



Hybrid materials for the removal of emerging pollutants in water: classification, synthesis, and properties

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ABSTRACT

In recent years, different approaches for achieve the removal of Contaminant of Emerging Concerns (CECs) from aqueous matrices were developed. Within this framework, the synthesis of new hybrid materials capable to combine different processes, such as photocatalysis, adsorption and enzyme catalysis, is an important issue. Therefore, to enhance performances and efficiency, and to reduce costs and environmental impact of these processes, different reusable materials were synthesized and tested towards both natural and spiked water matrices containing organic and inorganic pollutants. The aim of this review is to highlight the main strategies employed, to summarize the properties of these materials, and critically analyse their strengths and weaknesses.

1. Introduction

Water is a common good of humankind, and access to safe and clean water should be everyone's right. Unfortunately, water pollution is a widespread problem mainly due to anthropogenic sources and recently, in addition to traditional pollutants, the so-called "Contaminants of Emerging Concerns (CECs)" are becoming central for scientific research and legislation [1].

Pharmaceutically active compounds, personal care products, endocrine-disrupting chemicals and pesticides are some of CECs that have been increasingly detected in water. They are ubiquitous, very persistent and not easy to remove by classic wastewater treatment plants [2]. CECs may accumulate in the aquatic environment, but at present the lack of data on their environmental fate and ecotoxicological impact prevents a proper and complete evaluation of the risks associated with these organic compounds [3].

For this reason, more in-depth studies are needed on CECs physical and chemical properties, reactivity and metabolic pathways and the sharing of results within the scientific community, also through online platforms such as the Norman Network [4], should be a priority.

Even if CECs research topics mainly refer to the identification and characterization of new compounds, the evaluation of toxicological effects, the environmental fate and the associated human health risks, the development of proper analytical methods for their detection and novel

processes for their removal from water deserve to be studied as well [5]. Different removal techniques have been studied according to the type of contaminant: adsorption on activated carbon [6], Advanced Oxidation Processes (AOPs) involving ozone [7] or UV light, electro-oxidation techniques [8], enzymatic reactions [9], biological treatments [10], photocatalytic approaches [11–13] and so on. Despite the good results obtained with these techniques, in recent years many studies have been focusing on the synthesis of new hybrid materials, with the aim to improve their stability and durability, increase pollutants adsorption or removal capability, reduce environmental impact and toxicity of products by combining the properties of different materials.

It is not easy to define what a "hybrid material" is because this term has been used to express materials obtained by mixing different components, but they are also commonly called "composites" [14]. According to the IUPAC definition [15], a hybrid material is the result of an intimate mixture of inorganic and organic components, or both types of them, which interpenetrate on a scale of less than 1 μm . On the other hand, other definitions of hybrid materials are used, and different classifications, based on different criteria, were proposed.

In 2004, Makishima defined hybrid material as a mixture of two or more materials with newly-formed chemical-bonds and suggested a categorization based on the level of mixture [16], which was summarized in 2009 by Nanko as follows (examples are given in parentheses) [14]:

; AOPs, Advanced Oxidation Processes; CECs, Contaminants of Emerging Concerns; CMC, Carboxy Methyl Cellulose; GO, Graphene Oxide; HRP, Horseradish Peroxidase; MOF, Metal Organic Framework; NOM, Natural Organic Matter; SBP, Soybean Peroxidase.

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- **Composites:** Mixture of materials consisting of matrix and micron-level dispersion (fibre-reinforced polymers or glass-reinforced plastics).
- **Nanocomposites:** Sub-micron level mixture of similar kinds of materials (polymers or oxides mixture).
- **Hybrids:** Sub-micron level mixture of different kinds of materials (carbon nanotube/metal matrix composites).
- **Nanohybrids:** Atomic or molecular level mixture of different materials with chemical-bonds between their different materials (proteins covalently immobilized on inorganic supports).

Starting from the Makishima approach, Nanko also proposed a subdivision of hybrid materials in three different categories [14]:

- **Structurally Hybridized Materials:** composites with a hybridization of macroscopic mixture, such as a composite reinforced with almost two types of fibers. The resulting properties are the combination of the properties of their components.
- **Materials Hybridized in Chemical Bond:** inorganic/organic hybrids with chemical bonds between inorganic and organic materials. For example, organic-modified silicates with strong covalent bond, generated during the sol-gel processing, between silica and organic molecules.
- **Functionally Hybridized Materials:** materials created as a basis of the concept to harmonize each function of component material, resulting in new functions deriving from the hybridization of the functions of each material. For example, hybrid photocatalysts obtained by mixing a photocatalyst with an adsorbent (i.e., TiO₂ and SiO₂).

Other authors limited the term “hybrid materials” to organic-inorganic materials. Among them, Saveleva et al. [17] identified two different areas in the field of hybrid materials:

- Organic molecule-modified inorganic materials (organics-in-inorganics), which can be sub-divided in two sub-categories: (i) inorganic structures modified by organic molecules, and (ii) colloidal particles stabilized by organic molecules.
- Inorganic-modified organic materials (inorganics-in-organics).

In the “inorganics-in-organics” materials, the inorganic part can be mineral, clay, metal, semiconductor, carbon or ceramic, whereas the organic part can be biological (lipids, protein, polysaccharides, cells, bacteria or microorganisms) or chemical (hydrogels, brushes, polymers and block-copolymers).

A partial summary of the different categories of hybrid materials is reported in Fig. 1. Some of the main objectives of their synthesis are the synergistic action of different water treatment strategies, the reduction of costs and a lower environmental impact through the reuse of materials and their greater efficiency. The aim of this review is to highlight the main strategies employed so far, to summarize the properties of these materials, and analyse their strengths and weaknesses, focusing on two particular types: biopolymer- and enzyme-based hybrid materials.

2. Biopolymer-based hybrid materials

Adsorption is one of the simplest ways to remove pollutants from water. Historically the most common adsorbent materials belong to the class of activated carbons, a wide range of carbonized materials characterized by a high degree of porosity and high surface area. Activated carbons can be prepared by different sources, such as charcoal, wood, or agricultural wastes. Depending on the type of starting material, the process requires a preliminary carbonization followed by physical or chemical activation [18,19]. Physical activation is a dry oxidation which occurs in the presence of oxidizing gases and steam at high temperature (700–1100 °C) [20], while the chemical activation usually consists in a wet oxidation at relatively lower temperatures (400–900 °C) in the presence of alkali, acids, or inorganic salts as catalysts [21]. Despite an easy preparation and good adsorption capacities, this material suffers from the cost of regeneration and high attrition rate [22]. Moreover, it tends to adsorb organic chemicals indiscriminately, so hindering a selective recover of certain organic chemicals for reuse [22]. For these reasons, different low-cost materials have been widely produced.

In the past years, polymeric adsorbents have been considered as potential alternative to activated carbon thanks to their large surface area, pore size distribution and adjustable surface chemistry. Besides, polymer/inorganic hybrid adsorbents emerged as a new class of adsorbent materials for the complete removal of trace pollutants from water. In particular, biopolymers-inorganic hybrid materials are very interesting in order to develop new environmentally friendly techniques and

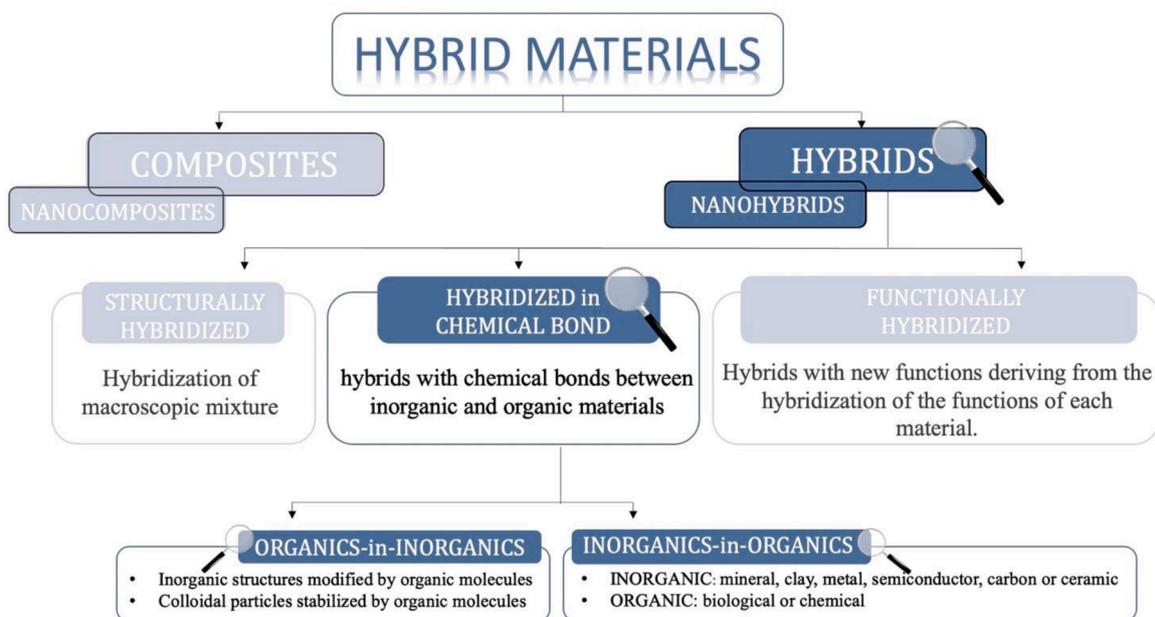


Fig. 1. A possible classification of hybrid-materials. Materials discussed in the review are highlighted.

to valorise biomass waste by recycling them.

Polysaccharides are the most studied biopolymers, in particular cellulose, chitosan and alginate. Cellulose is the most abundant polymer on Earth and it is present in cell walls of plants, in marine organisms and also generated by microbial biosynthesis [23]. Chitosan is produced commercially by deacetylation of chitin, that is the second most abundant polymer after cellulose [24], and it is usually obtained from natural sources such as the residues of shrimp, crab and lobster, fungal mycelia and green algae [25–27]. Alginate is a water-soluble linear polysaccharide extracted from brown seaweed [28]. Their use in hybrid materials is described in detail in the following paragraphs.

2.1. Alginate

Alginate is a biocompatible biopolymer, non-toxic, non-immunogenic and biodegradable, that can be described as an anionic copolymer of β -D-mannuronic acid (M blocks) and α -L-guluronic acid (G blocks) units arranged in an irregular blockwise pattern of GG, MG, and MM blocks in varying proportions. The mannuronic acid forms β (1 \rightarrow 4) bonds, so M block is linear and flexible, while guluronic acid gives rise to α (1 \rightarrow 4) bonds, and for this reason G block is structurally rigid [29].

Due to the surface rich in functional groups such as carboxyl and hydroxyl groups, alginate could capture metals or their ions. However, it is characterized by high rigidity and fragility with poor elasticity and mechanical properties [30]. In recent years, to improve mechanical and thermal stability and to enhance adsorbing capabilities, new materials were prepared in variable forms and with different methods (Fig. 2) by mixing alginate with other synthetic or natural polymers, such as polyacrylic acid [30] and chitosan [31], or adding biowaste-derived substances [32]. Moreover, many organic and inorganic-alginate materials have been synthesized and tested for the removal of some emerging contaminants, in particular antibiotics such as ciprofloxacin, tetracycline and norfloxacin. For this environmental purpose, three main classes of alginate-inorganic materials have been studied: (i) alginate-graphene oxide in fibers or hydrogels forms; (ii) magnetic

alginate-Fe₃O₄ composites; and (iii) alginate-MOF (metal organic frameworks).

2.1.1. Alginate-GO

Graphene oxide (GO), usually synthesized using the modified Hummer's method, is a carbon material characterized by a large specific surface area, excellent mechanical properties and unique physico-chemical properties [33]. Thanks to its two-dimensional sheet-like carbon structure and randomly distributed hydroxyl, epoxy, and carboxyl groups on its surface and edges, GO can be involved in hydrogen bonding, cation bonding interaction and π - π interactions which make it an interesting adsorbent material.

However, GO is nano-toxic, which can limit its environmental applications [34]. Encapsulation or introduction of Graphene Oxide in alginate-based hybrid material cannot only enhance alginate mechanical and physical properties, but also reduce GO nano-toxicity.

Hydrogels can be easily removed from water, making them particularly suitable for the treatment of aqueous matrices. Alginate is known to form hydrogels in the presence of divalent cations, such as Ca²⁺. Indeed, multivalent metal cations can act as crosslinkers between the carboxylic groups of alginate chains, building three-dimensional networks. But it was also shown that alginate can form acid gels at pH below the pK_a value of the uronic acid residues [35].

Alginate-graphene hydrogels can be synthesized by mixing sodium alginate and GO in water [36], so obtaining an encapsulation of GO into the material, or by dropping the mixed dispersion (GO, sodium alginate and polyvinyl alcohol) in a CaCl₂ solution. This second kind of hybrid material was also subjected to chemical and physical modification to improve its properties.

When alginate-GO beads were dipped in a solution of ascorbic acid, GO reduction occurs, and an alginate/graphene double network (GAD) is obtained [37]. In this case graphene oxide interpenetrates but remains independent from the alginate network and the resulting structure exhibits better mechanical properties, stability, and adsorption capacity than the single network. Moreover, to further increase adsorption

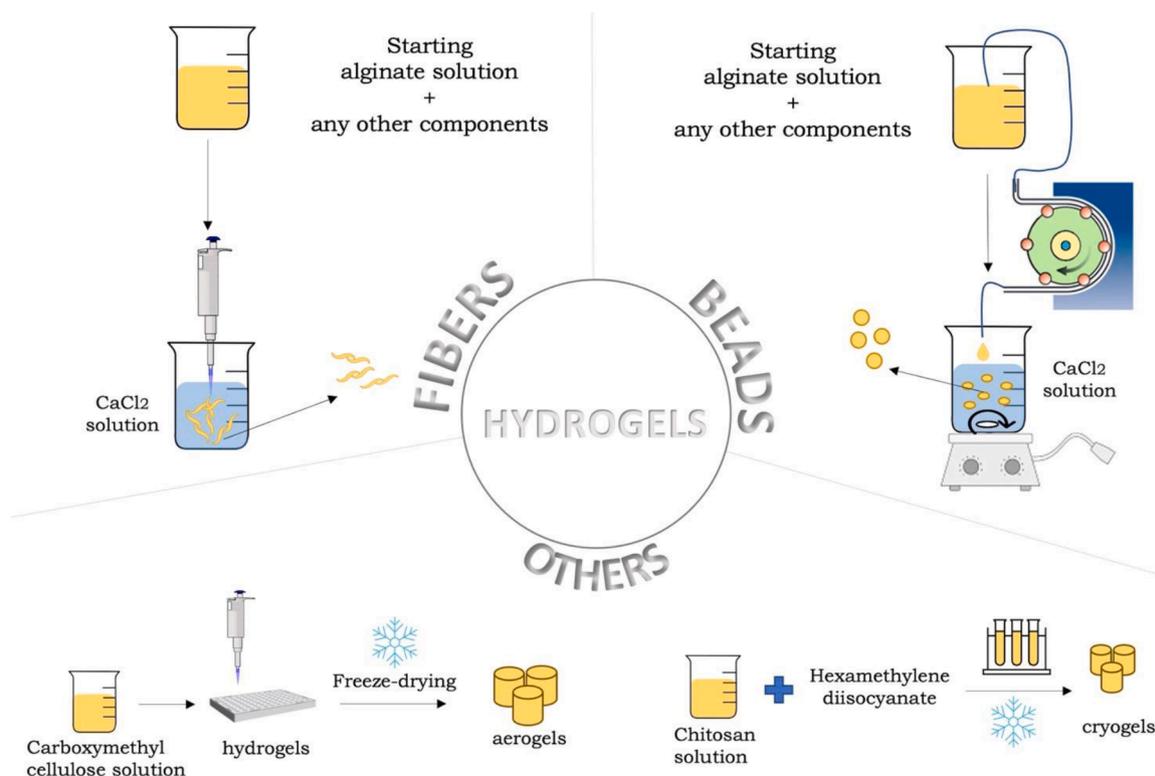


Fig. 2. Summary of different methods used in the preparation of alginate-based materials.

capacity, a porous material can be synthesized by adding CaCO_3 to the initial mixture of GO. After the synthesis, GAD was dipped into a HCl solution to generate CO_2 bubbles, so leading to the formation of pores in the structure of the material.

A further step can be done for the introduction of oxidized functional groups in the gel which consists in subjecting the hybrid material to a Fenton reaction by adding it to a solution of FeCl_3 and H_2O_2 .

These materials showed the highest adsorption capacity towards ciprofloxacin and tetracycline in acidic condition, whereas in alkaline environment gels structure is destroyed and the adsorbed substances are released [37]. Moreover, it is important to note that, at different pH values, the substances to be adsorbed can be in anionic, cationic or, sometimes, zwitterionic form with significant effects on the adsorbing capacity of the material.

Another critical factor is the ionic strength. GO-alginate hydrogels seem to be less efficient at higher ionic strength [36], whereas the adsorption capacity of GO-alginate double network porous hydrogels increases with NaCl concentration [37]. This may be due to both the anionic form of the two antibiotics tested and the ion exchange between Ca^{2+} in the hydrogel beads and Na^+ in the solution, which change the gel porosity. On the other hand, lyophilization of these hydrogels generates aerogels with similar properties, but with a reduced loss of efficiency as the ionic strength increases [36].

For environmental application, the reusability is also an important feature that should possess this kind of materials. For example, double network porous hydrogels after 10 cycles of use still show a high adsorption capacity for antibiotics [37].

Graphene oxide-alginate fibers were also produced by the wet spinning method and tested in the removal of ciprofloxacin from water [38]. In this method, powder alginate is added into graphene oxide solution and the stirred mixture is then injected with a very little needle into a CaCl_2 solution.

In this case, ciprofloxacin adsorption capability increases with pH increasing (with a maximum at $\text{pH} = 5.9$) and with the concentration of graphene oxide, probably due to the higher number of functional groups and micro-channels formed by GO which increase surface complexation capability and ion exchange capacity [38].

2.1.2. Alginate-magnetite

In the second class of inorganic-alginate materials, *i.e.*, magnetic alginate- Fe_3O_4 composites, magnetic component allows an easy removal from the aqueous matrix and improves both their thermal stability and mechanical properties. Moreover, the catalytic properties of iron ions towards the Fenton-like reactions can be used in the degradation of pollutants.

Fe_3O_4 nanoparticles are usually synthesized by using a conventional co-precipitation method (Fig. 3), where Fe^{3+} and Fe^{2+} salts are dissolved in hydroxide solution and shaken under an inert atmosphere.

Even this kind of hybrid materials can be synthesized in form both of fibers and core-shell nanoparticles. In the first case, wet spinning method described above can be used, both squeezing Fe_3O_4 /alginate mixture into CaCl_2 solution, and enfolding alginate solution into CaCl_2 before putting the fibers in contact with Fe_3O_4 nanoparticles [39]. On the contrary, hybrid nanoparticles were prepared by dispersing Fe_3O_4 into sodium alginate solution and then sonicating it [40]. The different modalities proposed for the synthesis of these hybrid materials are summarized in Fig. 3.

Alginate- Fe_3O_4 fibers were tested for the removal of ciprofloxacin and norfloxacin. In this case, adsorption capacity was higher in acidic conditions ($\text{pH} = 3$) since the charge repulsion between ionized COO^- groups are lower and intermolecular hydrogen bonding contributes to a greater extent to the stability of the hydrogel structure [39]. In this way a shrinkage of the polymeric network happens and Fe_3O_4 particles are exposed on the fibers surface. On the other hand, this material appears not to be stable in basic condition. Indeed, above $\text{pH} = 9$, cation exchanges between Ca^{++} and Na^+ , K^+ or NH_4^+ , that are non-gelling ions, can occur causing the destruction of fiber structure. It is interesting to note that the adsorption capability of the magnetic alginate- Fe_3O_4 fibers seems to be mainly due to the presence of iron oxide and not to the presence of alginate; indeed, the polar surface of Fe_3O_4 may give interactions with the polar groups present in the ciprofloxacin. However, alginate allows an easy separation of contaminants from solution, preventing the agglomeration of magnetic nanoparticles and ensuring the reusability of the hybrid material after washing of the fibers with pure water several time, soaking in MilliQ water for 24 h, and drying at 50°C [39].

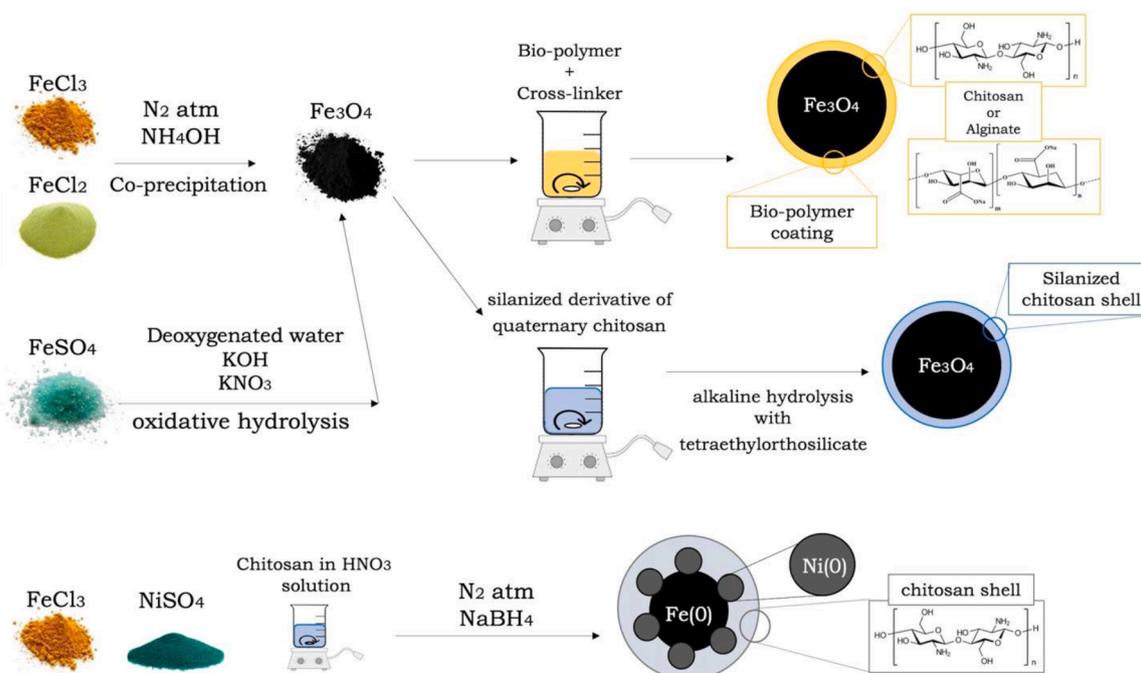


Fig. 3. Summary of methods for the synthesis of chitosan-alginate/ iron-based nanoparticles.

The case of alginate/Fe@Fe₃O₄ core/shell structured nanoparticles is more interesting because the presence of the iron-based core gives additional degradative properties to the material towards organic pollutants. In the literature, the cleavage of hydrogen peroxide, and the generation of reactive oxygen species catalyzed by Fe₃O₄ nanoparticles, was reported [41–43]. In the case of norfloxacin, it is hardly adsorbed on the surface of the hybrid material, but its complete removal was achieved in the presence of 0.4 g/L of hybrid nanoparticles at pH 3.5–6.5; its degradation proceeded through a defluorination pathway and the subsequent adsorption of the reaction products [40].

2.1.3. Alginate-MOF

A third class of alginate-inorganic hybrid materials includes metal organic frameworks (MOFs). MOFs are a class of crystalline materials consisting of metal centers and organic ligands self-assembled through coordination bonds to form network structures [44]. They are characterized by ultrahigh surface areas, thermal and mechanical stabilities, large pore volumes, excellent host-guest chemistry, and adaptable functionalities [45]; these properties make them useful in different fields, such as catalysis, drug delivery, energy storage, sensing, separation and remediation [46]. Incorporation of MOFs into three-dimensional polymer matrices is commonly used to obtain MOFs in spherical form or to immobilize them into hydrogels. For this purpose, alginate-MOF based hydrogel have been prepared following both one-step and two-step methods, and tested in the removal of tetracycline [47]. Results confirm that this kind of hybrid material exhibits excellent adsorption capacity and good reusability.

2.2. Chitosan

Chitosan is an amino polysaccharide, which is obtained from deacetylation of chitin (poly-N-acetyl-D-glucosamine) [48]. It is characterized by biodegradability, biocompatibility, hydrophilicity, non-toxicity, antimicrobial activity, low immunogenicity, inexpensiveness and accessibility [49].

Chitosan has been proved as a promising environmentally friendly adsorbent material and has been extensively used for the removal of dyes and heavy metals from aqueous solutions [50–52]. Furthermore, some studies reported the successful use of chitosan for the adsorption of emerging contaminants, such as pharmaceutical compounds [53,54], due to the presence of amino and hydroxyl groups capable of interacting with different types of molecules.

Chitosan can be employed as such for the synthesis of organic-inorganic hybrid materials [55]. Magnetic cross-linked chitosan nanoparticles have been easily prepared by adding chitosan, Fe₃O₄ magnetic nanoparticles, paraffin and glutaraldehyde into acetic aqueous solution and tested for the removal of diclofenac, carbamazepine and clofibrac acid. As mentioned above, pH values affect the surface properties of the adsorbent but also the adsorbate speciation in solution. In this case, sorption capacities for both clofibrac acid and diclofenac dropped when pH was beyond 7–8, and the highest removal efficiencies (59% and 98%, respectively) were obtained around pH = 4. Moreover, the ionic strength greatly affects the adsorption of clofibrac acid while do not change the sorption pattern of chitosan towards diclofenac, showing as the presence of ions can also affect the adsorption by changing the state of the ionizable groups of the adsorbate.

Another environmental factor, which needs to be considered, is natural organic matter (NOM). NOM is a complex matrix which includes organic substances, such as humic and fulvic acids; it can inhibit the binding sites on chitosan by competing with target compounds. For this reason, the magnetic chitosan should be modified again to get rid of the influence from NOM and use it in real waters.

Chitosan acts as an adsorbent thanks to the presence of amino and hydroxyl groups which make it possible to interact with different types of molecules. These groups also allow chitosan to be chemically modified to broaden its spectrum of action against a wide range of

contaminant and to obtain interesting hybrid materials. Grafting reactions lead to the introduction of new functional groups which make the biopolymer selective and with better adsorbing capacity, while cross-linking, usually made with glutaraldehyde, improves its resistance to extreme pH values [56].

Many recent environmental studies have been focused on the removal of pharmaceuticals from water. Since drugs and their metabolites are characterized by different physical and chemical properties, in particular hydrophilicity/hydrophobicity and pK_a, specific functional groups were introduced on chitosan surface to activate this biopolymer toward anionic or cationic compound. To make chitosan a specific adsorbent for cationic emerging contaminants, it is necessary to introduce anionic functionalities on its surface. Kyzas *et al.* reported the introduction of sulfonate groups by adding chitosan to a dichloroacetic acid/formamide solution, followed by the addition of a complex of chlorosulfonic acid and dimethylformamide [57]. Likewise, N-(2-carboxybenzyl) groups were introduced by adding 2-carboxybenzaldehyde, or acrylic acid groups were inserted by adding acrylic acid and potassium persulfate, as initiator for the polymerization, to chitosan dispersed in acetic acid solution [56,58].

Grafted chitosan can be used for the synthesis of inorganic-organic hybrid material by coupling it with GO. The graphene oxide/poly (acrylic acid) grafted chitosan nanocomposite was synthesized by adding glutaraldehyde and GO in alkaline condition and tested for the biosorption of pharmaceuticals such as dorzolamide from water [56]. It showed the utmost adsorption capability at pH = 3, while at higher pH values its performance decreases due to the presence on one side of –OH, –COOH and epoxy groups on the surface of GO, and on the other side of –OH, –NH₂ and –COOH groups on grafted chitosan's surface. This material shows a better performance when increasing temperature and it seems to be a promising candidate for a real application since only a 10% loss of efficiency was observed after 10 cycles of use.

Kyzas *et al.* [56] also investigated the mechanism of adsorption. It seems that the drug forms an amorphous nanodispersion within the adsorbent's matrix, probably caused by the strong interaction between the pharmaceutical compound and the hybrid material. It is interesting to note that in this case a real chemical bond is formed; in fact, in the FTIR spectrum a decrease in the intensity of the carboxyl groups peak at 1735 cm⁻¹ and the appearance of the band at 1660 cm⁻¹, attributable to the amide formation, was observed. In addition to the adsorption, the formation of bonds between the materials and the target molecules makes the material more efficient in removing the drug, although this mechanism could compromise the long-term regeneration of the material itself.

Recently other interesting materials with high affinity for anionic drugs have been developed and in a lot of cases they have been coupled with magnetic substrate to improve their removal and reusability. N-(2-hydroxypropyl)-3-trimethylammonium chitosan chloride is a quaternary derivative of the polysaccharide chitosan which can be obtained by adding glycidyltrimethylammonium chloride into chitosan previously dissolved in acetic acid solution under inert atmosphere [59]. It is characterized by the presence of a positive charge introduced by quaternization of amino group, as well as N,N,N-trimethylchitosan, which is studied for biomedical application, in particular as absorption enhancer in drug delivery [60].

These chitosan derivatives have been employed in the synthesis of hybrid material with a magnetic core and chitosan-based shell (Fig. 3). The coating step is often preceded by the synthesis of the alkoxy silane derivative, which is generated by the reaction with the silane coupling agent 3-(triethoxysilyl)propyl isocyanate (ICPTES). In literature two different coating methods were reported by Soares *et al.*: a two-step method [61] and a one-step sol-gel method [62]. In the first one, the initial step is the magnetic Fe₃O₄-core synthesis, carried out by alkaline oxidative hydrolysis of a Fe(II) salt under nitrogen stream. Successively, the magnetite core is encapsulated into amorphous silica shell by alkaline hydrolysis of a mixture of the alkoxy silane derivatives of chitosan

and tetraethyl orthosilicate (TEOS). The one-step sol-gel method consists in the hydrolytic co-condensation of a mixture of TEOS with the alkoxysilane derivatives of chitosan, carried on in the presence of the magnetic nanoparticles.

These hybrid materials were used for the adsorption of pollutants negatively charged in water at natural pH, such as diclofenac and sulfamethoxazole. As describe above, pH affects both the surface charge of the magnetic material and the compound present in the solution (depending on their pK_a). Focusing only on the adsorbent material, the adsorption capacity increases at lower pH values, following the trend of surface charge (i.e., surfaces more positively charged adsorb more negatively charged compound), while in alkaline condition the surface of the sorbent is negatively charged and an electrostatic repulsion towards other negative charges occurs. To evaluate this aspect with different pollutants it is important to know the zeta potential of the material.

Trimethylchitosan/siloxane-hybrid coated Fe_3O_4 nanoparticles were reused for several adsorption/desorption cycles in the removal of the contaminant (namely sulfamethoxazole), but a gradual decrease in drug adsorption in consecutive cycles was observed [62].

Zhou *et al.* [63] tried to synthesize an adsorbent capable of removing simultaneously hydrophilic and hydrophobic emerging contaminants and, at the same time, easily separable and regenerable. They developed a magnetic interpenetrating network of N-isopropylacrylamide/chitosan hydrogel. N-isopropylacrylamide was cross-linked by free radical polymerization in the presence of chitosan, N,N'-methylenebisacrylamide, glutaraldehyde and Fe_3O_4 particles previously synthesized by coprecipitation of $FeSO_4$ and $FeCl_3$. This hybrid material was tested against sulfamethoxazole (a hydrophilic antibiotic) and bisphenol A (a hydrophobic endocrine-disrupting compound) and the results showed that the optimal pH for maximum adsorption is in the range 5–9. As the adsorbent dosage was increased, the removal efficiency was enhanced, while the adsorption capacity per gram of adsorbent decreased since, with a higher adsorbent dosage, more adsorption sites are available but not all of them are fully utilized. An increase in ionic strength results in an inhibition of sulfamethoxazole adsorption, while it has no adverse effect on bisphenol A. Indeed, it enhances its adsorption probably due to the salting-out effect. The presence of other substances, such as inorganic ions and natural organic matters, does not influence the adsorption of hydrophobic drugs, while the adsorption of the hydrophilic one is affected by the competition with other anions. Therefore, the use of these hybrid hydrogels in real water matrices should be reconsidered. The regenerated hydrogel could be successfully reused for at least 5 cycles.

It is possible to produce chitosan-based hybrid materials capable of adsorbing and degrading the pollutants by means of a synergistic action between chitosan and the inorganic part, which can act as catalyst for oxidative degradation reactions. This is the case of the hybrid materials developed by Nisticò *et al.* [64], which tried to remove diclofenac from water by using magnetic materials containing chitosan. These materials have been prepared *via* coprecipitation synthesis starting from iron(II) and iron(III) inorganic salts in the presence of chitosan (acting as stabilizers of the iron-containing phase) and ammonium hydroxide. They can act as adsorbent when working in the dark and without hydrogen peroxide, while in presence of H_2O_2 in stoichiometric amount and under irradiation they can significantly reduce the diclofenac concentration. This effect was attributed to a photo-Fenton process, running despite the mild pH values used. The performances of these materials seem enhanced in experiments under simulated solar light, reasonably due to the large number of NH_2 groups capable to play some role in the iron availability.

Some pharmaceutical compounds, such as ciprofloxacin, pyrimethamine or sulfadiazine, are able to form strong complexes with multivalent metal ions. The stability of these complexes is greatly dependent on the nature of the metal ion involved and on the environmental conditions. This interaction between drugs and metals has been studied for

environmental application based on the possibility of immobilizing metals into chitosan-based matrices.

Chitosan contains nitrogen atoms, which can act as electron-donors, therefore this biopolymer can form polymer-metal complexes with many metal cations [65,66]. These complexes can be synthesized by adding cross-linked chitosan, for example in form of beads, to an aqueous solution of metals maintained under stirring to yield chitosan-metal complexation [67]. More recent synthetic procedures were carried out by dissolving chitosan in a metal ion aqueous solution [65], then spray-dried and cross-linked with glutaraldehyde to ensure the spherical shape of the particles [68]. It is important to take into consideration that the complexation capacity of chitosan towards metal ions is strongly affected by the pH of the solution, which must avoid the formation of positively charged nitrogen atoms (unfavourable for complexation).

Vieira *et al.* [67] used this hybrid material, synthesized with Cu(II) as metal at pH = 6, for pyrimethamine and sulfadiazine adsorption with promising results, as well as Rodrigues *et al.* [65] synthesized chitosan-iron (II and III) and chitosan-zinc particles at pH = 5 for ciprofloxacin adsorption. In the latter study was reported that drug initial concentration affects only Fe(III) and Zn(II) based nanoparticle equilibrium time, while for Fe(II) based particle it affects only the adsorption process. Indeed, an improvement of ciprofloxacin uptake was observed when its initial concentration increases. Moreover, no significant adsorption improvement can be observed for longer contact times. This study highlights the important role of metals which enhance equilibrium uptakes and adsorption yields. An important factor is the oxidation state of the metal which can affect the uptake mechanism and the shape of the adsorption isotherms.

Another way reported in literature for employ chitosan in metal immobilization is the synthesis of cryogels. Privar *et al.* [69] prepared supermacroporous cryogels starting from N-(2-carboxyethyl)chitosan and using hexamethylene diisocyanate as cross-linking agent. The mixture was put into plastic tubes, kept frozen, removed from tubes, washed, cut to cylinders, and dried in the vacuum oven to obtain monolith cryogels. The metal-chelated cryogel beads were obtained by adsorption of metal ions (Cu(II) and Al(III)) on the cryogel. Results showed that introduction of metal ions into the cryogel strongly enhance the efficiency of ciprofloxacin uptake which is > 90% in the pH range 7–10. At these pH values the electrostatic interaction between the surface of cryogels and ciprofloxacin is not efficient, so uptake efficacy can be related only to the metal-chelation effect. An important aspect of these materials is that there is a no significant metal release in water. In addition, they can be regenerated with NaOH solutions without loss in ciprofloxacin uptake efficacy.

In other kinds of chitosan-metal hybrid materials, the biopolymer was used as stabilizer of bimetallic nanoparticles [70]. Zero-valent iron nanoparticles have been recently studied for environmental remediation of antibiotics [71,72], dyes [73] and heavy metals [74–77]. They are characterized by large specific surface and high reactivity that can cause agglomeration or reaction with the surrounding media, resulting in a loss of reactivity. To solve this problem a possible strategy is to incorporate a second metal such as Pd or Ni, so obtaining bimetallic nanoparticles, further stabilized using chitosan.

The synthesis reported in several studies is carried out using a liquid-phase reduction method with chitosan as a stabilizer material [70,74,78]. Weng *et al.* [70] used chitosan-Fe/Ni nanoparticles to remediate water contaminated by amoxicillin. What emerges is the ability of this material to reduce the drug which, however, competes with metals dissolved into the solution.

2.3. Cellulose

Cellulose is the most abundant bio-based material from the biosphere and constitutes the main component of plant fibers, giving the plant rigidity [79]. It is a linear polysaccharide with long chains that consists of β -D-glucopyranose units joined by β (1 \rightarrow 4) glycosidic linkages [80].

Cellulose is widely studied thanks to its structural characteristics that comprise the presence of primary and secondary hydroxyl groups (at C-6 and at C-3 or C-4, respectively) that allow its use in different fields thanks to their hydrophilic character.

For environmental applications, the use of cellulose as adsorbent for the removal of aquatic pollutants has been widely reported in literature [79,81,82]. Adsorbent can be constituted by cellulose as it is or can be synthesized starting from cellulose derivatives obtained through chemical modifications.

In recent years nanocellulose has particularly attracted the researchers' interest. Cellulose nanomaterials encompass a wide spectrum of nano-scale cellulose-based particles having various shapes, sizes, surface chemistries and properties. Two main categories can be identified: nanostructured materials (cellulose microfibrils and microcrystalline cellulose) and nanofibers (cellulose nanocrystals, cellulose nanofibrils and bacterial cellulose) [83]. They exhibit unique characteristics due to their nanoscale size, fibril morphology and large surface area [84].

Many recent studies are focused on coupling cellulose, mainly in form of nanomaterials, with graphene oxide in order to obtain hydrogels, aerogels, or membranes able to remove a wide range of emerging pollutant from water through different mechanisms as π - π stacking, hydrogen bonding and electrostatic interactions.

Aerogels can be easily obtained by mixing graphene oxide and nanocellulose in water followed by ultrasonication, freezing and lyophilization. Cellulose nanofibrils can be employed for this synthesis [85], and the resulting hybrid material possesses interconnected 3D network microstructure, in which GO nanosheets were intimately grown along fibrils through hydrogen bonds. Their adsorption capability toward different classes of antibiotics follows the sequence: Tetracyclines > Quinolones > Sulfonamides > Chloramphenicols > β -Lactams > Macrolides. This behaviour can be explained considering structures and different amounts of hydroxyl groups that can interact with adsorbent surface.

Environmental conditions affect adsorption capabilities of aerogels. The adsorption decreases both with increasing pH, indicating that it depends on the aerogels surface charge, and the temperature, showing that it is an exothermic process. In addition, aerogels are porous material which can swell at high temperature with a consequent reduction in pores volume and in adsorption capacity.

An advantage of this kind of aerogels is the reusability. In fact, after alkaline desorption, they can be freeze-dried under vacuum and reused for 10 cycles [85].

Hydrogels can be obtained by mixing GO and nanocellulose in water and heating. Usually, GO self-assembly sponges are characterized by the lack of interconnectivity between pores and this contribute to the decrease in specific surface area. Addition of nanocellulose provides a robust scaffold to GO sponge structure allowing for a hybrid material ultra-strong and with a hierarchical pore structure and exceptional specific surface area.

Yousefi *et al.* also introduced Vitamin C in order to partially reduce graphene oxide and obtained a hierarchical structure of interconnected pores, which includes also millimeter-sized pores and micron-sized pores [86]. They tested their nanocrystal sponges toward sulfamethoxazole, tetracycline, diclofenac, 17- α -ethynylestradiol and Microcystin-LR via different cycles of adsorption/desorption. The results show that the adsorption capability only slightly decreases after each regeneration allowing a good reusability of the material.

In a very recent study [87], cellulose nanocrystals were incorporated into graphene oxide membranes with the purpose of employing them for water treatment not only for emerging contaminant removal, but also for maintaining useful nutrient and producing high-quality water directly usable in agriculture. For the membrane synthesis, GO nanosheets and cellulose nanocrystals were deposited onto a polyvinylidene fluoride support membrane via vacuum filtration. The resulting material has an increased surface hydrophilicity and a negative surface charge,

an enhanced crumpling surface structure, and an expanded GO structure for increased water transport. The negative surface charge ensures the electrostatic repulsion toward negatively charged pollutant such as sulfamethoxazole and levofloxacin, instead positively charged molecules such as norfloxacin could be adsorbed. In addition, hydrophobic repulsion of contaminant occurs but play a less significant role in exclusion of pollutant.

Cellulose-based hybrid materials can be also obtained starting from cellulose derivatives such as Carboxymethylcellulose (CMC). This cellulose-derivative is characterized by the presence of -OH and -COOH functional groups that can be a good starting point for obtaining compact aerogels. These 3D network structures can be used as support for metal organic frameworks (MOFs.), as already described for alginate in Section 2.1, or used for remediation purposes. In the literature, the removal of tetracycline from water using three-dimensional CMC aerogels decorated with Ni/Co-MOF was reported [88]. This material was obtained adding aerogels into DMF metals salts solution and then freezing them. At pH = 6 it showed the maximum adsorption capability against this antibiotic, while at higher pH value both adsorbent and drug are negatively charged, resulting in electrostatic repulsion.

Hybrid organic-inorganic cellulose-based materials can also be involved in photocatalytic degradation of pollutants when the inorganic part is a photocatalyst. TiO₂ is a well-known and widely studied photocatalyst which can be employed in environmental remediation; in fact, many recalcitrant organic pollutants, such as tetracycline [89], benzodiazepine [90] or other pharmaceutical compounds present in wastewaters [91] are photodegraded under UV-A or visible light irradiation using titanium dioxide. Usually, TiO₂ is employed in nanoparticle form in order to enhance its contact with the organic substrate; however, the removal of nano materials from aqueous matrices is not easy. For this reason, several studies focused on the research of good host material for this photocatalyst that can improve the stability, retain the special morphology, and control the growth of nanoparticles [92].

Films, microsphere, hydrogels, aerogels and monoliths are some of the possible hybrid materials that can be synthesized for this purpose:

- Cellulose/TiO₂ films can be easily obtained by sol-gel method from the hydrolysis of a precursor TiO₂ sol solution in the regenerated cellulose films prepared on the basis of cellulose dissolution at low temperature and successfully employed for phenol degradation under UV light [92].
- Cellulose/TiO₂ aerogels can be prepared by the *in situ* synthesis of TiO₂ nanoparticles in a cellulose matrix at a mild temperature which consist in the introduction of a precursor (tetrabutyl titanate) into cellulose hydrogels, subsequently converted into alcohol gels and then put into an acetic acid vapor atmosphere and hydrolysed [93].
- Cellulose/TiO₂ microsphere composites can be obtained by a one-step phase separation method using cellulose xanthate aqueous solution and sodium polyacrylate aqueous solution heated up and then frozen, as reported by Nagaoka *et al.* [94]. They show a higher efficiency in photodegradation of acetaldehyde than TiO₂ nanoparticles due to the organic pollutant concentration around the TiO₂ anchored on the composite surface.

In literature it is reported the application of cellulose/TiO₂ hybrid materials for the decomposition of emerging pollutants, such as paracetamol, activated by solar light [95]. In this study, an in-flow purification water system was developed. Cellulose nanofibrils (CNFs) were impregnated with TiO₂ nanoparticles using water as a solvent to obtain hybrid CNF/TiO₂ monoliths with 98% porosity. 30% of the paracetamol was degraded after 150 min due to the action of *in situ* generation of strongly oxidizing hydroxyl radicals (\bullet OH) by TiO₂ nanoparticles upon exposure to sunlight. In this case, cellulose has a support role, which prevent the release of particles in water and, at the same time, allows an easy handling and reuse of the photocatalytic membrane.

Graphitic carbon nitride (g-C₃N₄) could be a promising alternative to

TiO₂ as a conjugated semiconductor activated by visible light and thanks to its excellent photocatalytic performance for hydrogen formation, environmental decontamination and organic synthesis [96,97]. Despite this, also C₃N₄ present some drawbacks for its application, such as poor dispersion in water, easy aggregation and difficulty in recycling. Its immobilization on an appropriate support is an effective way to solve these problems and cellulose is a good candidate for this purpose.

Often reinforcing components or cross-linking points are introduced into the cellulose network to improve its mechanical component. Cellulose aerogels enhanced by cross-linked polyester fibers have been prepared by Chen *et al.* [98], following a three consecutive steps synthesis: dissolution, regeneration and freeze-drying. They have been tested against sulfaquinoxaline, carbamazepine and sulfadiazine, also taking into account the influence of various compounds that are present in wastewater. Addition of inorganic ions has a negligible effect on drug degradation, chloride ion is the only exception; it restrains the formation of hydroxyl radicals negatively affecting the reduction of pollutants. No significant interference was noted even when organic compounds such as urea and PEG (polyethylene glycol) were included in the reaction system, confirming that this kind of hybrid material shows a good photocatalytic performance also in the presence of a complex matrix. In addition, it exhibits a good reusability maintaining a high removal efficiency also after five recycle times.

2.4. Summary on CECs removal by biopolymer-based hybrid materials

To the best of our knowledge, polymer-based hybrid materials have been applied to the abatement of around twenty emerging pollutants, as summarized in Table 1. As largely discussed in the previous sections, the removal of these substances occurs mainly by adsorption after introduction of the adsorbent into water solution, and the research aimed at optimizing three factors: (i) good adsorbing capacity; (ii) easy separation of the material after use; (iii) easy and efficient reuse through adsorption / desorption cycles.

For some CECs, different studies indicate that the choice of diverse biopolymers and the addition of more components can improve the adsorbing properties. This is the case of diclofenac, where the promising results obtained by Zhang *et al.* in 2014 by using magnetic chitosan [55], were further improved in 2019, when Soares *et al.* synthesized magnetic nanoparticles coated with shells of a quaternary chitosan siliceous hybrid material [62]. In other cases, such as tetracycline, a significant improvement in the adsorption was also obtained by changing the structure of the material, passing from various types of hydrogels [37, 47,86] to aerogels [88].

Moreover, addition of a photocatalyst permitted to obtain better results as by coupling adsorption and photo-induced degradation. Nisticò *et al.* observed a synergistic removal of 80% of diclofenac in 60–90 min by applying this approach and its complete disappearance in 60 min when H₂O₂ was added to the system [64]. Similar results were also obtained for carbamazepine, sulfadiazine and sulfaquinoxaline by Chen *et al.* [98], and for paracetamol by Lucchini *et al.* [95].

These last results justify further studies to prepare new materials with the ability to simultaneously remove and degrade CECs. The studies pursuing this goal using enzymatic catalysis for the degradation of CECs are the subject of the second part of this review.

3. Enzymes-based hybrid materials

Attention to environmental issues is ever increasing and this is also reflected on the development of new biological remediation techniques that are competitive with traditional strategies but with a lower

environmental impact. Enzymes are considered highly efficient and green biocatalyst that can reduce the number of synthesis steps, use of toxic solvents, and activation energy [99].

Peroxidase and laccase are the most employed enzymes in bioremediation of wastewater because they can catalyse the oxidative degradation of many organic pollutants [100,101]. They have been successfully applied for dyes removal [102,103], degradation of pharmaceuticals and xenobiotics [104] and treatment of industrial effluents [105].

Peroxidases are heme-containing enzymes usually activated by hydrogen peroxide and divided into three classes according to the origin: (i) Class I, intracellular peroxidases, (ii) Class II, secretory fungal peroxidases, (iii) Class III, secretory plant peroxidases [106]. Some of the most studied peroxidases such as horseradish peroxidase (HRP) and soybean peroxidase (SBP) belong to Class III. Instead, laccases are multi-copper oxidases which can catalyse oxidation of substrates in the presence of molecular oxygen and that can be found in plants, fungi, and bacteria [107].

Enzymes in free form have a very high activity, but they are not usually stable in solution and can be easily inactivated; in addition, they are also characterized by high costs [108]. Several immobilization techniques have been developed to improve their stability, facilitate their reuse and reduce the costs [109–111]. However, in the immobilized form the enzymes generally lose some of their activity although they are more stable, but a synergistic action can be established between the enzyme and the support, thus obtaining real hybrid materials.

In recent years, different hybrid enzymatic-inorganic materials have been developed using metal oxides as inorganic part. This also allows exploiting the properties of the oxides in addition to the enzymatic action. Moreover, a particular new class of immobilized enzymes, the so called “enzymatic nanoflowers”, characterized by higher enzymatic activity, were obtained in the last years by coprecipitation of enzymes with Cu(II) or Fe(III) salts. Both these two groups of hybrid materials are reviewed in the following sections.

3.1. Enzymes-oxides

The first examples of this kind of hybrid enzymatic-inorganic materials are silica monoliths functionalised with different enzymes and oxides. Calza *et al.* [108] immobilized soybean peroxidase (SBP) extracted from soybean hulls on silica monoliths previously functionalised with (3-Aminopropyl)triethoxysilane (APTES) and glutaraldehyde and then used this material with TiO₂ to couple enzymatic action with the photocatalytic process. Through TiO₂ irradiation a production of hydrogen peroxide, used by SBP to catalyse oxidation reaction, was obtained. Results shows that by this hybrid approach also contaminants hardly oxidized by the SBP, such as carbamazepine, can be efficiently removed with a kinetic constant for the enzymatic-photocatalytic degradation 5 times higher than the photocatalytic process alone. Even if the reactions catalysed by immobilized SBP are slower than the corresponding degradation by SBP in solution, the possibility of reusing these catalysts is particularly appealing for applications to real wastewaters.

With a similar approach, Ji *et al.* [112] immobilized laccase from crude enzyme extracts of *P. ostreatus* culture on titania nanoparticles, and tested the material toward bisphenol A and carbamazepine in a hybrid membrane reactor. A rapid removal is observed for bisphenol A, with 90% of abatement achieved within 6 h of reaction using the immobilized enzyme, while the more recalcitrant carbamazepine was only slightly abated (10%) in a single-compound solution even after 48 h reaction. Carbamazepine degradation can be significantly improved in

Table 1
Emergent pollutants removal by biopolymer-based hybrid materials.

Emerging contaminant	Hybrid materials	Results	Reusability	Authors / Reference
amoxicillin	chitosan stabilized bimetallic Fe/Ni nanoparticles	93% abatement of a 60 mg/L solution in 60 min	3 cycles	Weng et al. 2013 [70]
bisphenol A	cellulose nanofibril/ Graphene Oxide hybrid aerogel	adsorption of 230.7 mg/g	10 cycles	Yao et al. 2017 [85]
carbamazepine	magnetic poly(N-isopropylacrylamide)/chitosan hydrogels	adsorption of 49-58 mg/g (60% efficiency max)	5 cycles	Zhou et al 2019 [63]
	magnetic cross-linked chitosan nanoparticles	no adsorption	-	Zhang et al. 2014 [55]
	g-C ₃ N ₄ @cellulose aerogel enhanced by cross-linked polyester fibers	total photochemical abatement in 120 min	5 cycles	Chen et al. 2019 [98]
chloramphenicol	cellulose nanofibril/ Graphene Oxide hybrid aerogel	adsorption of 421.2 mg/g	10 cycles	Yao et al. 2017 [85]
ciprofloxacin	hydrogels sodium alginate/GO beads	adsorption of 86,12 mg/g (hydrogels), or 55,55 mg/g (aerogels)	-	Yu et al. 2016 [36]
	alginate/graphene single (GAS) and double (GAD) network porous hydrogel	adsorption of 344,8 mg/g (GAD) or 308,6 mg/g (GAS)	10 cycles	Zhuang et al. 2017 [37]
	fibers of graphene oxide/calcium alginate	adsorption of 39.06 mg/g (with 6% in GO)	-	Wu et al 2013 [38]
	Cu(II) and Al(III)-chelated cryogels of N-(2-carboxyethyl)chitosan	adsorption of 280 mg/g with Cu(II) or 390 mg/g with Al(III)	-	Privar et al 2019 [69]
	magnetic alginate-Fe ₃ O ₄ hydrogel fibers	adsorption of 0.15–0.56 mg/g (in function of fibers type)	3 cycles	Konwar et al 2015 [39]
clofibrac acid	magnetic cross-linked chitosan nanoparticles	adsorption of 191.2 mg/g	-	Zhang et al. 2014 [55]
diclofenac	magnetic cross-linked chitosan nanoparticles	adsorption of 57.5 mg/g	-	Zhang et al. 2014 [55]
	magnetic quaternary chitosan hybrid nanoparticles	adsorption of 240.4 mg/g	-	Soares et al. 2019 [62]
	chitosan based magnetic materials	10-60% adsorption + 80% photodegradation in 90 min; photo-Fenton degradation close to 100% in 60 min	-	Nisticò et al. 2019 [64]
	reduced graphene oxide-cellulose nanocrystal sponges	adsorption of 129 mg/g	4 cycles	Yousefi et al. 2018 [86]
	graphite oxide/poly(acrylic acid) grafted chitosan nanocomposite	adsorption of 334 mg/g	10 cycles	Kyzas et al. 2014 [56]
dorzolamide	reduced graphene oxide-cellulose nanocrystal sponges	adsorption of 117 mg/g	4 cycles	Yousefi et al. 2018 [86]
erythromycin	cellulose nanofibril/ Graphene Oxide hybrid aerogel	adsorption of 291.8 mg/g	10 cycles	Yao et al. 2017 [85]
17- α -ethynylestradiol	cellulose nanocrystals incorporated into graphene oxide membranes	90,9% membrane rejection efficiency	-	Gao et al. 2021[87]
levofloxacin	reduced graphene oxide-cellulose nanocrystal sponges	adsorption of 22 mg/g	4 cycles	Yousefi et al. 2018 [86]
microcystin-LR	alginate/Fe@Fe ₃ O ₄ core/shell nanoparticles	total abatement in 60 min	-	Niu et al. 2012 [40]
norfloxacin	cellulose nanocrystals incorporated into graphene oxide membranes	97,2% membrane rejection efficiency	-	Gao et al. 2021 [87]
	titania-cellulose hybrid monolith	30% photodegradation in 150 min and 51% in 500 min	-	Lucchini et al. 2018 [95]
paracetamol	cellulose nanofibril/ Graphene Oxide hybrid aerogel	adsorption of 134.6 mg/g	10 cycles	Yao et al. 2017 [85]
pyrimethamine	chitosan containing complexed copper	adsorption of 22.4 mg/g	-	Vieira et al. 2007 [67]
sulfadiazine	chitosan containing complexed copper	adsorption of 25 mg/g	-	Vieira et al. 2007 [67]
	g-C ₃ N ₄ @cellulose aerogel enhanced by cross-linked polyester fibers	total photochemical abatement in 120 min	5 cycles	Chen et al. 2019 [98]
	trimethyl chitosan/siloxane-hybrid coated Fe ₃ O ₄ nanoparticles	adsorption of 42 mg/g	4 cycles	Soares et al. 2019 [61]
	cellulose nanofibril/ Graphene Oxide hybrid aerogel	adsorption of 228.9 mg/g	10 cycles	Yao et al. 2017 [85]
sulfamethoxazole	magnetic poly(N-isopropylacrylamide)/chitosan hydrogels	adsorption of 8 mg/g (max 90% adsorption efficiency)	5 cycles	Zhou et al 2019 [63]
	reduced graphene oxide-cellulose nanocrystal sponges	adsorption of 107 mg/g	4 cycles	Yousefi et al. 2018 [86]
	cellulose nanocrystals incorporated into graphene oxide membranes	74,8% membrane rejection efficiency	-	Gao et al. 2021 [87]
	g- C ₃ N ₄ @cellulose aerogel enhanced by cross-linked polyester fibers	2% adsorption + total photochemical degradation in 120 min	5 cycles	Chen et al. 2019 [98]
	cellulose nanofibril/ Graphene Oxide hybrid aerogel	adsorption of 219.6 mg/g	10 cycles	Yao et al. 2017 [85]
sulfaquinoxaline	alginate/graphene single (GAS) and double (GAD) network porous hydrogel	adsorption of 290.70 mg/g (GAD) or 247.52 mg/g (GAS)	10 cycles	Zhuang et al. 2017 [37]
	cellulose nanofibril/ Graphene Oxide hybrid aerogel	adsorption of 238.5 mg/g	10 cycles	Yao et al. 2017 [85]
tetracycline	3D alginate-based MOF hydrogel	364.89 mg/g MA-M 302.32 mg/g AM-M	10 cycles	Zhuang et al. 2019 [47]
	reduced graphene oxide-cellulose nanocrystal sponges	adsorption of 149 mg/g	4 cycles	Yousefi et al. 2018 [86]
	CMC aerogels decorated with Ni/Co-MOF	adsorption of 624.9 mg/g	-	Yang et al. 2019 [88]
	cellulose nanofibril/ Graphene Oxide hybrid aerogel	adsorption of 454.6 mg/g	10 cycles	Yao et al. 2017 [85]

the presence of bisphenol A, with 40% of removal after 24 h of treatment. Tests for reusability were carried out by running consecutive degradation cycles and the results showed that the removal of both bisphenol A and carbamazepine decreases gradually with a significant activity loss (over 75%) after five cycles.

In order to improve the reusability of these materials and to enhance their removal action toward emerging contaminants and metals, Pylypchuk *et al.* [113] synthesized core-shell magnetic submicro-particles with iron oxide core and silica shell as substrate for immobilization of different functions. The synthesized magnetite has been treated to obtain a silica shell and then functionalized with APTES, with diethylenetriaminepentaacetic dianhydride (DTPA anhydride), and finally with glutaraldehyde. These particles were used as support for immobilization of commercial laccase from *Trametes versicolor*. Each of these functions allows different actions: DTPA gives the particles activity towards metals, APTES is involved in enzymes immobilization and laccase is used to degrade organic pollutant.

This hybrid material was tested toward Cd(II), acetaminophen and diclofenac. Adsorption of cadmium ions was performed from a test solution containing 0.1 μM of Cd(II) and results show that the hybrid material was capable to remove metal ions from solution without any loss in enzymatic activity. During 10 adsorption cycles of Cd(II), the composite material revealed an average of 78% of metal removal from the solution. Heavy metal could be desorbed by the adding of nitric acid because immobilized laccase is stable under this acid environment up to pH 3 and does not decrease its activity. The removal of acetaminophen and diclofenac was tested both on single pollutants and on their mixture. The material was able to remove up to 99% of acetaminophen in 1 mg/mL solution in 18 h. Removal greater than 85% were reached for both contaminants in acetaminophen/diclofenac mixtures after contact with composite material for 18 h. When also Cd(II) ions are present in the mixture, a removal greater than 95% was achieved for both molecules. It seems that acetaminophen is polymerized by immobilized laccase and its by-products could be hydrophobic and be adsorbed on the magnetic adsorbent surface.

More complex hybrid materials were also synthesized and tested. Sarro *et al.* [114] combined soybean peroxidase and oxide nanoparticles with poly(styrene-co-maleic anhydride) nanofibers. ZnO nanoparticles, synthesized by the hydrothermal method, were dispersed into the polymer solution and coupled with SBP by adding the enzyme in the same solution or by dipping already formed fibers into a 1 mg/mL enzyme solution in PBS buffer at pH = 7.4. This hybrid material was tested against diclofenac, naproxen, iopamidol, imidacloprid, bisphenol A and 2,4-dichlorophenol. Experiments with SBP in aqueous solution confirm the good capability of peroxidases in the degradation of 2, 4-dichlorophenol and bisphenol A, whereas the abatement of the other compounds is slower. The photocatalytic efficiency of the pristine and cerium-doped ZnO was also evaluated and the results show that the Ce-ZnO system led to the fastest degradation of all compounds, in particular for iopamidol (the most recalcitrant compound). The role of cerium in zinc oxide is crucial in the formation of interfaces that seem to be the active site during the irradiation process. In the case of composite nanofibers, the best performance was achieved with the Ce-ZnO composite, which led to the complete abatement of diclofenac and 2, 4-dichlorophenol, 90% of naproxen, 85% of imidacloprid and 70% of iopamidol and bisphenol A within 24 h. The synergistic action is due to the generation of a greater concentration of highly reactive radicals, such as superoxide anions and hydroxyl radicals, during the photocatalytic process, with the formation of H_2O_2 , capable to activate the

catalytic cycle of SBP. Some tests were carried out in wastewater, where the synergistic effect is more remarkable; while the photocatalytic activity of the semiconductors is negatively influenced by the presence of dissolved organic matter in wastewater, which could act as a scavenger of radical species, the enzyme activity is less influenced by them.

An alternative way to provide *in situ* hydrogen peroxide is the electro-generation from oxygen in aqueous solution. The combination of enzymatic catalysis and electro-generation of H_2O_2 is called electro-enzymatic process; it was used in enzymatic fuel-cells or in synthetic processes [115], but also in the degradation of phenolic pollutants [116, 117].

To avoid problems, such as enzyme inactivation during the storage, some researchers have used hemin as catalytic site of mimetic enzymes used as peroxidase substitute [118]. In recent years, this molecule has been widely used in chemical sensors and electrodes coupled with graphene because it can accelerate the electron transfer between substrate and enzyme. This synergistic effect has been used for different purposes, such as colorimetric detection of single-nucleotide polymorphism [119], electrochemical biosensors for determining L-tyrosine [120] or specific oxidation of C—H bond [121].

Cheng *et al.* [122] proposed GO-hemin hybrid materials for the electro-enzymatic degradation of diclofenac. Graphene oxide, obtained from graphite powder, was dissolved in 2% solution of chitosan in acetic acid with commercial hemin to synthesize hybrid material. For the electrode preparation, graphite sheet was polished with emery papers, washed with distilled water, and dried with nitrogen gas. Graphite electrode surface was coated with graphene-hemin solution and exposed to air at room temperature to form a membrane electrode. This system was initially tested with a solution of methyl orange and Na_2SO_4 by applying a bias potential of -0.4 V. Results show that after 120 min of electroenzymatic treatment, 95% of methyl orange solution was decolorated. After these preliminary tests, the hybrid material was used to degrade diclofenac in similar conditions and the removal efficiency reached ca. 96% after 11 h of treatment, even if the efficiency decreases with high diclofenac concentration (> 20 mg/L).

3.2. Nanoflowers

Nanoflowers are particular hybrid organic-inorganic materials accidentally discovered some years ago by mixing copper(II) sulphate and bovine serum albumin in phosphate buffered saline (PBS) at pH = 7.4 and 25 °C [123]. In the original experiment, a stable precipitate appeared after three days from the mixture showing a porous flower-like structure. A similar procedure was then successfully applied to obtain different types of nanoflowers by using other metal ions and proteins [124–127] (Fig. 4).

The most relevant properties of nanoflowers are their stability and catalytic properties. In particular, enzymes containing nanoflowers, unlike most enzyme-based materials, seem to preserve or even enhance the enzymatic activity due to the positive interactions between the enzyme molecules, the effect of metal ions, and the great surface area of nanoflowers [124,128,129]. In some cases, the observed increase in enzymatic activity was high, as reported for example by Ocoy *et al.* which recorded an activity around 700% compared to the free enzyme [128].

Some oxidoreductive enzymes, such as laccases and peroxidases, were employed in the preparation of nanoflowers. One of the most used enzymes was horseradish peroxidase. The nature and morphology of HRP containing nanoflowers were studied by employing different

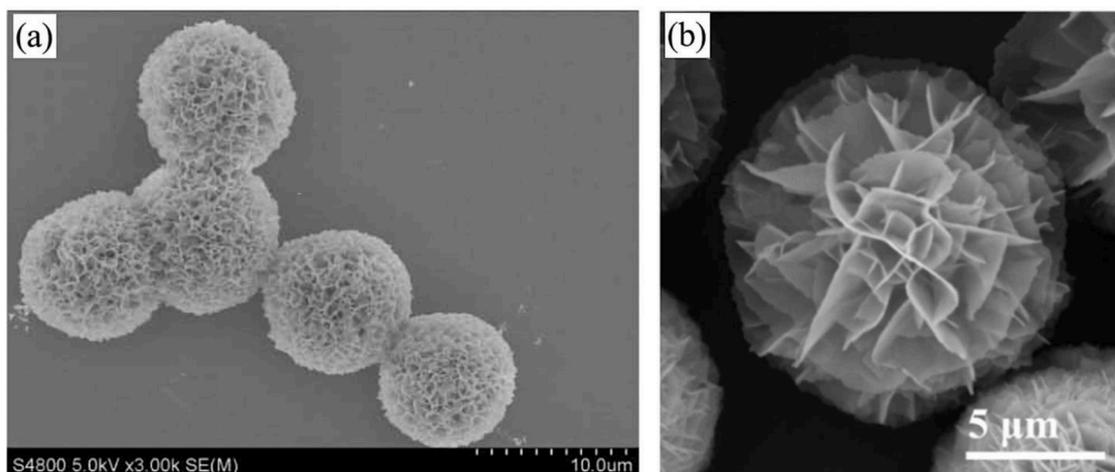


Fig. 4. SEM images of enzyme- $\text{Cu}_3(\text{PO}_4)_2$ hybrid nanoflowers: a) laccase (image reprinted with permission from reference [126]); b) horseradish peroxidase (image reprinted with permission from reference [125]).

techniques and their stability and activity were analysed in diverse conditions, confirming the positive effects due to the incorporation of the protein in the hybrid material [130]. Moreover, HRP was also employed for the preparation of nanoflowers in the presence of Fe(II) instead of Cu(II) ions [128]. In this case, a concomitant increase in stability was also recorded for nanoflowers stored 30 days at room temperature.

Furthermore, bi-enzymatic nanoflowers, containing both glucose oxidase and HRP, were prepared by Sun *et al.* aimed to obtain a colorimetric sensor for the detection of glucose [131]. The results showed that the proximity of the two enzymes greatly reduces the diffusion and decomposition of H_2O_2 produced by glucose oxidase and greatly enhances the sensitivity of glucose detection. An improvement of this system was recently proposed by Yuan *et al.*, where a hypersensitive sensor with a $0.5 \mu\text{M}$ limit of detection was obtained by replacing HRP with a peroxidase mimic peptide [132].

There are still a few examples of nanoflowers employed in the degradation of pollutants. Fang *et al.* obtained 80% removal of a 0.2 mM

2,4-dichlorophenol solution (with a residual activity around 58% after 6 reaction cycles) by using nanoflowers containing 2,4-dichlorophenol hydroxylase [133], whereas other authors observed the degradation of different dyes, such as malachite green (complete degradation of 25 mg/L dye solution by 1.5 g/L nanoflowers solution in 15 min) [126], crystal violet (40-100% removal of 2.5 mg/L dye solution in 8 days) and neutral red (20-100% removal of 7.5 mg/L dye solution in 8 day) [134], bromophenol blue, Coomassie Brilliant Blue R-250 and xylene cyanol (41-56%, 73-91% and 73-93% decolorization respectively in 48h) by laccase-based nanoflowers [135]. Similar results were also obtained by Rong *et al.* in the degradation of Congo Red, with 95% of decolorization of a 10 mg/L dye solution in 3 h [136], but in this case a peculiar procedure was used for the preparation of the materials. Indeed, in this study laccase hybrid microspheres were loaded on copper-phosphate nanoflowers synthesized on the surface of copper foils. Crystal violet complete degradation was also obtained by chloroperoxidase containing nanoflowers [137], whereas Turkish black radish peroxidase was used in the degradation of Victoria Blue dye obtaining more than 90%

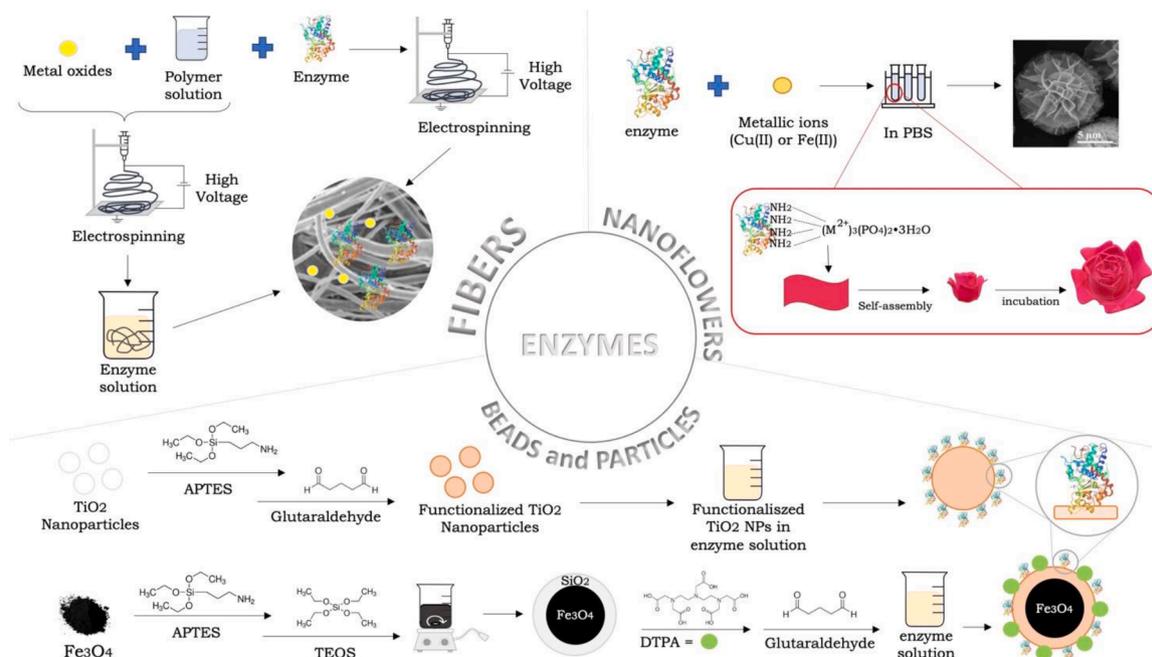


Fig. 5. Summary of methods for the synthesis of enzymes-based hybrid materials.

Table 2
Emergent pollutants removal by enzyme-based hybrid materials.

Emerging contaminant	Hybrid materials	Results	Reusability	Authors / Reference
carbamazepine	soybean peroxidase immobilized on silica monoliths and titanium dioxide	complete abatement in 60 min	-	Calza et al. 2016 [108]
bisphenol A	laccase immobilized on titania nanoparticles	40% abatement after 24 h	5 cycles	Ji et al. 2017 [112]
	laccase immobilized on titania nanoparticles	90% abatement after 6 h	5 cycles	Ji et al. 2017 [112]
	combined soybean peroxidase (SBP) and oxide nanoparticles with poly (styrene-co-maleic anhydride) (SMA) nanofibers	70% abatement in 24 h	-	Sarro et al. 2018 [114]
	laccase-loaded magnetic nanoflowers	total abatement of < 25 mg/L solution in 5 min	5 cycles	Fu et al. 2019 [139]
	laccase-based hybrid nanoflowers	93.2 % abatement in 8 h	8 cycles	Yang et al. 2021 [140]
	magnetic HRP-based nanoflowers	92/ abatement	8 cycles	Han et al. 2019 [129]
diclofenac	laccase Immobilized on Fe3O4/SiO2-DTPA Hybrid Nanocomposites	85% abatement in 18 h	-	Pylypchuk et al. 2018 [113]
	combined soybean peroxidase (SBP) and oxide nanoparticles with poly (styrene-co-maleic anhydride) (SMA) nanofibers	complete abatement in 24 h	-	Sarro et al. 2018 [114]
	integration of graphene-hemin hybrid materials in an electroenzymatic system	96% abatement in 11 h	-	Cheng et al. 2016 [122]
acetaminophen (paracetamol)	laccase Immobilized on Fe3O4/SiO2-DTPA Hybrid Nanocomposites	99% abatement in 18 h	-	Pylypchuk et al. 2018 [113]
naproxen	combined soybean peroxidase (SBP) and oxide nanoparticles with poly (styrene-co-maleic anhydride) (SMA) nanofibers	90% abatement in 24 h	-	Sarro et al. 2018 [114]
iopamidol	combined soybean peroxidase (SBP) and oxide nanoparticles with poly (styrene-co-maleic anhydride) (SMA) nanofibers	70% abatement in 24 h	-	Sarro et al. 2018 [114]
imidacloprid	combined soybean peroxidase (SBP) and oxide nanoparticles with poly (styrene-co-maleic anhydride) (SMA) nanofibers	85% abatement in 24 h	-	Sarro et al. 2018 [114]
2,4-dichlorophenol	combined soybean peroxidase (SBP) and oxide nanoparticles with poly (styrene-co-maleic anhydride) (SMA) nanofibers	complete abatement in 24 h	-	Sarro et al. 2018 [114]

decolorization in 1 h [138]. Moreover, bisphenol A was successfully removed (more than 90%) by Han *et al.* by using magnetic nanoflowers prepared adding a flower-like surface structure containing HRP on a core-shell made of magnetic composite microspheres [129]. Bisphenol A complete degradation was also obtained by laccase containing magnetic nanoflowers prepared by Fu *et al.* [139], whereas Yang *et al.* obtained similar results with succinic anhydride-modified laccase co-crystallized with Cu(II) phosphate [140].

3.3. Summary on CECs removal by enzyme-based hybrid materials

A summary diagram of the methods employed for the synthesis of enzyme-based hybrid materials is shown in Fig. 5. Despite the scarce number of studies currently available (Table 2), the use of these materials for the degradation of CECs is very interesting since the enzymatic degradation is usually obtained in milder conditions compared to the conventional chemical methods. Moreover, the combination of different processes permits a faster and more complete removal of these species and suggests that this approach could be successfully applied in the future for the degradation of other recalcitrant pollutants.

4. Conclusions

The management of wastewater and pollution of water resources has led to the development of new and more efficient methods for the treatment of CECs, especially considering the specific problems in the removal of these substances which are stable, recalcitrant to traditional methods and present in small concentrations. These new strategies aim to be both more sustainable for the environment and to reduce costs by using recycled and reusable sources for the synthesis of more performing hybrid materials.

In many cases, this approach led to the synthesis of hybrid materials showing improved adsorbing properties towards water pollutants. Moreover, to employ these materials in real situations, the influence of three fundamental factors must be taken into consideration: *i*) pH of the aqueous solution and pK_a of the substrates; *ii*) ionic strength, *iii*)

presence of Natural Organic Matter or other organic contaminants.

These three parameters can inhibit the removal of contaminants by competing with them for adsorption sites or can affect the structure of the material itself as in the case of alginate-based materials for which the presence of non-gelling ions leads to the destruction of the gel. The dissolved organic matter present in water can also act as a scavenger of radical intermediates and so can negatively affect photocatalytic activity of semiconductors. Furthermore, the organic fraction introduced in hybrid-materials often behaves as the adsorbent component, also following functionalization reactions aimed at increasing the affinity towards anionic or cationic contaminants, but in some cases it also acts as stabilizer for the inorganic fraction, *i.e.* in the case of magnetic alginate-Fe₃O₄ fibers [39].

The greatest interest was raised by hybrid materials that also possess degradative capacity due to the presence of photodegradative oxides, such as TiO₂, semiconductors activated by visible light, such as C₃N₄, or enzymes. The use of biological techniques in the environmental field is becoming more and more widespread and studies on enzymes for emerging contaminants treatments, as shown in Table II, are at present only a few but rapidly increasing. The main reasons for this growing interest are linked to the milder reaction conditions and the elimination of hazardous chemical solvents; in short, the use of enzymes directs water treatment towards approaches near to "green chemistry" objectives. Obviously, despite these encouraging aspects, the use of enzymes is hindered by their limited stability and, therefore, a compromise between stability and activity is required and it is the main goal of research of new immobilization techniques.

Reuse is a very interesting aspect that characterizes many of the hybrid materials described in this work and, in some cases, it is preceded by a regeneration step based on washing with pure water or buffered solution, treatments with alcohols (methanol or ethanol), strong acids or basis. However, only in a few studies the regeneration procedures were described in detail, therefore a discussion about this point has to be postponed in the future once more studies will be available. Nevertheless, it is important to underline that the choice of the solvent for hybrid materials regeneration is certainly related with the nature of the

material itself and the properties of contaminants adsorbed, but also with the environmental impact of the entire treatment. This latter aspect is relevant as one of the objectives of the development of new wastewater treatment techniques is to achieve the sustainability of the whole process.

This review highlights how, through a proper optimization of all the factors that affect the process, hybrid materials can be an alternative to traditional water treatment techniques, both in terms of effectiveness toward many emerging contaminants, and reusability, so becoming an important path toward the circular economy and green chemistry perspectives.

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.

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