrid materials are subject to repeating usage for multiple cycles under identical conditions

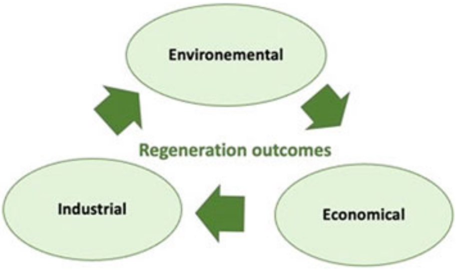

Fig. 2 The outcomes of hybrid materials regeneration

to enable a clear insight of hybrid materials shelf life and maximum performances. Whereas, regeneration is ensured by several techniques to revive the spent exhausted hybrid materials to diminish significantly virgin materials usage in favor of regenerated materials (Fig. 2). Depending on the hybrid material type and formulation, the regeneration could be using ultrasounds [26], thermal energy [27], electrochemical [28], and chemical treatments [15]…etc.

Testing the hybrid material's reusability and its ability to be regenerated is an essential prerequisite at the lab scale. However, the usefulness of the data collected from these experiments is limited and doesn't reflect necessarily what may take place at larger scale. By way of explanation, most, if not all, of the lab-scale experiments are done in batches. The transition from static mode (lab-scale) to dynamic continuous processes (larger scale) is usually associated with many risk factors that come into play: the effect of flowing rate, and the severe operating conditions of larger scale that may be conducive to degradation of the hybrid materials. Thus, shortening their shelf life to a much-reduced duration compared to what was estimated when in static mode.

In the light of the above considerations and for better practicability, hybrid materials should be able to stand up to the toughest use and conditions. Thereby, more relevant consideration should therefore be taken into account while transiting from a static, closed, and controllable system to a dynamic, open, and uncontrollable large system.

3.4 Interferences

Contaminated water has at its disposal a broad panoply of co-existing pollutants none of which are considered harmless to human health, viz. pathogenic organisms, organic and inorganic contaminants, metallic elements, oils, radioactive elements, etc. [6]. Knowing this, hybrid material's efficacy is better appraised if they have a demonstrated ability to remove various contaminants parallelly.

Most studies carried out on this vein using hybrid materials focused on the removal of water pollutants taken separately in solutions. Nevertheless, few studies shed light on the importance of assessing the effect of the co-existing ions on the pollutants removal [29]. It is fairly typical for inorganic co-existing ions to predominate in wastewater in high quantities. According to current scientific studies, these ions have a significant influence over pollutants removal mechanisms: they may help to speed up, slow down, or even stop the decontamination process.

Predictably and according to the literature, the simultaneous presence of co-existing ions has a significant negative influence on pollutants removal [13]. This is mostly because competitive reactions may take place over the hybrid materials binding sites between the target pollutants and co-existing ions, which leads to a certain decline in terms of hybrid materials affinity and their decontamination performances.

As mentioned above, polluted waters like wastewaters (sewage) are a complex cocktail of pollutants. Ergo, to permit a more accurate evaluation of the prepared hybrid materials and considering possible interferences within polluted water, simulating wastewater at lab scale is an indispensable step not to mispresent the contaminated water conditions, but basically to fully state them to infer the hybrid material's behavior. Then pass to the second step that is to test the hybrid materials on real wastewater samples for a thorough investigation of their real ability to decontaminate water. To this extent, all possible interferences are being already taken into consideration at the lab scale as well as understanding the functioning of these materials; this makes it possible to make conclusions based on sound science and valid data.

3.5 Cost-Effectiveness

In comparing hybrid materials, account shall be taken of their effectiveness in removing pollutants, and their costs. In fact, the cost-effectiveness analysis is a crucial component of environmental initiatives to maximize environmental benefits at the lowest possible cost. Thus, ensuring an economically viable alternative for water treatment at larger scale.

Of all the literature reviewed, the cost estimation of hybrid materials for water treatment is seldom or never clearly defined. Generally, estimating the cost of certain elaborated material for a certain application may depend on a range of factors, including precursors accessibility and their pre-treatment, elaboration methods and processing, the materials recyclability, energy consumption, etc.

In the case of hybrid materials based on bio-resources like biopolymers, their starting materials are commonly available, natural, and inexpensive, making their larger-scale practicability possible [30, 31]. However, more focus must be put upon optimal natural resources management and exploitation to benefit from the environment, yet preserving its resources.

For the case where hybrid materials are based on nanoparticles and nanomaterials, providing large quantities of these nanomaterials at reasonable costs is among the main concerns of nanotechnology application for water decontamination. Hence, finding suppliers that fill the needs while offering lower prices or at least in reasonable limits would be beneficial for these materials implementation on the existing conventional wastewater sector as effective, and attractive alternatives.

3.6 Sustainability and Toxicity

Biodegradable, non-toxic, biocompatible, eco-friendly, ecological, etc. are the attractive most-used terms describing hybrid materials for water treatment in the literature [13, 15, 32]. Tobridge the gap between these good promises and the reality, measuring the sustainability and the "non-toxicity" of these materials is a must before their larger-scale applications. However, there is a lack of studies regarding this issue.

Only a few reports addressed the biodegradability or the sustainability metrics of already prepared hybrid materials by analyzing quantitatively and qualitatively their potential environmental influences [32], or by evaluating their biodegradability [33]. In the case of adsorption, the spent hybrid materials are considered secondary waste as long as they are not regenerated. Indeed, adsorbents full of toxic pollutants as heavy metals even on a small scale are deemed to pose many threats to human health and the environment, and this risk would be magnified by switching to the larger scale.

Further research and risk/benefit analysis are required to corroborate the non-toxicity assumptions of hybrid materials. Using polymers or natural resources in the processing of hybrid materials does not endow them with a guaranteed sustainability label. There is a significant concern over the usage of nanoparticles within the biopolymeric matrix. These nanoparticles exert their effect making the hybrid materials high-performing yet less benign as expected. That is where the concern stems from, and ironically no studies are reasserting specifically about the potential toxicity of hybrid materials incorporating nanoparticles for water decontamination. All the focus is usually geared toward the effectiveness of removing pollutants without paying enough attention to the harmful effects of nanoparticles. Another issue that has to be addressed is the possible leaching of these persistent insoluble nanoparticles into water and hence seeping into the soil [5, 34].

4 Conclusion and Future Perspectives

The rising number of studies devoted to water decontamination employing hybrid materials is the best proof of their suitability and high effectiveness which is reflected in encouraging results over the other conventional materials. Despite this, hybrid materials testing so far have been at a small lab-scale, requiring further consideration and research for the assessment of their potential applications at larger-scale on the one hand, and determining the optimal procedures besides risk management measures on the other hand. The remaining key challenges for evolving hybrid materials from lab scale to industrial wastewater sector are diversified, i.e. the mass scale synthesis should be preferably continuous and scalable for a high yield sustainable production, improving the selectivity of these materials towards target pollutants, and evaluating their effectiveness over long periods using representative samples of real wastewater.

Last but not least, the underlying objective behind conducting these researches is elaborating new materials for water decontamination and restoring its purity for further reuse towards a sustainable future with the least possible environmental damage. Otherwise, we will be introducing new sorts of pollutants to the environment.

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