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Desorption Strategies and Reusability of Biopolymeric Adsorbents and Semisynthetic Derivatives in Hydrogel and Hydrogel Composites Used in Adsorption Processes

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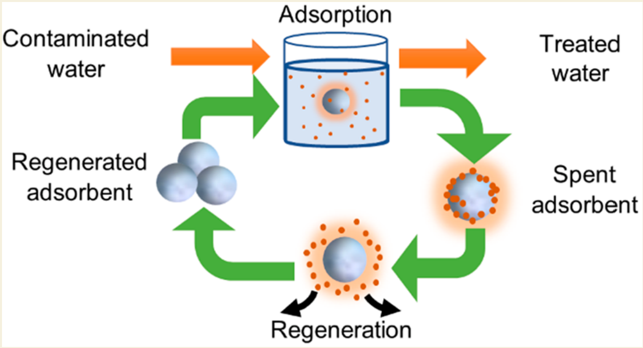
ABSTRACT: Adsorption is a promising technique for the removal of persistent contaminants, since it is a relatively cheap process with low energy requirements and does not produce secondary contamination. However, the large-scale implementation of an adsorption process usually involves a dual column process for either pressure swing or temperature swing operations. Therefore, the reusability of adsorbents is a key characteristic to consider and evaluate but is often overlooked during the development of new materials. To be reused, the adsorbent should successfully release the contaminant by a desorption or regeneration step without compromising the chemical and physical stability of the matrix. The efficiency of desorption/regeneration methods depends greatly on the chemical characteristics of the contaminants, the nature of the adsorbents, and the adsorption mechanisms responsible for the adsorbent−adsorbate interactions. This review focuses on the desorption strategies that have been used for the regeneration of biobased hydrogels and hydrogel composites, materials that have been successfully applied in the adsorption of wastewater contaminants. The strategies can be divided into chemical and physical methods. The chemical methods include the use of desorption agents, photocatalytic oxidation, and CO_2 bubbling; and the physical methods include thermal and ultrasonic treatments. These regeneration strategies have shown different efficiencies as well as specific advantages and drawbacks that need to be considered to select the most suitable method for a specific application.



KEYWORDS: *biopolymers, hydrogel composites, reusability, regeneration strategies, desorption, wastewater contaminants, desorption mechanism, chemical regeneration, physical regeneration*

1. INTRODUCTION

Water is a vital resource for mankind; however, anthropogenic activity has significantly affected its quality and availability. According to the WHO, around 829 000 people die every year from illness or infections related to drinking unsafe water.[1] To mitigate water stress, it is necessary to develop effective strategies to improve water quality, removing contaminants that have detrimental effects on humans, animals, and plants.

Different types of contaminants have been found in wastewater depending on the origin. Domestic/municipal wastewater usually contains contaminants, such as paper, household cleaners, detergents, garbage, and a high biological load. On the other hand, industrial, agricultural, and hospital/pharmaceutical wastewaters usually contain a wide variety of highly toxic organic and inorganic contaminants, for instance heavy metals, dyes, salts, pharmaceuticals, and agrochemicals, including various nitrogen and phosphorus species like nitrates and phosphates, to name a few.[2] These contaminants are of great concern due to their high persistence in the environment, their toxicity, and their ability to bioaccumulate in plants and fish. Exposure to these pollutants is normally associated with severe health problems, including metabolic syndromes, different types of cancers, and reproductive disorders in humans and animals.[3−6]

Wastewater pollutants have different chemical structures, functional groups, charge, solubility, hydrophilicity, thermal properties, and photostability; hence, their presence and

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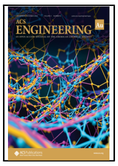

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persistency vary. Many of these chemical contaminants are persistent molecules with a low degradability. Therefore, different treatments are used in wastewater treatment plants for their elimination. Secondary and tertiary treatments are applied to either remove or degrade toxic chemicals with different efficiencies.[2] Many conventional methods like chemical precipitation, coagulation, electrocoagulation, and membranes are meant to remove contaminants; however, it has been observed that conventional wastewater treatments do not efficiently recover a great variety of emerging persistent pollutants.[7] Therefore, in the past decades, more sophisticated methods have been developed and adapted to efficiently degrade pollutants, methods like biological treatments and advanced oxidation processes (AOP) have been used, including strategies like Fenton reactions, gamma irradiation, photocatalysis, ozonation or cavitation methods, like ultrasound, and hydrodynamic cavitation.[8,9] Yet, another drawback might be associated with novel destructive methods. Biological treatments or Fenton reactions, for example, might generate secondary contamination by toxic sludge, and it has been reported that some AOP, like photocatalysis, generate toxic intermediate products that are often equally or more toxic than the parent compound.[10] Moreover, advanced destructive methods might require more sophisticated facilities and a higher investment. These problems are exacerbated in low and middle-income countries, where the lack of instrumentation and facilities impedes the application of proper implementation of advanced procedures.[11] However, some methods, such as hydrodynamic cavitation, are relatively simple in design and technological requirements, in addition to having low energy requirements. Hydrodynamic cavitation seems to be very effective for the degradation of toxic organic contaminants with minimal generation of secondary pollution. It is considered a very promising technique but is still not implemented at the commercial level or in larger scale applications, and its use is still limited. Despite its advantages, there is an entire hydrodynamic theory and physicochemical effects behind the foundations of said method that must be understood before its implementation and that are essential for its design, scale-up, and optimization.[9] Therefore, a lot of effort is still put into the improvement of well-known, conventional methods that are already well characterized, understood, and widely used at different scales for the removal of persistent contaminants.

Adsorption is a relatively cheap process, simple in theory, design and operation and with low energy requirements.[2] Adsorption involves the accumulation of molecules from a liquid or gas phase on the surface of a solid substrate, normally a porous matrix, following a mass transfer process. The molecules that interact and attach to the solid surface are called adsorbates, while the solid matrix is called adsorbent.[12] Selection of the adsorbent material is key to the applicability of the process. Commercial activated carbons (AC) are widely used adsorbents; however, AC has generally low selectivity and efficiency toward nonconventional contaminants, or pollutants at trace levels.[13] Therefore, a great deal of research has focused on the synthesis of novel, efficient, and inexpensive adsorbents. These novel adsorbents often rely on strategies such as waste and biomass valorization for obtaining inexpensive materials.[14−17] Biobased materials, such as biobased hydrogels and hydrogel composites, have gained attention in recent years for their versatility and their relatively high adsorption efficiencies. Moreover, their chemical structures result in high affinity toward many different water contaminants, making them ideal adsorbents.[18]

However, when these novel adsorbents become saturated after being used for the removal of wastewater contaminants, the removal efficiency becomes negligible in subsequent adsorption cycles, and the material can no longer be used.[19] This means that new material must be available for each adsorption process and the saturated adsorbent must be discarded. The continuous generation and disposal of saturated adsorbents may even become a source of contamination.[20] Therefore, the adsorbent materials should not only have high adsorption capacity and high specificity toward targeted contaminants but also be reusable. It has been observed that reusing the adsorbent may improve the long-term economical feasibility of adsorption treatments. For example, Mariño-Peacock et al.[21] performed an economic evaluation of granular activated carbon (GAC) adsorption treatment for a projected time of 11 years. It was reported that reusing the material may decrease up to 74% of the original cost of the process. Additionally, the projection showed a reduction of about 6 tons of spent GAC disposed as landfill after that period of time, which means that secondary contamination might be significantly reduced.[21]

Reusability depends on a desorption or regeneration step that should successfully break the adsorbent−adsorbate interaction, while the adsorbent structure remains intact for successive adsorption steps. Reusability is directly affected by the nature of the adsorbent material, the nature of the contaminant, and the interaction between them.

Despite the importance of reusability for the evaluation of long-term viability, many papers addressing the synthesis of new adsorbent materials do not assess this parameter. Therefore, this review focuses on regeneration strategies applied to hydrogels or composite hydrogels synthesized with one or more biobased components, including biopolymers and semisynthetic derivatives. This also includes materials in copolymerization with synthetic polymers or composites with matrices of different nature. A brief description of the different adsorbent materials is included along with an overview of the wastewater contaminants that have been successfully removed by these materials. Lastly, the different desorption and regeneration strategies for biopolymeric materials are explored, as well as their corresponding efficiencies for desorption of various water contaminants. Finally, some future perspectives on this topic are addressed.

2. ADSORBENT MATERIALS

In current times, there is a wide variety of adsorbent materials that have been successfully used for the removal of conventional contaminants. These adsorbents may include, for example, activated carbons,[22] zeolites,[23] agro-waste like citrus peels,[24] etc. However, for the removal of more specific, complex emerging contaminants, these adsorbents may have some limitations such as relatively low affinity and low reusability or progressive loss of removal capacity. To overcome these drawbacks, new adsorbents have been developed, with hydrogels being a viable option.

2.1. Hydrogels

Hydrogels are 3D polymeric structures with a hydrophilic nature, which are able to swell and retain large volumes of water. The high swelling capacity is given by the functional groups in the polymeric structure, with groups such as

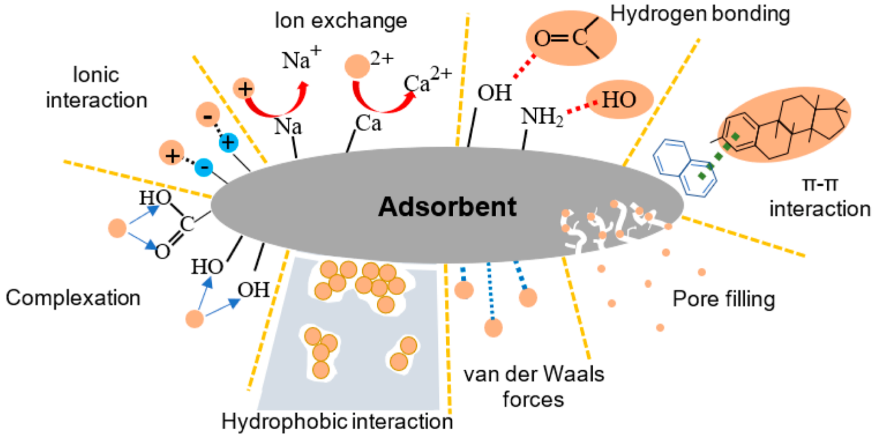

Figure 1. Adsorption mechanisms for the removal of contaminants.

hydroxyl (−OH), carboxyl (−COOH), amidic (−CO + NH$_2$), for example, contributing significantly to this property. Thanks to their high swelling capacity, hydrogels have huge potential in separation technology and water remediation.[25] Hydrogels have been shown to successfully remove water-soluble contaminants, acting as adsorbents. Their chemical structures allow them to interact with contaminants, attaching them to the surface of the hydrogel. They can be synthesized with either natural or synthetic sources, requiring monomer(s), initiator(s), and cross-linker(s).[25] Synthetic hydrogels are usually stable and possess relatively high adsorption capacities and a good mechanical strength. For example, poly(vinyl alcohol) gels and acrylamide/acrylate/acrylic acid−based gels are commonly found in literature.[26−29] On the other hand, natural hydrogels are composed of biopolymers, including polysaccharides or proteic structures that, unlike their synthetic counterparts, tend to have greater biodegradability and lower toxicity, allowing them to fit a range of agricultural, medical and environmental applications.[25,30,31] Most common biopolymers include carbohydrates, such as starches,[32] cellulose,[33,34] chitin/chitosan,[35] carrageenan,[33] and alginate;[36] as well as proteins, such as collagen, keratin, zein, and gelatin, to name a few.[33,37,38] There is also a wide variety of hydrogels produced with semisynthetic derivatives of these biological materials. They still represent a greener alternative than using synthetic polymers and also a strategy for the valorization of biological and/or agricultural waste. All these natural or semisynthetic polymeric materials can be used alone in homopolymers, in combination to form copolymers, or with other different phases and matrices to form composites.

2.2. Hydrogel Composites

Composites are broadly defined as engineered multiphase materials. They are composed of two or more phases, a primary continuous matrix phase, and at least one dispersed discontinuous phase (also referred to as filler). The dispersed phase is physically and chemically distinct to the matrix, conferring new mechanical or functional properties to the composite material.[39,40] Hydrogel composites have been reported in literature with the addition of different discontinuous phases like carbonaceous materials, clay minerals, some fibers and metals or metal oxides.[41] The addition of these fillers tends to increase the adsorption capacities and results also in firmer structures, more resistant to deformation and degradation.[42]

2.2.1. Carbon-Based Composite Hydrogels. Carbon-based materials may have high porosity and large surface areas, which make them very effective for the adsorption of water pollutants.[22] Carbonaceous materials that are normally included in hydrogel composites may include petrochemical-based AC and charcoal, as well as more environmentally friendly alternatives, such as biochar, that has shown potential for the removal of various water contaminants, including dyes[43] and heavy metals like Pb^{2+}.[44] More advanced engineered materials include carbon nanotubes or two-dimensional graphene, with or without surface group modifications.[45] Most carbon-based composite hydrogels adsorbents are used for organic contaminant removal, such as pharmaceuticals,[19,46] dyes,[47,48] plastic additives,[49] and pesticides.[50]

2.2.2. Clays and Mineral-Based Hydrogel Composites. Clay is a naturally forming fine-grained soil that contains a range of hydrous aluminosilicates, often with various metals dispersed throughout.[51] They are an extremely broad category of adsorbent materials for wastewater treatment due to the wide range of minerals, chemical modifications, and pretreatments.[52] One of the most common clay materials is montmorillonite, which has an anisotropic nature, multiple Al−OH groups, small size, and high surface energy that favors its dispersion in heterogeneous systems such as composites.[53] In most of the cases, montmorillonite is used in the production of nanoparticles, either with biopolymers or synthetic polymers, mainly for the removal of dyes and heavy metals.[53−55]

Minerals have also been used in hydrogel preparation; one of the examples is hydroxyapatite (HAP). This mineral is the main nonorganic component of hard tissue, like bones and teeth. HAP is rich in Ca^{2+} and OH$^-$ groups that contribute to a high adsorption capacity, particularly toward divalent metal ions. When incorporated into hydrogel composites, it has shown to increase the removal capacity and to improve mechanical properties of the polymeric adsorbent material.[56] HAP has been successfully incorporated into adsorbents with biopolymers like xanthan gum and chitosan for the removal of dyes like methylene blue (MB)[57] or congo red (CR),[56] respectively.

2.2.3. Natural Fiber-Based Composite Hydrogels. A large range of natural fibers including edible, nonedible, agro-wastes, and chemically modified derivatives of fibers, have all been tested for pollutant adsorption due to their environmental friendliness and economic viability.[58,59] Some examples are straws, grasses, peels, coconut and corn husks, sawdust and other wood waste, and wool-based products.[59] However, the removal efficiency of these materials tends to be significantly lower than other engineered adsorbent materials or more complex composites, reaching maximum adsorption capacities of <100 mg/g,[60] when other complex materials may go up to few hundreds.[60,61] However, natural fibers can also be incorporated into composite hydrogels. For example, Ma et al.[62] incorporated agarwood fruit husks into sodium alginate (SA) and chitosan hydrogels, to improve the mechanical properties and removal capacity of dyes. According to authors, the composite material not only showed better mechanical properties but also exhibited higher adsorption capacities than the husks, SA, and chitosan adsorbents individually.[62] Similarly Zhou et al.[42] synthesized a porous double network jute/poly(acrylic acid) (Jute/PAA) gel for the adsorption of Cd^{2+} and Pb^{2+}. This hydrogel showed a high adsorption capacity, removing up to 401.7 mg/g for Cd^{2+} and 542.9 mg/g for Pb^{2+}. This material exhibited high stability and good mechanical strength.

3. DESORPTION METHODS/REGENERATION STRATEGIES

The selection of a desorption method will depend on different factors, such as the material's chemical characteristics and strength, the chemical nature of the adsorbate, and mainly the adsorption mechanism that governs the adsorbate−adsorbent interaction. Water pollutants may be adsorbed by different mechanisms, and the adsorbate−adsorbent interaction may be driven by a combination of several mechanisms (Figure 1). Electrostatic interactions and ion exchange, which consist in the attraction between two oppositely charged species, are key in the adsorption of ionic molecules, such as heavy metals, phosphates, nitrates, and ionic dyes to name a few.[63] Heavy metals may also be adsorbed by other mechanisms like complexation, which is the capacity of heavy metals to form multiatomic structures when they interact with metal−ligands or chelating agents, normally oxygen-containing functional groups in the adsorbent material.[64] Some other hydrogen-, nitrogen-, oxygen-, and fluorine-containing contaminants may be successfully adsorbed by hydrogen bonding. However, H-bonding is considered a weak interaction as compared to ionic bonds.[65] The adsorption of organic molecules, such as PACs, dyes, and agrochemicals, may take place by $\pi-\pi$ interactions, thanks to their aromatic rings containing π bonds. This mechanism has been observed especially when carbonaceous materials are used.[66] On the other hand, for contaminants with neutral, unpolarized, and unmagnetized atoms, van der Waals forces may be responsible for their adsorption. For these mechanisms, increasing the distance between the two species diminishes the interaction.[67]

Another adsorption mechanism that can be observed in materials, particularly porous ones is pore filling. This mechanism is commonly found in carbonaceous materials like biochar. Materials with micro and mesoporous structures (<2 nm and 2−50 nm pores, respectively) can physically trap molecules into their pores. Therefore, adsorption is highly dependent on the size of both the pores and the targeted molecules.[68] All of these mechanisms and interactions vary in terms of strength and reversibility, affecting the efficiency of the regeneration. Therefore, different chemical and physical methods have been developed for efficient adsorbent regeneration.

One of the most common regeneration methods for conventional adsorbents, like AC or zeolite, is the application of high temperature in the range of 150 to 850 °C.[69−71] However, hydrogels have relatively sensitive structures that can be damaged with aggressive conditions such as temperature, agitation, or pH. Therefore, desorption strategies with mild conditions may have better outcomes in hydrogels' regeneration. Besides, the environmental and economical implications of the desorption step cannot be ignored, which means that eco-friendly and cost-effective methods are ideal.[72] Different chemical and physical regeneration methods have been evaluated in biopolymeric adsorbents and hydrogel composites with good results. The most common chemical methods are the use of desorption agents,[73] photochemical regeneration,[74] and CO_2 bubbling,[75] while physical methods include ultrasonication[76] and thermal regeneration.[77]

The performance of desorption and regeneration strategies is difficult to analyze and compare since it has been evaluated from different approaches in literature. The first approach is to evaluate the desorption from the solid matrix, meaning that the concentration of the adsorbate attached to the adsorbent is measured before and after the desorption step, and the percentage that was removed is reported (eq 1).

$$\text{contaminant desorption (\%)} = \frac{C_0 - C_i}{C_0} \times 100 \tag{1}$$

where C_0 is the concentration of the contaminant attached to the adsorbent material and C_i is the concentration after desorption step.[73]

On the other hand, the desorption process may be evaluated considering the reusability of the adsorbent, defined as regeneration capacity or regeneration efficiency. In other words, it evaluates to what extent the functionality of the adsorbent is affected by the desorption strategy. Regeneration capacity (RE) is given by the difference between the adsorption capacity of an adsorbent material after the desorption cycles, compared to its original adsorption capacity, calculated according to eq 2.[78]

$$\text{RE (\%)} = \frac{q_r}{q_0} \times 100 \tag{2}$$

where q_r is the adsorption capacity of a given adsorbent after a regeneration process and q_0 is its original adsorption capacity.[79]

The utilization of different approaches impedes comparison among the methods and strategies. However, both approaches may be necessary for a better understanding of the process and a clearer overview of the performance of a given regeneration strategy: first, to define how well the desorption process removes the contaminant from the adsorbent surface and, second, to determine if the regeneration compromises the adsorption capacity of the adsorbent for the following cycles. Nonetheless, both approaches are rarely applied together in hydrogels and biopolymeric materials. Therefore, it may be difficult to select the best fitting regeneration strategy for a given adsorbent−adsorbate system.

3.1. Chemical Methods

Chemical regenerations involve some kind of chemical reagent to either destabilize the adsorbate−adsorbent interaction, modify the characteristics of the adsorbent's surface, or

Table 1. Regeneration of Biopolymeric Adsorbents and Hydrogel Composites Using Acidic Eluents

Adsorbent	Contaminant	Adsorption mechanism	Desorption strategy	Cycles	Desorption efficiency	Regeneration efficiency	Ref
Alginate/carbon films	Diclofenac	van der Waals forces H bonding Electrostatic interaction	Acetic acid 50% v/v	5	-	66.70%	19
Chitosan/poly(acrylic acid) hydrogel	Ciprofloxacin enrofloxacin	Electrostatic interaction	0.1 M HCl 120 rpm 2 h 30 °C	5	-	~100% CIP ~85% ENR	89
Chitosan-coated sand	Cu(II) Pb(II)	Chemisorption	HCl (pH 1) 50 rpm	1	93% 88%	-	85
Carboxymethylated chitosan beads	Cu(II)	Chemisorption	HCl ($pH < 2$) continuous stirring	6	>99.9%	-	90
Polyaniline grafted cross-linked chitosan	Cd(II) Pb(II)	Chemisorption (covalent bonding)	0.5 M HCl 3 h	5	98.95% 97.50%	-	91
Bentonite/sodium alginate/dextrin cross-linked poly(acrylic acid) hydrogel	Paraquat (PQ)	Electrostatic interaction	0.01 N HCl 2 h	6	-	73.70%	92
Poly(methacrylic acid)-grafted chitosan microspheres	Cd(II)	Electrostatic interaction Complexation Ionic exchange	1 M HNO_3 25 °C 150 rpm 1 h	5	>95%	96.89%	93
Triethylenetetramine-modified cross-linked chitosan beads	Ni(II)	Complexation	1 M H_2SO_4 stirring for 24 h	4	-	95%	94
Molybdate-impregnated chitosan beads	As(III) As(V)	Complexation Electrostatic interaction, ion exchange	1 M H_2SO_4	20	95% 99%	-	95
Chitosan/itaconic acid (Ch-*g*-IA) Chitosan/crotonic acid (Ch-*g*-CA)	Cu(II)	Electrostatic interaction	1 M HNO_3 150 rpm 48 h	4	-	~50%	96
Chitosan	Cr(IV)	-	0.1 M H_2SO_4 0.01 N HCl 0.01 M acetic acid 0.01 M citric acid	1	88% 80% 45% 47%	-	73
Sodium alginate/polyethylenimine SA/PEI	MB	Chelation	0.1 M HNO_3 in ethanol	4	79.40%	63.20%	97
LS-*g*-AA hydrogels	MB	Electrostatic interaction	HCl (pH 4)	1	51%	-	98
		Ion exchange	0.1 M HCl (pH 1)	1	65%	-	
				4	-	79%	
PAA/XG/HAP	MB	H bonds Electrostatic interaction	0.01 M HCl 2 h	10	-	86%	99
Polyanionic xanthan gum-based hydrogels	MB	Electrostatic interaction	0.1 M HCl 90 min	20	-	95%	100
Ethylenediamine-modified calcium alginate aerogel (ECAA)	Pb(II) Cu(II)	Ion exchange Chelation	0.1 M HCl	10	-	~90%	101
Chitosan/ethyl acrylate (CEA)	Pb(II) Cd(II) Zn	Physisorption	0.6 M HCl	1	98%	-	102
Methylcellulose/tannic acid complex coated on alginate/poly(acrylic acid)	MB Quinoline (QUI)	H bonding Electrostatic interaction π−π interaction	0.1 M HCl (MB) 10% acetic acid (QUI) in methanol	3	-	~75%	103
Graphene Oxide/alginate hydrogel membranes	Cr(III)	Electrostatic interaction	1 M HCl	5	-	56%	104
	Pb(II)	Ion exchange Chelation	0.3 M HCl		-	93%	
Starch-based hydrogel	Cu(II) Ni(II) Pb(II)	Electrostatic interaction	0.1 N HCl	3	92.70% 90.80% 89.40%	91.80% 95.20% 78%	105
Polyaspartic acid/carboxymethyl *Salix psammophila* powder (PASP/CMS) hydrogel	Pb(II) Cd(II)	Electrostatic interaction	0.08 M HNO_3 60 °C 90 min	1	35% 53.11%	-	106
Xanthan gum/poly(acrylic acid) /hydroxyapatite (XG/PAA/HAP)	MB	H bonding Electrostatic interaction	0.01 M HCl 2 h	10	-	86%	107

Table 1. continued

Adsorbent	Contaminant	Adsorption mechanism	Desorption strategy	Cycles	Desorption efficiency	Regeneration efficiency	Ref
CMC/PAA/GO	MB	π−π interaction H bonding Electrostatic interaction	0.01 M HCl 2 h	9	-	90%	108
Starch/Polyacrylic acid	MB	H bonding Electrostatic interaction π−π interaction	0.1 M HCl	5	85%	∼72%	109
Sugar cane cellulose (SBC)/sodium carboxymethylcellulose with carbon nitride (g-C3N4)	MB	Electrostatic interaction H bonding π−π interaction	6 M HCl 30 min	7	∼90%	-	110
Husk of agarwood fruit (HAF)/sodium alginate (SA)	Crystal violet (CV)	Electrostatic interaction H bonding	4.4 M acetic acid 10 min	5	-	98.31%	62
Molybdate impregnated chitosan beads (MICB)	As (V)	Complexation	0.01 M citric acid (pH 2.06)	1	100%	-	111
			0.01 M tartaric acid (pH 2.55)		80%		
			0.1 M H_3PO_4	3	87%		

degrade the contaminant. They include the use of desorption agents, advanced oxidation methods, and a promising eco-friendly technique based on CO_2 regeneration.

3.1.1. Desorption Agents. This method consists of immersing the saturated adsorbent in an eluent (an aqueous solution or desorption agent) to recover the contaminants in the liquid phase. The efficiency of the eluent is influenced by many factors, including the nature of the adsorbent and adsorbate, the adsorbate−adsorbent interaction, and the desorbing agent that is used. Some of the most common desorption agents include acids, alkalis, salts, chelating agents, and solvents.[78]

Acids and Alkalis. pH is a critical factor for adsorption mechanisms and adsorbent efficiency toward many contaminants, especially when the bonding depends on the anionic, cationic, or zwitterionic nature of the molecules involved in the process.[80] The pH of the medium directly affects the charge and ionization of the adsorbents and adsorbates by protonation or deprotonation of the chemical structures.

The acid or alkali regeneration of adsorbents is the most common method in the literature for hydrogels and polymeric adsorbents. It is generally performed with strong acids and alkalis at low concentrations. In acidic eluents, the cations H^+ and H_3O^+ will be present in excess, whereas basic eluents will have OH^- anions in high concentration. The excess ions may protonate or deprotonate the active sites of the solid phase, so the contaminants might be released into the medium.[81] This means that acidic and alkaline eluents are particularly effective when the adsorbate−adsorbent interaction is mainly driven by electrostatic forces. As described in Table 1, acidic eluents have multiple applications, being particularly effective in the desorption of heavy metals and cationic dyes, such as MB. In contrast, as shown in Table 3, alkalis are effective in the desorption of anionic species like phosphates,[82] perchlorate,[83] or anionic dyes.[84]

The most common acid desorbing agents in the literature are hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and nitric acid (HNO_3). HCl has shown particularly good results for desorption of various heavy metals. Wan et al.[85] studied the desorption efficiency of Cu^{2+} and Pb^{2+} with HCl solutions (pH 1 and 3) from chitosan-coated sand. In their experiment, the desorption efficiency was over 93% for Cu and 88% for Pb at pH 1. In contrast, the authors reported lower desorption values with higher pH and very low removal at neutral conditions (5% and 30% for Cu and Pb, respectively). This effect is explained by the point of zero charge (PZC): the pH value at which a given material has a neutral charge. When the pH < PZC, the adsorbent is protonated and has a positive charge. In contrast, when the pH > PZC, the adsorbent becomes deprotonated.[86] However, in many cases, the PZC is not considered during desorption experiments. In the case of the chitosan-coated sand adsorbent, the PZC was not reported, but the high desorption efficiency at low pH confirms that the material got protonated, in other words, pH< PZC.[85] Conversely the low desorption toward neutral pH indicates that the material remained deprotonated (pH > PZC) and the electrostatic interaction between the metal ions and the adsorbent was maintained; therefore, the contaminant was not released.[85]

In most of the cases, as described in Tables 1−2, the desorption step is performed at a fixed acid or alkali concentration, instead of considering a pH range or the PZC. As it can be observed, the concentration varies normally from 0.01 to 1 M, having different results on the desorption efficiency and number of cycles that can be successfully performed. But considering the PZC may be more specific for the material and less damaging for the adsorbent's structure.

Organic acids have also been evaluated for adsorbent regeneration. Acetic acid, for example, has been used for diclofenac desorption from alginate/carbon films.[19] The performance was evaluated in terms of adsorption efficiency, having an average of 83% diclofenac removal from the first to the fourth cycle. After the fifth cycle, the adsorption decreased to 66.7%. According to the authors, the acid treatment may have caused chemical and textural modifications that reduced the adsorption capacity of the material. However, as the desorption efficiency was not reported, it should not be assumed that the decrease in the adsorption efficiency was only a consequence of the material's degradation. Diclofenac may have accumulated in the adsorbent's surface through successive adsorption−desorption cycles.[19] In some cases, it has been

Table 2. Regeneration of Biopolymeric Adsorbents and Hydrogel Composites Using Alkaline Eluents

Adsorbent	Contaminant	Adsorption mechanism	Desorption strategy	Cycles	Desorption efficiency	Regeneration efficiency	Ref
Chitosan/biochar hydrogel beads (CBHB)	Ciprofloxacin	$\pi-\pi$ interaction H bonding Hydrophobic interaction	1 N NaOH	6	-	>64%	46
Poly(vinyl alcohol)-g-poly(acrylic acid)/cassava starch-gpoly(acrylic acid) hydrogel	MB	H bonding Electrostatic interaction	0.5 M NaOH 24 h and washing 24 h	5	-	>70%	112
Amine Functionalized Egg albumin hydrogel (ALB/PEI)	Diclofenac	Electrostatic interaction H bonding $\pi-\pi$ interaction	0.5 M NaOH 1 h	4	72.40%	34%	113
Chitosan lanthanum (CS/La) hydrogel beads	Phosphorus (P)	Electrostatic interaction Ion exchange	3.5 M NaOH 60 °C 2 00 rpm 24 h	5	80%[a]	90%[a]	114
Graphene oxide/locust bean gum (GO/LBG) aerogels	Rhodamine-B (RhB)	$\pi-\pi$ interaction H bonding Electrostatic interaction	0.1 M NaOH	10	-	70.8−92.4%	115
Polyvinyl alcohol-copper alginate (PVA-CA) gel beads	Tetracycline (TC)	H bonding $\pi-\pi$ interaction	0.01 M NaOH 3 h (posterior Cu cross-linking)	4	-	76.41%	116
Chitosan/zeolite composite aerogels	Indigo carmine (IC)	Electrostatic interactions H bonding	0.1 M NaOH	3	-	∼100%	117
Chitosan/hyper-cross-linked polymer (CS/HCP) hydrogel	IC Sunset yellow (SY)	-	0.1 M NaOH	3	-	>95%	84
Zr(IV)-cross-linked carboxymethyl cellulose/carboxymethyl chitosan hydrogel	P	Electrostatic interactions Ligand exchange Ion exchange	0.8% NaOH (w/v)	6	-	∼90%	82
Cu−Fe embedded cross-linked 3D cellulose hydrogel	Cr(VI)	Reduction Complexation	0.1 M NaOH 2 h	5	88%	86.60%	118
Epichlorohydrin cross-linked chitosan hydrogel beads	Perchlorate	Electrostatic interaction	0.1 M NaOH 16 h	12	∼100%	-	83
HAF/Chitosan (CS)	Reactive blue 4 (RB4)	Electrostatic interaction H bonding	4.4 M ammonia solution 10 min	5	-	∼80%	62
Alginate/carboxymethylcellulose/aluminum hydrogel beads	P	Electrostatic interaction Ion exchange	KOH (pH 9.5)	1	60%	-	119

[a] Percentage calculated based on previous cycle instead of initial value.

observed that organic acids may not be as efficient as other strong inorganic agents. For Cr^{6+} desorption from saturated chitosan, acetic and citric acid had a desorption efficiency of 45% and 47%, respectively, whereas H_2SO_4 and HCl showed 88% and 80% Cr^{6+} desorption, respectively. However, as the adsorption capacity was not evaluated, there is no information regarding the integrity of the adsorbent after successive cycles.[73]

For the alkaline eluents, some common agents are NaOH, ammonia, and KOH, as shown in Table 2. NaOH has shown good results, for example, on indigo carmine (IC) and sunset yellow (SY) from chitosan-based hydrogels.[84] Salzano de luna et al.[84] evaluated the performance of the method in terms of regeneration capacity. The material could maintain more than 95% of the original adsorption capacity after 3 adsorption−desorption cycles for both dyes. Those results may indicate that the material did not undergo major changes during the desorption process.

Occasionally, the desorption process may result in the denaturation of the adsorbent; thus, regeneration would require one or more than one extra step to restore the structure of the material or prevent denaturation. A common strategy is to use a combination of desorption agents in successive treatments. For example, Hu et al.[87] reported the regeneration of a chitosan lactate (CL) hydrogel cross-linked to salecan (an anionic polysaccharide produced by *Agrobacterium sp.*) saturated with Ni^{2+}. This material was regenerated with 0.1 M NaOH solution followed by 0.1 M HCl solution and finally washed with deionized water until neutrality. After 5 regeneration cycles, the hydrogel maintained an adsorption capacity of 95.3% when compared to its initial value, indicating that neutralization successfully prevented the denaturation of the material.[87] In another example reported by Natarajan et al.,[88] the removal of acetaminophen from chitosan encapsulated magnetic nanoparticles coated with rhamnolipids (Rh-cMNP) was evaluated. It was observed that acidic desorption conditions (pH 3) caused dissociation of the magnetic nanoparticles. Therefore, they were subjected to basic conditions to perform the reencapsulation before starting a new adsorption step. Regardless of the denaturation, the material had an adsorption capacity of around 75% after 8 regeneration cycles.

Chelating Agents. Chelating agents are molecules ligands that interact with metal ions to form a complex. These molecules can donate electron pairs to form two or more covalent bonds with a central metal ion. For their capacity to sequester metallic species, chelators may be used for the regeneration of adsorbents loaded with heavy metals. To successfully use a chelator as desorbing agent, an important factor to consider is the formation constant (log K) of the agent toward the metallic ion to desorb. As shown in Table 3, the most widely known chelating agent is ethylenediaminetetraacetic acid (EDTA), and it is widely used in industry to improve the stability of products by the sequestration of trace metals to prevent catalytic reactions. It is also used in agriculture to enhance the availability and transport of metal nutrients.[120] EDTA has been used to recover Hg^+ ions from spent aminated chitosan beads, reaching a desorption ratio of around 95%.[121] According to the authors, EDTA was more efficient for Hg recovery compared to acidic eluents such as HCl and HNO_3, widely used in the desorption of heavy metals. Moreover, the beads maintained their adsorption capacity at around 90% after 5 consecutive adsorption−desorption cycles. EDTA had also been used for the desorption of Pb ions from spent carboxylated alginic acid with a desorption efficiency of 75%.[122] Other chelating agents have been tested, with positive results. In the same study, nitrilotriacetic acid (NTA) was tested for the regeneration of the exhausted carboxylated alginic acid with a removal efficiency of around 80%.

Another molecule with great potential to be used as a desorbing agent is [S,S]-ethylenediaminedisuccinic acid (EDDS). EDDS has been considered as an acceptable biodegradable replacement of EDTA for certain environmental applications.[123] This chelating agent has been reported to extract heavy metal ions (Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+}) from contaminated soil as a decontamination strategy, removing up to 66% of Cu from the soil matrix. Those results indicate that it could also be a good option to desorb heavy metals from spent adsorbents.[124]

However, one of the disadvantages of chelators is that in general, they may be more expensive than other desorbing agents and the cost of the processes might increase. Even though these chelators were evaluated in single use, chelating agents have the potential to be reused, which may decrease the cost of this desorbing method. EDTA, for example, has shown reusability for the chelation of heavy metals after being treated with $Na_2S/Ca(OH)_2$[125] or electrochemical separation.[126]

Salts. The use of salts has also been investigated for their potential as desorbing agents. Saturated salt solutions destabilize the adsorbate−adsorption interactions and favor the release of the contaminants toward the liquid phase due to ionic exchange. Salts may affect the adsorbent−adsorbate interaction governed by electrostatic interaction since salts in solution affect the ionic strength of the system.

NaCl is one of the main salts used as regenerating agent (Table 3); it has been used, for example, for the regeneration of spent cellulose-derived adsorbents with metal ions (Pb^{2+} and Cd^{2+}).[127] According to the authors, saturation of Na ions leads to the exchange between Na ions and metals. In this study, the regenerated materials with NaCl presented high regeneration efficiency, maintaining the adsorption capacity of the material intact after 2 regeneration cycles. However, it decreased to 80% of its original value after the third cycle. NaCl was also used for regeneration of a cellulose-based adsorbent with 75% of Cd desorption.[8] In the same study, $NaNO_3$ and CH_3COONa were also evaluated, yielding around 85% and 65% desorption of Cd respectively after one adsorption−desorption cycle. Compared to other eluents like HCl, salts are generally considered mild agents that compromise the integrity of the adsorbent in a lesser extent.[8] However, it is important to highlight that the salts were not tested for multiple regeneration cycles; thus, the effects on the adsorption capacity and the integrity of the material were not assessed in many cases. Additionally, according to Anirudhan et al.[8] salts may show relatively low efficiencies (≤85%) when compared to acidic eluents (98% efficiency) after only one cycle. However, salts seem to be particularly effective to desorb ionic contaminants from ion-exchange resins not only in batch systems but also in columns.[128] Ion-exchange resins are very efficient in the removal of contaminants like heavy metals and dyes, and they are very useful for the demineralization of hard water. And even though they are not widely exploited in combination with biopolymeric materials, and biobased hydrogels, they have a lot of potential to be included in composites for their ease of regeneration and their multi ion adsorption capacity.[128]

Solvents. The use of organic solvents as regeneration agents has been reported. Organic solvents do displace contaminants from the surface of the adsorbent as the solvent penetrates the material. This regeneration strategy strongly depends on the porosity of the adsorbent and the nature of the organic solvent. Small solvent molecules have better penetration into the micropores of the adsorbent matrix. Another important factor is the solubility of the adsorbate in the solvent to be successfully extracted into the liquid phase.[129]

Different solvents have been used, in conventional materials including acetone,[130] methanol,[131] ethanol,[132] and benzene.[129] In an example with activated carbon saturated with chlorophenols, it has been observed that ethanol extracted around 38% of the adsorbate, being the highest percentage among the above-mentioned solvents, while the less efficient agent was benzene.[129] In another example, Wang et al.[133] reported the use of methanol to desorb perfluorooctanesulfonate (PFOS) from a spent hydrogel made of carbon-dots (nanosized photoluminescent carbon material), removing more than 90% of the adsorbate from the adsorbent material.[133] The authors reported that after 5 adsorption−desorption cycles, the adsorption capacity of the material did not experience significant changes.

Solvents have also shown to be excellent desorbing agents for organic contaminants, namely, for dyes and organic phenols (Table 4). Gul et al.[130] performed regeneration steps for a magnetic chitosan-graphene oxide composite after the adsorption of an anionic (Alizarin Yellow, AY) and a cationic dye (methyl violet, MV). The authors compared the performance of acetonitrile, acetone, and ethanol as eluents; however, values for acetonitrile and ethanol were not reported. According to Gul et al., acetone was the best agent for the desorption of dyes. The adsorption capacity of MV remained unchanged after 4 cycles, while the adsorption of AY slightly decreased.[130] As previously mentioned, the solubility of the adsorbate influences the efficiency of the agent during desorption, with MV being more soluble in acetone than AY.

Table 3. Regeneration of Biopolymeric Adsorbents and Hydrogel Composites with Chelating Agents and Salts

Adsorbent	Contaminant	Adsorption mechanism	Desorption strategy	Cycles	Desorption efficiency	Regeneration efficiency	Ref
Chitosan	Cr(IV)	-	0.1 M EDTA	1	78%	-	73
Amino-functionalized nanocellulose aerogel	Cu(II)	Ion Exchange Complexation	0.05 M EDTA−2Na 3 h	4	∼95%	-	137
Aminated chitosan beads	Mg(II)	Biosorption	0.1 M EDTA	5	95%	90%	121
Chitosan cross-linked with epichlorohydrin−triphosphate	Cu(II)	Electrostatic interactions	0.01 M EDTA 200 rpm 3 h	1	84.99% Cu(II)	-	138
	Cd(II)				88% Cd(II)		
			0.1 M EDTA 200 rpm 3 h			-	
				1	87.6% Cu(II)		
					88.2% Cd(II)		
Wood-inspired nanocellulose aerogel	Pb(II)	Complexation	0.05 M EDTA−2Na 3 h	5	-	90%	139
2-Mercaptobenzamide modified itaconic acid-grafted-magnetite nanocellulose composite	Cd (II)	Precipitation	0.1 M NaCl	1	75.30%	-	8
		Electrostatic interaction	0.1 M $NaNO_3$		69.40%	-	
			0.1 M CH_3COONa		65.50%	-	
Chitosan/zeolite composite aerogels	MB	H bonding Electrostatic interaction	1 M NaCl	3	-	>60%	117
Cross-linked chitosan beads	P	Electrostatic interaction	50 mM NaCl	4	-	∼100%	140

In this case, a lower desorption efficiency could have been obtained with AY, which may help to explain the decrease in adsorption capacity.

Adsorption of MB has been widely studied in the last years, and ethanol has been used as a desorbing agent for hydrogels and polymeric adsorbents. Ethanol was used for the regeneration of carboxymethyl cellulose/poly(acrylic acid) hydrogel saturated with MB. The adsorption capacity of the material was not significantly reduced after the first 2 cycles and it maintained about 96% of its initial capacity after 4 adsorption−desorption cycles.[134] In a different study, a xanthan gum/hydroxyapatite (XG/HAP) derivative saturated with MB was treated with 95% ethanol. After 5 successive cycles, the material maintained 81% of the original adsorption capacity.[57] In both cases, the desorption efficiency of ethanol was not reported; therefore, it is not clear if the materials reduced their adsorption capacity due to the accumulation of irreversible adsorbate−adsorbent bonds or because of the modifications of the adsorbent's surface. However, according to Chen et al.,[57] the adsorption mechanism of MB on the surface of XG/HAP may be mainly driven by electrostatic interaction in relatively weak bonds; therefore, the formation of irreversible interactions seems less likely.

Compared to other desorption agents, the major drawback of using organic solvents is that they are less eco-friendly and could be potentially toxic, like in the case of methanol or benzene. The adsorption process is generally perceived as a green method for water remediation, and researchers are pushing forward the use of biodegradable and biobased adsorbent materials. Therefore, the use of solvents that may have environmental repercussions may not be congruent. An alternative that has not been explored in this type of adsorbent is the use of green solvents. The term "green solvents" may include biosolvents (also called biorenewable solvents) such as bioethanol and supercritical fluids like CO_2 as the main examples. Also, solvents with better environmental, health, and safety properties are considered green solvents.[135] In these cases, the replacement of organic and potentially toxic reagents with greener options may reduce the environmental impact of these desorbing agents.

The use of eluents is usually the most common method in the literature for the regeneration of biobased hydrogels, their semisynthetic derivatives, and hydrogel composites. Compared to other strategies that will be explained in later sections, eluent use has simple technological requirements and is usually very easy to adapt and scale up for batch and column processes, having relatively high desorption and regeneration efficiencies.

As can be observed in Tables 1−4, the performance of the different desorption agents varies greatly. This variability can be attributed to different factors; first, and as it was mentioned before, the desorption efficiency is directly affected by the nature of the contaminant, the adsorbent, and the type of interaction between them. In general, acid eluents are highly efficient in the desorption of cationic species adsorbed mainly by electrostatic interactions. Alkalis tend to be efficient in the desorption of contaminants that are negatively charged. Salts and chelators are particularly effective to remove heavy metals, considering that chelators unlike acid eluents, can desorb metal ions adsorbed by complexation. And finally, solvents have shown to be very effective in the desorption of organic contaminants such as dyes.

However, other factors related to the desorption step, such as the concentration of the agent, contact time, and agitation, affect the results as well. In many cases, those processing conditions were considered and reported, but this is not always the case. Additionally, one factor has been frequently omitted by the authors, the solid to liquid ratio (adsorbent:eluent). The solid to liquid ratio affects the kinetics of the desorption and the equilibrium of the system.[80] If the ratio is high, the eluent may be rapidly saturated, leading to incomplete desorption. On the other hand, a low solid to liquid ratio may be more efficient to remove the contaminants; however, it may be inconvenient and costly to deal with larger processing volumes.

Table 4. Regeneration of Biopolymeric Adsorbents and Hydrogel Composites Using Solvents

Adsorbent	Contaminant	Adsorption mechanism	Desorption strategy	Cycles	Desorption efficiency	Regeneration efficiency	Ref
Chitosan–halloysite nanotubes hydrogel beads	MB MG (Malachite green)	Chemisorption	0.5 M NaOH and acetone	1		>92% (MB) <55% (MG)	141
Xanthan gum/hydroxyapatite derivative	MB	Electrostatic interaction H bonding	95% ethanol	5	-	81%	57
Sodium alginate/polyethylenimine SA/PEI	MB	Chelation	0.1 M HNO_3 in ethanol	4	79.40%	63.20%	97
Methylcellulose/tannic acid complex coated on alginate/poly(acrylic acid)	Quinoline (QUI)	H bonding π–π interaction	10% Acetic Acid in methanol	3	-	75%	103
Agar/κ-carrageenan hydrogel	MB	H bonding Electrostatic interaction	Ethanol Deionized water N,N-dimethylformamide 48 h 150 rpm	5 1 1	~45% <5% ~59%	-	142
Alanine functionalized/graphene oxide Cu-Aln/GO Alanine functionalized/graphene oxide/alginate hydrogel Cu-Aln/GO@Alg	Organic phenols	Hydrophobic Interaction π–π interaction	75% ethanol 6 h 30 °C	4	97% 82.53%	- -	143
Magnetic chitosan/graphene oxide (Fe3O4©GO)	Methyl violet (MV) Alizarin yellow (AY)	Electrostatic interaction π–π interaction	Acetone	4	-	~95% ~84%	130
Magnetic β-cyclodextrin–chitosan/graphene oxide	MB	Electrostatic interaction	Ethanol 72 h	5	-	>65%	132
$FeCl_3$-activated seaweed carbon/MCM-41/alginate hydrogel	Basic blue (BB) Bisphenol A (BPA)	H bonding	Ethanol	5	-	72% 83.33%	49
Cellulose nanocrystal–alginate hydrogel	MB	H bonding van der Waals forces	1 M HCl in 98% ethanol	5	-	~97%	144
Chitosan/hyper-cross-linked polymer (CS/HCP)	Rhodamine (RH)	-	Ethanol	3	-	>95%	84
Chitosan-polyaniline/zirconium biopolymer	Fluoride	Electrostatic interaction	Distilled water	5	-	~40%	145
Magnetic chitosan grafted graphene oxide nanocomposite (MCGO)	Ciprofloxacin (CIP)	Electrostatic interaction π–π interaction	Ultrapure water–methanol	4	-	72%	131
Cyclodextrin-functionalized graphene oxide/poly(N-isopropylacrylamide) nanocomposite hydrogel	Phenolic compounds	H bonding	1:1 ammonia and methanol	5	-	74%	146

One major issue that is rarely addressed in the literature is the management and disposal of the final eluent. Once the contaminants are released from the adsorbent, they are resuspended in the eluent, which means they have returned to an aqueous medium that now must be managed and disposed of with care, or it might become an environmental risk itself. In some specific cases, the contaminant might be recovered and reused for other industrial or agricultural applications. For example, Jóźwiak et al.[136] reported the recovery of P in a basic eluent (NaOH, pH 12–13), that was evaporated to obtain a sediment rich in water-soluble phosphate salts. This sediment has the potential to be used in agricultural industry.[136] However, not all contaminants can be easily recovered from the eluents, so other strategies are needed for better management and disposal.

3.1.2. Oxidation/Degradation of Contaminants. Oxidation/degradation methods have been used for the elimination of water contaminants for a long time. For their capacity to successfully degrade molecules, these chemical methods have also been tested in saturated adsorbents for the regeneration of the materials. Fenton reaction, electro-oxidation-H_2O_2, and an electro-Fenton reaction, for examples, have been used in adsorbent carbonaceous materials, like biochar, for the removal of sulfamethoxazole and methylparaben with positive results.[147] However, in materials such as biopolymeric adsorbents, hydrogels, and hydrogel composites, a degradation method that has exhibited positive results is photocatalytic oxidation. It involves the oxidation and reduction of photocatalysts and photosensitizers after the application of light, generating free radicals ($OH^\bullet$ and $O_2^{\bullet-}$). The free radicals degrade the pollutants attached to the surface of the adsorbent to regenerate the material. In general, photocatalytic regeneration may be performed in different ways, depending on how the material comes into contact with the photocatalyst. First, the adsorbents can be impregnated with photocatalysts before being in contact with the targeted contaminant; they can be submerged in a photocatalyst suspension while illuminated once they are saturated (Figure 2); or the adsorbents can be synthesized with cross-linked photocatalysts.[74,148,149] The saturated material may be exposed to light, UV light, or sunlight depending on the photocatalyst. The system can be operated at room temperature, as the

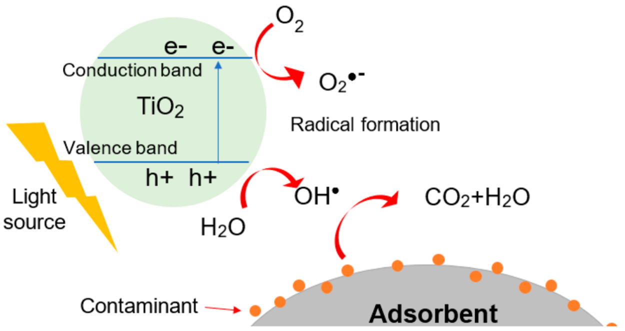

Figure 2. Photocatalytic regeneration of adsorbents with TiO_2 as photocatalyst.

reactions are driven by photonic activation.[148] In the literature, a common photocatalyst is TiO_2, which has been successfully used for the regeneration of many different matrices, including activated carbon,[148] modified agro-wastes,[150] and biobased polymers,[74] to name some.

According to Myint et al.,[149] this regeneration strategy is particularly useful for hydrogel materials, since their cross-linking capacity allows to incorporate photocatalyst in their structure. For a commercial starch-based hydrogel saturated with MB, TiO_2/UV photocatalysis was shown to be the best regeneration method, maintaining around 90% of its initial adsorption capacity when compared to regeneration by desorption agents, like HCl, dipropylamine, and EDTA. Similarly, TiO_2 was incorporated in carboxymethyl cellulose-chitosan-montmorillonite nanosheets composite hydrogel. In this study, MB was eliminated at 97% from the hydrogel's surface, maintaining more than 95% of its original adsorption capacity after 5 regeneration cycles of 20 h.[53] Photocatalytic regeneration seems to be particularly well-suited for dyes, which become colorless after the irradiation process.[74]

There is limited information on photocatalytic regeneration in biobased hydrogels or their semisynthetic derivatives loaded with contaminants other than dyes. However, photochemical oxidation has shown a good regeneration efficiency toward other organic contaminants such as PAC's[151] or bisphenol A[152] in synthetic hydrogels. Therefore, this method could be successfully applied for the regeneration of biobased hydrogels and composites. Nonetheless, it is important to consider the photostability of a given material before the application of this regeneration strategy. It has been observed that the method might be aggressive for the adsorbent material, oxidating not only the contaminant but also the polymeric structure. According to Arayaphan et al.[112] biopolymers seem to be more susceptible to photodegradation than their synthetic counterparts.

Additionally, a major drawback of this method is that it requires specific equipment and set up that may represent a significant investment compared to simpler chemical desorption strategies. Considering only the photocatalyst, the cost of chemical reagents is significantly higher compared to desorption agents. The cost per tonne of two of the most widely used agents, hydrochloric acid and sodium hydroxide, can be around the hundreds of dollars,[153] whereas the most used photocatalyst, titanium dioxide, can reach prices up to a few thousands of dollars per tonne.[154] Apart from the photocatalyst, the reactor design, the light intensity, and the irradiation times influence greatly the total cost of the photocatalytic process at a laboratory scale.[155,156] Additionally, the set ups may require auxiliary equipment for continuous monitoring, maintenance and recalibration of the light source, since the performance of the photoreactor may be affected by irregular light emission of lamps.[157] Therefore, careful economical analysis of these factors must be done before scaling-up. Plaza et al.[155] recommend evaluating the prospect of using solar radiation instead of synthetic light in large scale applications.[155] Nonetheless, the average sunlight intensity of the location should be considered. For example, Muthukumar et al.[158] positively evaluated the feasibility of photodegradation of 4-nitrophenol under natural sunlight. However, this experiment took place in the United Arab Emirates where the annual average sunlight intensity is 90−120 klx for around 10 h per day. The authors highlighted that unexpected circumstances that may affect the sunlight availability may limit the process.[158] Therefore, this process configuration may not be as effective in geographical locations with lower sunlight intensity.

3.1.3. CO_2 Regeneration.

This regeneration method consists of the injection of CO_2 into a system where the spent adsorbent is suspended in aqueous solution. The gas dissolves in water producing carbonic acid. This process requires CO_2-responsive polymers that react when protonated, producing carbamate or bicarbonates. This interaction may change the charge of the material, affecting self-assembly and hydrophilicity, releasing the contaminant (Figure 3). The protonation may be reversed by the injection of another gas, like N_2 purging, or simply by mild heating (∼60 °C), processes that may push the CO_2 out of the solution.[75,159]

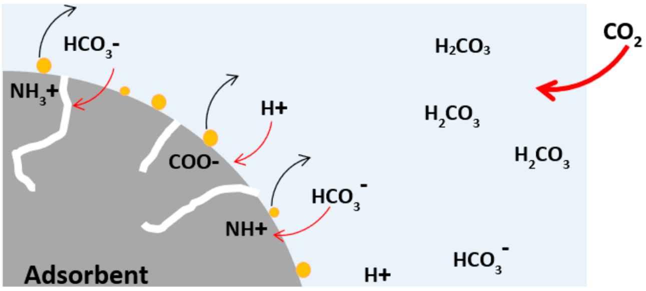

Figure 3. Regeneration of adsorbent materials via CO_2 injection.

Responsive materials must have nitrogen and oxygen rich functional groups to interact with the CO_2 including amino, carboxylic, amidine, and guanidine, having a particularly good response to tertiary amino groups ($-N-(CH_3)_2$).[75,160] Therefore, some polymers and hydrogel materials have a CO_2 responsive properties. One example is poly(2-dimethylamino-ethyl methacrylate) (PDMAEMA) that reacts to form ammonium bicarbonates via protonation of the amino groups.[161] Fan et al.[75] developed a CO_2 responsive hydrogel by cross-linking PDMAEMA with poly(acrylic acid) and chitosan. This material was used for Cu^{2+} adsorption and its regeneration capacity by CO_2 bubbling was evaluated over 6 consecutive cycles of 6 h. The hydrogel desorbed 85.1% of Cu^{2+} after the first regeneration step, decreasing to around 75% after the sixth cycle. Similarly, the adsorption capacity of the gel showed a slight reduction, reaching 70% of its initial capacity after 6 cycles. According to the authors, the gel may have formed strong adsorbent−adsorbate interactions, leading to an incomplete desorption and progressive reduction of the adsorption capacity.[75] However, the material still maintained a relatively high percentage of its initial removal efficiency.

Compared to other chemical methods, CO_2 regeneration may be considered a relatively eco-friendly method that does not require additional inorganic and/or toxic chemicals as desorbing agents. The method is relatively simple to apply compared to photocatalysis, but it has higher technological requirements than desorbing agents since CO_2 regeneration requires a gas injection method and a heating system for later degassing.

The disposal and management of the eluent solution have not been addressed by the regeneration experiments. Therefore, further steps will be required for the treatment of the eluent, or it might become an environmental risk.

3.2. Physical Methods

3.2.1. Thermal Regeneration. As temperature directly affects the molecular interactions and alters the active sites on the surface of the adsorbents, in some cases, the temperature increases the mobility of the contaminants and weakens the adsorbent−adsorbate interactions.[36] Thermal regeneration is suitable for adsorbent materials that resist high temperatures, such as activated carbon, zeolites, etc. In these cases, the process is performed at a range between 150 and 800 °C, temperatures that may oxidize, denature, or carbonize the pollutants. However, mild temperature conditions can also be efficient for regeneration of more delicate materials, like hydrogels. It has been reported that the use of thermal regeneration a thermo-magneto-responsive poly(*N*-isopropylacrylamide)-*co*-acrylic acid composite loaded with Cr^{3+} reached complete desorption at 50 °C.[77] According to the authors, desorption in this composite system was largely attributed to the enthalpy-driven dissociation of hydrated Cr^{3+} from the hydrogel surface once the medium cooled to room temperature. As explained by Chen et al.,[77] the increase in temperature not only affected the stability of the adsorbent−adsorbate interaction but also the arrangement of the composite network. As the temperature increased, the hydrogel presented more stable inner H bonds, which increased the rigidity of the polymeric network. Moreover, at higher temperature, repulsion between the metal ions and the acrylic acid carboxylates increased.[77]

The application of this strategy is still limited for biobased hydrogels and composite hydrogels with biopolymeric components or semisynthetic derivatives, but some examples can be found in literature. Wang et al.[162] synthesized a thermoresponsive cyclodextrin-encapsulated-Mxene composite hydrogel for the adsorption of phenolic compounds, including pentachlorophenol and 4-nonylphenol.[162,163] This material maintained an adsorption capacity of around 82% of its initial value after 5 cycles at 35 °C for 200 h. According to the authors, the hydrogel showed changes in its adsorption capacity and physicochemical characteristics upon exposure to temperatures beyond 35 °C. This response may be a major drawback for possible *in situ* application, considering that contaminant removal will not take place at high temperatures; the hydrogel may not be suitable for warm, tropical, and subtropical environments.

These results indicate that temperature regeneration may have potential for desorption of pollutants as long as the adsorbent material resists mild temperatures with no significant modification. The great advantage of this strategy is that reagents are not needed for desorption, making it a greener option than chemical methods. However, the energy requirement for heating large processing volumes may be a major drawback that needs to be carefully evaluated, considering that the desorption may require long processing times.

3.2.2. Ultrasonic Regeneration. Ultrasound is an oscillating sound pressure wave that operates at frequencies from 20 kHz to several GHz, which is beyond the human hearing range. Ultrasound is divided into low and high intensity. High-intensity ultrasound (from 20 to 40 kHz) is generally used for altering properties of materials.[164] The waves produce compression and expansion alternations, forming bubbles that collapse asymmetrically with the solid surface (Figure 4). The process generates surface sonication that may break the boundary layer and affect the properties of the material. Surface sonication is the main principle that drives ultrasonic regeneration, the compression−expansion alternation may break the adsorbent−adsorbate interaction.[76,165] Additionally, the sound waves increase the turbulence, reducing the laminar sublayer, and the acoustic energy dissipation increases the bulk temperature.[164] With the mechanical and thermal effects generated by the cavitation, the contaminants may be not only released, but also degraded.[10] Ultrasonic regeneration may be efficient when physisorption is involved in the adsorption (van der Waals forces and H bonding).

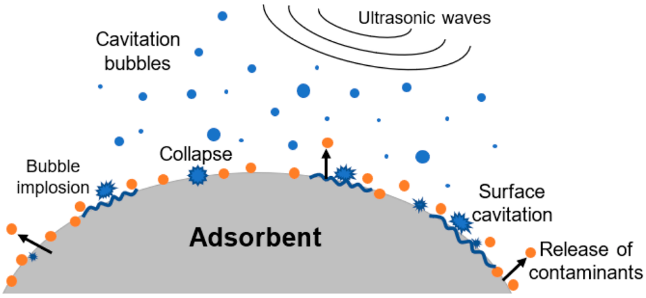

Figure 4. Ultrasonic regeneration of adsorbents.

This technique efficiently regenerated nanocomposite hydrogels based on polymers of intrinsic microporosity, cellulose acetate and graphene oxide (CA/PIM-1/GO) used for adsorption of neonicotinoids.[76] A treatment at 80 kHz and 20 W power in bath sonication was applied for 1.5 min to the spent adsorbent. According to Alammar et al.,[76] the adsorption capacity of the material remained constant for over 10 adsorption−desorption cycles. The authors compared the ultrasonic regeneration of CA/PIM-1/GO with two desorption methods: ethanol as desorption agent and thermal regeneration (40 °C). The three desorption treatments maintained more than 96% of the original adsorption capacity, with process efficiency being ranked as ethanol < temperature < ultrasound in ascending order. However, the processing time of ultrasound treatment was significantly shorter. Ethanol washing and temperature regeneration took place for 8 h, while ultrasound required 1.5 min. According to the authors, these results may represent an advantage for ultrasound application from the practical point of view.[76] However, it is important to consider that processing times, frequency, and power of ultrasound treatments should be carefully considered and optimized, since surface sonication may alter the structure of the adsorbent. In the same experiment, the authors reported that the morphology of (CA/PIM-1/GO) may be changed from bead-like to fiber-like structure with relatively long processing times; therefore, the adsorption capacity of the adsorbent may be affected.[76] This aligns with recent suggestions made by Girard et al.,[166] indicating that for ultrasound processes experimental details must be reported more precisely. It is ideal to report not only the power normalized to the mass of the material but also the volume of solution to account for geometric effects and acoustics.

Like other methods that require a particular set up, ultrasound regeneration may represent a challenge to adapt and scale up for real life applications. Moreover, the degradation that ultrasonic cavitation generates may release toxic byproducts. Therefore, its used is still limited to laboratory scale.[10] However, this method is highly promising, considering the efficiency it has in terms of processing time, having high desorption efficiencies after a few minutes, whereas the other chemical and physical desorption strategies often require between 2 and 24 h.

4. CONCLUSIONS AND FUTURE PERSPECTIVES

The methods covered in this review show variable performances in terms of efficiency, time, and number of cycles for biopolymeric adsorbents and semisynthetic derivatives in hydrogel and hydrogel composites. Despite the abundance of information regarding desorption, the way it has been reported over the years has hindered the evaluation and comparison of different strategies. First and foremost, it is important to consider the approach used to evaluate the desorption and regeneration efficiencies. Both approaches provide different information that can complement each other for better evaluation of the performance of a given method.

In general, some methods tend to be more effective on specific contaminants or toward certain adsorption mechanisms. For example, electrostatic interactions are efficiently interrupted using desorbing agents, with HCl being the most widely used eluent. Different regeneration strategies may successfully desorb the same contaminant, regardless of the matrices. For example, MB may be efficiently removed by desorbing agents including acids, alkalis, and solvents and by photocatalytic regeneration. However, desorption performance and number of cycles that a material can undergo varies.

Parameters such as eco-friendliness and simplicity will also impact the overall evaluation of a given method; in other words, desorption efficiency should not be considered on its own. In many cases, the evaluation of a desorption strategy does not consider the processing times or technological requirements, aspects that may significantly increase the overall cost of application. As previously mentioned, the economical feasibility of acid regeneration of GAC has been evaluated. According to the projections of 11 years of adsorption treatment, reusing the adsorbent materials can reduce the costs by up to 74%, when compared to purchasing new materials for the same period of time.[21] These results are based on the price of the adsorbent and the efficiency and cost of the regeneration method. GAC is a common commercial adsorbent material which has a low to medium cost, ranging between 0.67 to 75 USD per kg. However, it is important to highlight that this sort of evaluation has not been performed for the types of materials covered in this review. According to Gkika et al.,[167] polymeric adsorbents might also have a low to medium cost, but the incorporation of other matrices like graphene oxides, carbon nanotubes, minerals like hydroxyapatite or cross-linkers might significantly increase the cost, to several hundred USD per kg.[167] Therefore, the evaluation of the economical feasibility of the adsorption process as water treatment for more sophisticated materials becomes critical, and cost-efficient regeneration methods are an essential need. However, there are no sufficient studies addressing the economical aspect of regeneration methods. Thus, studies of the implementation and maintenance costs as well as long-term projections are still needed for assessing real life application.

There is limited information related to optimization and the desorption kinetics of the different regeneration methods. There are a few studies that have assessed the kinetics of chemical regeneration by desorbing agents of various biobased adsorbents. However, the desorption kinetics of biopolymeric matrices, semisynthetic derivatives, biobased hydrogels, and composites are rarely followed or reported appropriately. The most widely used kinetic models are pseudo-first-order (PFO) and pseudo-second-order (PSO), being PSO, in many cases the best fitting model for some dye-saturated biobased adsorbents, like jujube shells or golden thistle stalks.[167] However, there are limited studies regarding other nonconventional adsorbent−adsorbate combinations and virtually no studies regarding the desorption kinetics of the different methods covered in this review for the selected type of adsorbents. The lack of information about desorption kinetics represents a significant gap and a key opportunity to improve the evaluation and understanding of regeneration methods. Also, kinetics is an essential tool for the optimization of processing times and projecting maximum desorption capacities, which are important parameters for the evaluation of real-life application.

Moreover, there is limited information regarding how and to what extent a particular method affects these types of materials. Through mechanisms of desorption or regeneration, the effects may sometimes be easily observed or inferred such as the use of strong desorption agents or the application of an ultrasonication treatment. However, in many cases, there are no studies to confirm the integrity of the regenerated adsorbent at the chemical, morphological, or textural level. Therefore, a recharacterization of the materials should be considered to better predict long-term performance.

Integrating all of these factors and considerations during regeneration studies will help to produce useful information related to the efficiencies, effects, and the real applicability of the regeneration strategies. Hence it will be easier to evaluate and select the best fitting method for a given adsorption system.

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Fabiola Alcalde Garcia, PhD. student, drafted the manuscript. Prof. Marie-Josée Dumont, supervisor of the student, and Prof. Jason Robert Tavares and Prof. Shiv Prasher, cosupervisors of the student, contributed to all aspects of this work, including their research expertise, manuscript review and editing, and funding. Prof Serge Kaliaguine provided comments and knowledge on some technical aspects of the manuscript. CRediT: **Fabiola Alcalde-Garcia** conceptualization, data curation, writing-original draft, writing-review & editing; **Shiv Prasher** supervision, writing-review & editing; **Serge Kaliaguine** writing-review & editing; **Jason Robert Tavares** funding acquisition, supervision, writing-review & editing; **Marie-Josée Dumont** funding acquisition, supervision, writing-review & editing.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) World Health Organization (WHO) *Drinking water*. https://www.who.int/news-room/fact-sheets/detail/drinking-water (accessed 2022/04/13).

(2) Ali, I.; Naz, I.; Peng, C.; Abd-Elsalam, K. A.; Khan, Z. M.; Islam, T.; Pervez, R.; Amjed, M. A.; Tehrim, A.; Perveen, I.; Sehar, S., Chapter 2 - Sources, classifications, constituents, and available treatment technologies for various types of wastewater: An overview. In *Aquananotechnology*; Abd-Elsalam, K. A., Zahid, M., Eds.; Elsevier: 2021; pp 11−46.

(3) Fu, Z.; Xi, S. The effects of heavy metals on human metabolism. *Toxicology Mechanisms and Methods* **2020**, *30* (3), 167−176.

(4) Järup, L. Hazards of heavy metal contamination. *British Medical Bulletin* **2003**, *68* (1), 167−182.

(5) Gautam, R. K.; Sharma, S. K.; Mahiya, S.; Chattopadhyaya, M. C., Chapter 1 Contamination of Heavy Metals in Aquatic Media: Transport, Toxicity and Technologies for Remediation. In *Heavy Metals In Water: Presence, Removal and Safety*; The Royal Society of Chemistry: 2015; pp 1−24.

(6) Tchounwou, P. B.; Yedjou, C. G.; Patlolla, A. K.; Sutton, D. J. Heavy metal toxicity and the environment. *Exp Suppl* **2012**, *101*, 133−164.

(7) Kasonga, T. K.; Coetzee, M. A. A.; Kamika, I.; Ngole-Jeme, V. M.; Benteke Momba, M. N. Endocrine-disruptive chemicals as contaminants of emerging concern in wastewater and surface water: A review. *Journal of Environmental Management* **2021**, *277*, 111485.

(8) Anirudhan, T. S.; Shainy, F. Adsorption behaviour of 2-mercaptobenzamide modified itaconic acid-grafted-magnetite nanocellulose composite for cadmium(II) from aqueous solutions. *Journal of Industrial and Engineering Chemistry* **2015**, *32*, 157−166.

(9) Ranade, V. V.; Bhandari, V. M.; Nagarajan, S. *Hydrodynamic Cavitation*; Wiley, 2022; pp 1−20.

(10) Kaleekkal, N. J., Advanced Oxidation Techniques for Wastewater Treatment. In *Sustainable Technologies for Water and Wastewater Treatment*; CRC Press: Boca Raton, FL, 2021; p 412.

(11) Murtaza, G.; Ghafoor, A.; Qadir, M.; Owens, G.; Aziz, M. A.; Zia, M. H.; Saifullah. Disposal and Use of Sewage on Agricultural Lands in Pakistan: A Review. *Pedosphere* **2010**, *20* (1), 23−34.

(12) Karge, H. G.; Weitkamp, J. *Adsorption and Diffusion*; Springer: Berlin, Germany, 2008; Vol. 7, p 411.

(13) Crini, G.; Lichtfouse, E.; Wilson, L. D.; Morin-Crini, N. Conventional and non-conventional adsorbents for wastewater treatment. *Environmental Chemistry Letters* **2019**, *17* (1), 195−213.

(14) Akram, M.; Xu, X.; Gao, B.; Wang, S.; Khan, R.; Yue, Q.; Duan, P.; Dan, H.; Pan, J. Highly efficient removal of phosphate from aqueous media by pomegranate peel co-doping with ferric chloride and lanthanum hydroxide nanoparticles. *Journal of Cleaner Production* **2021**, *292*, 125311.

(15) Flores-Céspedes, F.; Villafranca-Sánchez, M.; Fernández-Pérez, M. Alginate-based hydrogels modified with olive pomace and lignin to removal organic pollutants from aqueous solutions. *Int. J. Biol. Macromol.* **2020**, *153*, 883−891.

(16) Mu, Y.; He, W.; Ma, H. Enhanced adsorption of tetracycline by the modified tea-based biochar with the developed mesoporous and surface alkalinity. *Bioresour. Technol.* **2021**, *342*, 126001.

(17) Bouhcain, B.; Mansouri, F. E.; Brigui, J.; Ruiz, S. G.; Alonso, J. M. Q.; Dekkaki, H. C.; Zerrouk, M. H. Study of elimination of emerging contaminants by adsorption using activated carbon of coconut (Amoxicillin−Penicillin−Theobromine). *AIP Conf. Proc.* **2021**, *2417*, No. 020001.

(18) Godiya, C. B.; Martins Ruotolo, L. A.; Cai, W. Functional biobased hydrogels for the removal of aqueous hazardous pollutants: Current status, challenges, and future perspectives. *Journal of Materials Chemistry A* **2020**, *8* (41), 21585−21612.

(19) Shamsudin, M. S.; Azha, S. F.; Sellaoui, L.; Badawi, M.; Bonilla-Petriciolet, A.; Ismail, S. Performance and interactions of diclofenac adsorption using Alginate/Carbon-based Films: Experimental investigation and statistical physics modelling. *Chem. Eng. J.* **2022**, *428*, 131929.

(20) Baskar, A. V.; Bolan, N.; Hoang, S. A.; Sooriyakumar, P.; Kumar, M.; Singh, L.; Jasemizad, T.; Padhye, L. P.; Singh, G.; Vinu, A.; Sarkar, B.; Kirkham, M. B.; Rinklebe, J.; Wang, S.; Wang, H.; Balasubramanian, R.; Siddique, K. H. M. Recovery, regeneration and sustainable management of spent adsorbents from wastewater treatment streams: A review. *Science of The Total Environment* **2022**, *822*, 153555.

(21) Mariño Peacok, T.; Crespo Sariol, H.; Puente Torres, J.; Yperman, J.; Sánchez Roca, Á.; Carleer, R.; Salomón García, L. Mathematical Tool Based on Breakthrough Curves to Evaluate the Economic Advantages of Chemical Regeneration of Activated Carbon in Power Plants: A Comparative Study. *Applied Sciences* **2021**, *11* (24), 11786.

(22) Perrich, J. R. *Activated Carbon Adsorption for Wastewater Treatment*; CRC Press, Taylor & Francis Group: Boca Raton, 2018; p 260.

(23) Erdem, E.; Karapinar, N.; Donat, R. The removal of heavy metal cations by natural zeolites. *J. Colloid Interface Sci.* **2004**, *280* (2), 309−314.

(24) Inagaki, C. S.; Caretta, T. O.; Alfaya, R. V. S.; Alfaya, A. A. S. Mexerica mandarin (Citrus nobilis) peel as a new biosorbent to remove Cu(II), Cd(II), and Pb(II) from industrial effluent. *Desalination and Water Treatment* **2013**, *51* (28−30), 5537−5546.

(25) Thakur, S.; Thakur, V. K.; Arotiba, O. A., History, Classification, Properties and Application of Hydrogels: An Overview. In *Hydrogels: Recent Advances*; Thakur, V. K., Thakur, M. K., Eds.; Springer: Singapore, 2018; pp 29−50.

(26) Kongseng, P.; Amornpitoksuk, P.; Chantarak, S. Development of multifunctional hydrogel composite based on poly(vinyl alcohol-g-

acrylamide) for removal and photocatalytic degradation of organic dyes. *React. Funct. Polym.* **2022**, *172*, 105207.

(27) Kaur, K.; Jindal, R.; Saini, D. Synthesis, optimization and characterization of PVA-co-poly(methacrylic acid) green adsorbents and applications in environmental remediation. *Polym. Bull.* **2020**, *77* (6), 3079−3100.

(28) Pille, A.; Dumont, M.-J.; Tavares, J. R.; Roy, R. The effect of foaming additives on acrylic acid/acrylamide hydrogels. *Journal of Environmental Chemical Engineering* **2022**, *10* (2), 107310.

(29) Abdeen, Z.; Moustafa, Y. M. M. Treatment of Oily Wastewater by Using Porous PVA Hydrogels as Oil Adsorbent. *J. Dispersion Sci. Technol.* **2016**, *37* (6), 799−805.

(30) Jun Loh, X.; A. Scherman, O. Chapter 1: Introduction. In *Polymeric and Self Assembled Hydrogels: From Fundamental Understanding to Applications*; The Royal Society of Chemistry, 2013; pp 1−6.

(31) Hwang, D.-C.; Damodaran, S. Chemical modification strategies for synthesis of protein-based hydrogel. *Journal of Agricultural and Food Chemistry* **1996**, *44* (3), 751−758.

(32) Abd El-Ghany, N. A.; Elella, M. H. A.; Abdallah, H. M.; Mostafa, M. S.; Samy, M. Recent Advances in Various Starch Formulation for Wastewater Purification via Adsorption Technique: A Review. *Journal of Polymers and the Environment* **2023**, *31* (7), 2792−2825.

(33) Russo, T.; Fucile, P.; Giacometti, R.; Sannino, F. Sustainable removal of contaminants by biopolymers: A novel approach for wastewater treatment. current state and future perspectives. *Processes* **2021**, *9* (4), 719.

(34) Olivera, S.; Muralidhara, H. B.; Venkatesh, K.; Guna, V. K.; Gopalakrishna, K.; Kumar K., Y. Potential applications of cellulose and chitosan nanoparticles/composites in wastewater treatment: A review. *Carbohydr. Polym.* **2016**, *153*, 600−618.

(35) Karimi-Maleh, H.; Ayati, A.; Davoodi, R.; Tanhaei, B.; Karimi, F.; Malekmohammadi, S.; Orooji, Y.; Fu, L.; Sillanpää, M. Recent advances in using of chitosan-based adsorbents for removal of pharmaceutical contaminants: A review. *Journal of Cleaner Production* **2021**, *291*, 125880.

(36) Sutirman, Z. A.; Sanagi, M. M.; Wan Aini, W. I. Alginate-based adsorbents for removal of metal ions and radionuclides from aqueous solutions: A review. *Int. J. Biol. Macromol.* **2021**, *174*, 216−228.

(37) Kayan, G. Ö.; Kayan, A. Composite of Natural Polymers and Their Adsorbent Properties on the Dyes and Heavy Metal Ions. *Journal of Polymers and the Environment* **2021**, *29* (11), 3477−3496.

(38) Ni, N.; Dumont, M.-J. Protein-Based Hydrogels Derived from Industrial Byproducts Containing Collagen, Keratin, Zein and Soy. *Waste and Biomass Valorization* **2017**, *8* (2), 285−300.

(39) Thakur, V. K.; Thakur, M. K.; Kessler, M. R. *Handbook of Composites from Renewable Materials, Nanocomposites: Science and Fundamentals*; John Wiley & Sons, Incorporated: Somerset, United States, 2017.

(40) Callister, W. D., Jr.; Rethwisch, D. G.; Rethwisch, D. G. *Fundamentals of Materials Science and Engineering: An Integrated Approach*, 4th ed.; Wiley: Hoboken, N.J., 2012; p 910.

(41) Dutt, M. A.; Hanif, M. A.; Nadeem, F.; Bhatti, H. N. A review of advances in engineered composite materials popular for wastewater treatment. *Journal of Environmental Chemical Engineering* **2020**, *8* (5), 104073.

(42) Zhou, G.; Luo, J.; Liu, C.; Chu, L.; Crittenden, J. Efficient heavy metal removal from industrial melting effluent using fixed-bed process based on porous hydrogel adsorbents. *Water Res.* **2018**, *131*, 246−254.

(43) Praveen, S.; Jegan, J.; Bhagavathi Pushpa, T.; Gokulan, R.; Bulgariu, L. Biochar for removal of dyes in contaminated water: an overview. *Biochar* **2022**, *4* (1), 10.

(44) Bardestani, R.; Roy, C.; Kaliaguine, S. The effect of biochar mild air oxidation on the optimization of lead(II) adsorption from wastewater. *Journal of Environmental Management* **2019**, *240*, 404−420.

(45) Raza, A.; Altaf, S.; Ali, S.; Ikram, M.; Li, G. Recent advances in carbonaceous sustainable nanomaterials for wastewater treatments. *Sustainable Materials and Technologies* **2022**, *32*, No. e00406.

(46) Afzal, M. Z.; Sun, X. F.; Liu, J.; Song, C.; Wang, S. G.; Javed, A. Enhancement of ciprofloxacin sorption on chitosan/biochar hydrogel beads. *Sci. Total Environ.* **2018**, *639*, 560−569.

(47) Gonçalves, J. O.; da Silva, K. A.; Rios, E. C.; Crispim, M. M.; Dotto, G. L.; de Almeida Pinto, L. A. Single and Binary Adsorption of Food Dyes on Chitosan/Activated Carbon Hydrogels. *Chem. Eng. Technol.* **2019**, *42* (2), 454−464.

(48) Mittal, H.; Al Alili, A.; Morajkar, P. P.; Alhassan, S. M. GO crosslinked hydrogel nanocomposites of chitosan/carboxymethyl cellulose − A versatile adsorbent for the treatment of dyes contaminated wastewater. *Int. J. Biol. Macromol.* **2021**, *167*, 1248−1261.

(49) Marrakchi, F.; Fazeli Zafar, F.; Wei, M.; Wang, S. Cross-linked FeCl3-activated seaweed carbon/MCM-41/alginate hydrogel composite for effective biosorption of bisphenol A plasticizer and basic dye from aqueous solution. *Bioresour. Technol.* **2021**, *331*, 125046.

(50) Utzeri, G.; Verissimo, L.; Murtinho, D.; Pais, A. A. C. C.; Perrin, F. X.; Ziarelli, F.; Iordache, T. V.; Sarbu, A.; Valente, A. J. M. Poly(β-cyclodextrin)-activated carbon gel composites for removal of pesticides from water. *Molecules* **2021**, *26* (5), 1426.

(51) Barton, C. D., Clay Minerals. In *Encyclopedia of Soil Science*; Lal, R., Ed.; Marcel Dekker: New York, NY, 2002, 187−192.

(52) Barakan, S.; Aghazadeh, V. The advantages of clay mineral modification methods for enhancing adsorption efficiency in wastewater treatment: a review. *Environmental Science and Pollution Research* **2021**, *28* (3), 2572−2599.

(53) Wang, W.; Ni, J.; Chen, L.; Ai, Z.; Zhao, Y.; Song, S. Synthesis of carboxymethyl cellulose-chitosan-montmorillonite nanosheets composite hydrogel for dye effluent remediation. *Int. J. Biol. Macromol.* **2020**, *165*, 1−10.

(54) Barati, A.; Asgari, M.; Miri, T.; Eskandari, Z. Removal and recovery of copper and nickel ions from aqueous solution by poly(methacrylamide-co-acrylic acid)/montmorillonite nanocomposites. *Environmental Science and Pollution Research* **2013**, *20* (9), 6242−6255.

(55) Sarkar, N.; Sahoo, G.; Swain, S. K. Nanoclay sandwiched reduced graphene oxide filled macroporous polyacrylamide-agar hybrid hydrogel as an adsorbent for dye decontamination. *Nano-Structures & Nano-Objects* **2020**, *23*, 100507.

(56) Hou, H.; Zhou, R.; Wu, P.; Wu, L. Removal of Congo red dye from aqueous solution with hydroxyapatite/chitosan composite. *Chem. Eng. J.* **2012**, *211−212*, 336−342.

(57) Chen, X.; Li, P.; Zeng, X.; Kang, Y.; Wang, J.; Xie, H.; Liu, Y.; Zhang, Y. Efficient adsorption of methylene blue by xanthan gum derivative modified hydroxyapatite. *Int. J. Biol. Macromol.* **2020**, *151*, 1040−1048.

(58) Buenaño Bautista, B. B.; Vera Calle, E. R.; Aldás Sandoval, M. B. Study of coagulating/flocculating characteristics of organic polymers extracted from biowaste for water treatment. *Ingenieria e Investigación* **2019**, *39* (1), 24−35.

(59) Wahi, R.; Chuah, L. A.; Choong, T. S. Y.; Ngaini, Z.; Nourouzi, M. M. Oil removal from aqueous state by natural fibrous sorbent: An overview. *Sep. Purif. Technol.* **2013**, *113*, 51−63.

(60) Aruna; Bagotia, N.; Sharma, A. K.; Kumar, S. A review on modified sugarcane bagasse biosorbent for removal of dyes. *Chemosphere* **2021**, *268*, 129309.

(61) Czarny, K.; Szczukocki, D.; Krawczyk, B.; Gadzała-Kopciuch, R.; Skrzypek, S. Toxicity of single steroid hormones and their mixtures toward the cyanobacterium Microcystis aeruginosa. *Journal of Applied Phycology* **2019**, *31* (6), 3537−3544.

(62) Ma, C. M.; Yang, B. Y.; Hong, G. B. Husk of agarwood fruit-based hydrogel beads for adsorption of cationic and anionic dyes in aqueous solutions. *Molecules* **2021**, *26* (5), 1437.

(63) Adamczyk, Z. Potential Interactions Among Particles. In *Interface Science and Technology*; Adamczyk, Z., Ed.; Elsevier: 2006; Vol. *9*, pp 15−196.

(64) Shaaban, M.; Abid, M. Biochar as a sorbent for organic and inorganic pollutants. In *Sorbents Materials for Controlling Environmental Pollution*; Núñez-Delgado, A., Ed.; Elsevier: 2021; pp 189−208.

(65) Sivakumar, R.; Lee, N. Y. Adsorptive removal of organic pollutant methylene blue using polysaccharide-based composite hydrogels. *Chemosphere* **2022**, *286*, 131890.

(66) Peng, B.; Chen, L.; Que, C.; Yang, K.; Deng, F.; Deng, X.; Shi, G.; Xu, G.; Wu, M. Adsorption of Antibiotics on Graphene and Biochar in Aqueous Solutions Induced by *π*-*π* Interactions. *Sci. Rep.* **2016**, *6* (1), 31920.

(67) Buhmann, S. Y. Introduction: Dispersion Forces. In *Dispersion Forces I: Macroscopic Quantum Electrodynamics and Ground-State Casimir, Casimir−Polder and van der Waals Forces*; Springer: Berlin, 2012; pp 1−43.

(68) Wang, X.; Guo, Z.; Hu, Z.; Zhang, J. Recent advances in biochar application for water and wastewater treatment: a review. *PeerJ.* **2020**, *8*, No. e9164.

(69) Marques, S. C. R.; Marcuzzo, J. M.; Baldan, M. R.; Mestre, A. S.; Carvalho, A. P. Pharmaceuticals removal by activated carbons: Role of morphology on cyclic thermal regeneration. *Chem. Eng. J.* **2017**, *321*, 233−244.

(70) Sun, Z.; Li, C.; Wu, D. Removal of methylene blue from aqueous solution by adsorption onto zeolite synthesized from coal fly ash and its thermal regeneration. *J. Chem. Technol. Biotechnol.* **2010**, *85* (6), 845−850.

(71) Li, J.; Chen, G.; Chang, J.; Zhang, L.; Wang, T.; Song, Z.; Ma, C. Study on sulfur migration and carbon consumption during regeneration of SO_2-loaded activated carbon: Effect of alkali/alkaline earth metals. *Journal of the Energy Institute* **2022**, *102*, 118−127.

(72) Vakili, M.; Deng, S.; Cagnetta, G.; Wang, W.; Meng, P.; Liu, D.; Yu, G. Regeneration of chitosan-based adsorbents used in heavy metal adsorption: A review. *Sep. Purif. Technol.* **2019**, *224*, 373−387.

(73) Bhuvaneshwari, S.; et al. Regeneration of chitosan after heavy metal sorption. *Journal of Scientific Industrial Research* **2012**, *71* (4), 266−269.

(74) Dhodapkar, R.; Rao, N. N.; Pande, S. P.; Nandy, T.; Devotta, S. Adsorption of cationic dyes on Jalshakti®, super absorbent polymer and photocatalytic regeneration of the adsorbent. *React. Funct. Polym.* **2007**, *67* (6), 540−548.

(75) Fan, S.; Chen, J.; Fan, C.; Chen, G.; Liu, S.; Zhou, H.; Liu, R.; Zhang, Y.; Hu, H.; Huang, Z.; Qin, Y.; Liang, J. Fabrication of a CO2-responsive chitosan aerogel as an effective adsorbent for the adsorption and desorption of heavy metal ions. *J. Hazard. Mater.* **2021**, *416*, 126225.

(76) Alammar, A.; Park, S.-H.; Ibrahim, I.; Arun, D.; Holtzl, T.; Dumee, L. F.; Lim, H. N.; Szekely, G. Architecting neonicotinoid-scavenging nanocomposite hydrogels for environmental remediation. *Appl. Mater. Today* **2020**, *21*, 100878.

(77) Chen, J. J.; Ahmad, A. L.; Lim, J. K.; Ooi, B. S. Adsorption-desorption characteristic of thermo-magneto-responsive poly(N-isopropylacrylamide)-co-acrylic acid composite hydrogel towards chromium (III) ions. *Journal of Water Process Engineering* **2019**, *32*, 100957.

(78) Chatterjee, A.; Abraham, J. Desorption of heavy metals from metal loaded sorbents and e-wastes: A review. *Biotechnol. Lett.* **2019**, *41* (3), 319−333.

(79) Sun, K.; Jiang, J.-c.; Xu, J.-m. Chemical Regeneration of Exhausted Granular Activated Carbon Used in Citric Acid Fermentation Solution Decoloration. *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)* **2009**, *28* (4), 79−83.

(80) Worch, E. *Adsorption Technology in Water Treatment*. De Gruyter: Berlin, 2021; p 363.

(81) Bilal, M.; Ihsanullah, I.; Younas, M.; Ul Hassan Shah, M. Recent advances in applications of low-cost adsorbents for the removal of heavy metals from water: A critical review. *Sep. Purif. Technol.* **2021**, *278*, No. 119510.

(82) Wang, J.; Wei, J. Facile synthesis of Zr(IV)-crosslinked carboxymethyl cellulose/carboxymethyl chitosan hydrogel using PEG as pore-forming agent for enhanced phosphate removal. *Int. J. Biol. Macromol.* **2021**, *176*, 558−566.

(83) Yu, X.; Zhang, J.; Zheng, Y. Perchlorate adsorption onto epichlorohydrin crosslinked chitosan hydrogel beads. *Sci. Total Environ.* **2021**, *761*, 143236.

(84) Salzano de Luna, M.; Castaldo, R.; Altobelli, R.; Gioiella, L.; Filippone, G.; Gentile, G.; Ambrogi, V. Chitosan hydrogels embedding hyper-crosslinked polymer particles as reusable broad-spectrum adsorbents for dye removal. *Carbohydr. Polym.* **2017**, *177*, 347−354.

(85) Wan, M.-W.; Kan, C.-C.; Rogel, B. D.; Dalida, M. L. P. Adsorption of copper (II) and lead (II) ions from aqueous solution on chitosan-coated sand. *Carbohydr. Polym.* **2010**, *80* (3), 891−899.

(86) Bakatula, E. N.; Richard, D.; Neculita, C. M.; Zagury, G. J. Determination of point of zero charge of natural organic materials. *Environmental Science and Pollution Research* **2018**, *25* (8), 7823−7833.

(87) Hu, X.; Yan, L.; Wang, Y.; Xu, M. Smart and functional polyelectrolyte complex hydrogel composed of salecan and chitosan lactate as superadsorbent for decontamination of nickel ions. *Int. J. Biol. Macromol.* **2020**, *165*, 1852−1861.

(88) Natarajan, R.; Anil Kumar, M.; Vaidyanathan, V. K. Synthesis and characterization of rhamnolipid based chitosan magnetic nanosorbents for the removal of acetaminophen from aqueous solution. *Chemosphere* **2022**, *288*, 132532.

(89) Wang, N.; Xiao, W.; Niu, B.; Duan, W.; Zhou, L.; Zheng, Y. Highly efficient adsorption of fluoroquinolone antibiotics using chitosan derived granular hydrogel with 3D structure. *J. Mol. Liq.* **2019**, *281*, 307−314.

(90) Yan, H.; Dai, J.; Yang, Z.; Yang, H.; Cheng, R. Enhanced and selective adsorption of copper(II) ions on surface carboxymethylated chitosan hydrogel beads. *Chem. Eng. J.* **2011**, *174* (2), 586−594.

(91) Igberase, E.; Osifo, P. Equilibrium, kinetic, thermodynamic and desorption studies of cadmium and lead by polyaniline grafted cross-linked chitosan beads from aqueous solution. *Journal of Industrial and Engineering Chemistry* **2015**, *26*, 340−347.

(92) Thakur, S.; Verma, A.; Raizada, P.; Gunduz, O.; Janas, D.; Alsanie, W. F.; Scarpa, F.; Thakur, V. K. Bentonite-based sodium alginate/ dextrin cross-linked poly (acrylic acid) hydrogel nanohybrids for facile removal of paraquat herbicide from aqueous solutions. *Chemosphere* **2022**, *291*, 133002.

(93) Huang, L.; Yuan, S.; Lv, L.; Tan, G.; Liang, B.; Pehkonen, S. O. Poly(methacrylic acid)-grafted chitosan microspheres via surface-initiated ATRP for enhanced removal of Cd(II) ions from aqueous solution. *J. Colloid Interface Sci.* **2013**, *405*, 171−182.

(94) Liao, B.; Sun, W.-y.; Guo, N.; Ding, S.-l.; Su, S.-J. Equilibriums and kinetics studies for adsorption of Ni(II) ion on chitosan and its triethylenetetramine derivative. *Colloids Surf., A* **2016**, *501*, 32−41.

(95) Chen, C.-Y.; Chang, T.-H.; Kuo, J.-T.; Chen, Y.-F.; Chung, Y.-C. Characteristics of molybdate-impregnated chitosan beads (MICB) in terms of arsenic removal from water and the application of a MICB-packed column to remove arsenic from wastewater. *Bioresour. Technol.* **2008**, *99* (16), 7487−7494.

(96) Bal, A.; Özkahraman, B.; Acar, I.; Özyürek, M.; Güçlü, G. Study on adsorption, regeneration, and reuse of crosslinked chitosan graft copolymers for Cu(II) ion removal from aqueous solutions. *Desalination and Water Treatment* **2014**, *52* (16−18), 3246−3255.

(97) Godiya, C. B.; Xiao, Y.; Lu, X. Amine functionalized sodium alginate hydrogel for efficient and rapid removal of methyl blue in water. *Int. J. Biol. Macromol.* **2020**, *144*, 671−681.

(98) Yu, C.; Wang, F.; Zhang, C.; Fu, S.; Lucia, L. A. The synthesis and absorption dynamics of a lignin-based hydrogel for remediation of cationic dye-contaminated effluent. *React. Funct. Polym.* **2016**, *106*, 137−142.

(99) Hosseini, H.; Pirahmadi, P.; Shakeri, S. E.; Khoshbakhti, E.; Sharafkhani, S.; Fakhri, V.; Saeidi, A.; McClements, D. J.; Chen, W.-H.; Su, C.-H.; Goodarzi, V. A novel environmentally friendly nanocomposite aerogel based on the semi-interpenetrating network of polyacrylic acid into Xanthan gum containing hydroxyapatite for

efficient removal of methylene blue from wastewater. *Int. J. Biol. Macromol.* **2022**, *201*, 133−142.

(100) Njuguna, D. G.; Schönherr, H. Smart and regeneratable Xanthan gum hydrogel adsorbents for selective removal of cationic dyes. *Journal of Environmental Chemical Engineering* **2022**, *10* (3), 107620.

(101) Huang, Y.; Wang, Z. Preparation of composite aerogels based on sodium alginate, and its application in removal of Pb^{2+} and Cu^{2+} from water. *Int. J. Biol. Macromol.* **2018**, *107*, 741−747.

(102) Maleki, A.; Pajootan, E.; Hayati, B. Ethyl acrylate grafted chitosan for heavy metal removal from wastewater: Equilibrium, kinetic and thermodynamic studies. *Journal of the Taiwan Institute of Chemical Engineers* **2015**, *51*, 127−134.

(103) Abebe, M. W.; Kim, H. Methylcellulose/tannic acid complex particles coated on alginate hydrogel scaffold via Pickering for removal of methylene blue from aqueous and quinoline from non-aqueous media. *Chemosphere* **2022**, *286*, 131597.

(104) Bai, C.; Wang, L.; Zhu, Z. Adsorption of Cr(III) and Pb(II) by graphene oxide/alginate hydrogel membrane: Characterization, adsorption kinetics, isotherm and thermodynamics studies. *Int. J. Biol. Macromol.* **2020**, *147*, 898−910.

(105) Sarmah, D.; Karak, N. Starch based mechanically tough hydrogel for effective removal of toxic metal ions from wastewater. *Journal of Cleaner Production* **2022**, *344*, 131074.

(106) Wang, H.; Zhao, B.; Wang, L. Adsorption/desorption performance of Pb^{2+} and Cd^{2+} with super adsorption capacity of PASP/CMS hydrogel. *Water Sci. Technol.* **2021**, *84* (1), 43−54.

(107) Benhalima, T.; Ferfera-Harrar, H.; Lerari, D. Optimization of carboxymethyl cellulose hydrogels beads generated by an anionic surfactant micelle templating for cationic dye uptake: Swelling, sorption and reusability studies. *Int. J. Biol. Macromol.* **2017**, *105*, 1025−1042.

(108) Hosseini, H.; Zirakjou, A.; McClements, D. J.; Goodarzi, V.; Chen, W. H. Removal of methylene blue from wastewater using ternary nanocomposite aerogel systems: Carboxymethyl cellulose grafted by polyacrylic acid and decorated with graphene oxide. *J. Hazard. Mater.* **2022**, *421*, 126752.

(109) Chen, L.; Zhu, Y.; Cui, Y.; Dai, R.; Shan, Z.; Chen, H. Fabrication of starch-based high-performance adsorptive hydrogels using a novel effective pretreatment and adsorption for cationic methylene blue dye: Behavior and mechanism. *Chem. Eng. J.* **2021**, *405*, 126953.

(110) Chen, Z.; Pan, Y.; Cai, P. Sugarcane cellulose-based composite hydrogel enhanced by g-C3N4 nanosheet for selective removal of organic dyes from water. *Int. J. Biol. Macromol.* **2022**, *205*, 37−48.

(111) Dambies, L.; Guibal, E.; Roze, A. Arsenic(V) sorption on molybdate-impregnated chitosan beads. *Colloids Surf., A* **2000**, *170* (1), 19−31.

(112) Arayaphan, J.; Maijan, P.; Boonsuk, P.; Chantarak, S. Synthesis of photodegradable cassava starch-based double network hydrogel with high mechanical stability for effective removal of methylene blue. *Int. J. Biol. Macromol.* **2021**, *168*, 875−886.

(113) Godiya, C. B.; Kumar, S.; Xiao, Y. Amine functionalized egg albumin hydrogel with enhanced adsorption potential for diclofenac sodium in water. *J. Hazard. Mater.* **2020**, *393*, 122417.

(114) Koh, K. Y.; Chen, Z.; Zhang, S.; Chen, J. P. Cost-effective phosphorus removal from aqueous solution by a chitosan/lanthanum hydrogel bead: Material development, characterization of uptake process and investigation of mechanisms. *Chemosphere* **2022**, *286*, 131458.

(115) Li, K.; Lei, Y.; Liao, J.; Zhang, Y. A facile synthesis of graphene oxide/locust bean gum hybrid aerogel for water purification. *Carbohydr. Polym.* **2021**, *254*, 117318.

(116) Liao, Q.; Rong, H.; Zhao, M.; Luo, H.; Chu, Z.; Wang, R. Strong adsorption properties and mechanism of action with regard to tetracycline adsorption of double-network polyvinyl alcohol-copper alginate gel beads. *J. Hazard. Mater.* **2022**, *422*, 126863.

(117) Marotta, A.; Luzzi, E.; Salzano de Luna, M.; Aprea, P.; Ambrogi, V.; Filippone, G. Chitosan/zeolite composite aerogels for a fast and effective removal of both anionic and cationic dyes from water. *Polymers* **2021**, *13* (11), 1691.

(118) Wang, Y.; Lin, N.; Gong, Y.; Wang, R.; Zhang, X. Cu−Fe embedded cross-linked 3D hydrogel for enhanced reductive removal of Cr(VI): Characterization, performance, and mechanisms. *Chemosphere* **2021**, *280*, 130663.

(119) Malicevic, S.; Garcia Pacheco, A. P.; Lamont, K.; Estepa, K. M.; Daguppati, P.; van de Vegte, J.; Marangoni, A. G.; Pensini, E. Phosphate removal from water using alginate/carboxymethylcellulose/aluminum beads and plaster of paris. *Water Environment Research* **2020**, *92* (9), 1255−1267.

(120) Nowack, B.; VanBriesen, J. M. Chelating Agents in the Environment. In *Biogeochemistry of Chelating Agents*; American Chemical Society: 2005; Vol. *910*, pp 1−18.

(121) Jeon, C.; Ha Park, K. Adsorption and desorption characteristics of mercury(II) ions using aminated chitosan bead. *Water Res.* **2005**, *39* (16), 3938−3944.

(122) Jeon, C.; Park, J. Y.; Yoo, Y. J. Characteristics of metal removal using carboxylated alginic acid. *Water Res.* **2002**, *36* (7), 1814−1824.

(123) Jones, P. W.; Williams, D. R. Chemical speciation used to assess [S,S′]-ethylenediaminedisuccinic acid (EDDS) as a readily-biodegradable replacement for EDTA in radiochemical decontamination formulations. *Applied Radiation and Isotopes* **2001**, *54* (4), 587−593.

(124) Yang, R.; Luo, C.; Zhang, G.; Li, X.; Shen, Z. Extraction of heavy metals from e-waste contaminated soils using EDDS. *Journal of Environmental Sciences* **2012**, *24* (11), 1985−1994.

(125) Zeng, Q. R.; Sauvé, S.; Allen, H. E.; Hendershot, W. H. Recycling EDTA solutions used to remediate metal-polluted soils. *Environ. Pollut.* **2005**, *133* (2), 225−231.

(126) Voglar, D.; Lestan, D. Electrochemical separation and reuse of EDTA after extraction of Cu contaminated soil. *J. Hazard. Mater.* **2010**, *180* (1), 152−157.

(127) Yu, X.; Tong, S.; Ge, M.; Wu, L.; Zuo, J.; Cao, C.; Song, W. Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals. *Journal of Environmental Sciences* **2013**, *25* (5), 933−943.

(128) Hu, Y.; Boyer, T. H. Removal of multiple drinking water contaminants by combined ion exchange resin in a completely mixed flow reactor. *Journal of Water Supply: Research and Technology-Aqua* **2018**, *67* (7), 659−672.

(129) Ferro-García, M. A.; Utrera-Hidalgo, E.; Rivera-Utrilla, J.; Moreno-Castilla, C.; Joly, J. P. Regeneration of activated carbons exhausted with chlorophenols. *Carbon* **1993**, *31* (6), 857−863.

(130) Gul, K.; Sohni, S.; Waqar, M.; Ahmad, F.; Norulaini, N. A. N.; A. K., M. O. Functionalization of magnetic chitosan with graphene oxide for removal of cationic and anionic dyes from aqueous solution. *Carbohydr. Polym.* **2016**, *152*, 520−531.

(131) Wang, F.; Yang, B.; Wang, H.; Song, Q.; Tan, F.; Cao, Y. Removal of ciprofloxacin from aqueous solution by a magnetic chitosan grafted graphene oxide composite. *J. Mol. Liq.* **2016**, *222*, 188−194.

(132) Fan, L.; Luo, C.; Sun, M.; Qiu, H.; Li, X. Synthesis of magnetic β-cyclodextrin−chitosan/graphene oxide as nanoadsorbent and its application in dye adsorption and removal. *Colloids Surf., B* **2013**, *103*, 601−607.

(133) Wang, W.-R.; Chen, P.-Y.; Deng, J.; Chen, Y.; Liu, H.-J. Carbon-dot hydrogels as superior carbonaceous adsorbents for removing perfluorooctane sulfonate from water. *Chem. Eng. J.* **2022**, *435*, 135021.

(134) Malatji, N.; Makhado, E.; Ramohlola, K. E.; Modibane, K. D.; Maponya, T. C.; Monama, G. R.; Hato, M. J. Synthesis and characterization of magnetic clay-based carboxymethyl cellulose-acrylic acid hydrogel nanocomposite for methylene blue dye removal from aqueous solution. *Environmental Science and Pollution Research* **2020**, *27* (35), 44089−44105.

(135) Capello, C.; Fischer, U.; Hungerbühler, K. What is a green solvent? A comprehensive framework for the environmental assessment of solvents. *Green Chem.* **2007**, *9* (9), 927−934.

(136) Jóźwiak, T.; Kowalkowska, A.; Filipkowska, U.; Struk-Sokołowska, J.; Bolozan, L.; Gache, L.; Ilie, M. Recovery of phosphorus as soluble phosphates from aqueous solutions using chitosan hydrogel sorbents. *Sci. Rep.* **2021**, *11* (1), 16766.

(137) Mo, L.; Pang, H.; Tan, Y.; Zhang, S.; Li, J. 3D multi-wall perforated nanocellulose-based polyethylenimine aerogels for ultra-high efficient and reversible removal of Cu(II) ions from water. *Chem. Eng. J.* **2019**, *378*, 122157.

(138) Laus, R.; de Fávere, V. T. Competitive adsorption of Cu(II) and Cd(II) ions by chitosan crosslinked with epichlorohydrin−triphosphate. *Bioresour. Technol.* **2011**, *102* (19), 8769−8776.

(139) Mo, L.; Pang, H.; Lu, Y.; Li, Z.; Kang, H.; Wang, M.; Zhang, S.; Li, J. Wood-inspired nanocellulose aerogel adsorbents with excellent selective pollutants capture, superfast adsorption, and easy regeneration. *J. Hazard. Mater.* **2021**, *415*, 125612.

(140) Mahaninia, M. H.; Wilson, L. D. Cross-linked chitosan beads for phosphate removal from aqueous solution. *J. Appl. Polym. Sci.* **2016**, *133* (5), 42949.

(141) Peng, Q.; Liu, M.; Zheng, J.; Zhou, C. Adsorption of dyes in aqueous solutions by chitosan−halloysite nanotubes composite hydrogel beads. *Microporous Mesoporous Mater.* **2015**, *201*, 190−201.

(142) Duman, O.; Polat, T. G.; Diker, C. Ö.; Tunç, S. Agar/κ-carrageenan composite hydrogel adsorbent for the removal of Methylene Blue from water. *Int. J. Biol. Macromol.* **2020**, *160*, 823−835.

(143) El-Fawal, E. M.; Zaki, T. Taguchi Optimization Study for Efficient Removal of Phenolic Pollutants from Wastewater Using Cu-Alanine Functionalized Graphene Oxide and Their Grafted Alginate Microbeads: Isotherm Modeling. *Journal of Polymers and the Environment* **2022**, *30* (3), 971−987.

(144) Mohammed, N.; Grishkewich, N.; Berry, R. M.; Tam, K. C. Cellulose nanocrystal−alginate hydrogel beads as novel adsorbents for organic dyes in aqueous solutions. *Cellulose* **2015**, *22* (6), 3725−3738.

(145) Muthu Prabhu, S.; Meenakshi, S. Defluoridation of water using dicarboxylic acids mediated chitosan-polyaniline/zirconium biopolymeric complex. *Int. J. Biol. Macromol.* **2016**, *85*, 16−22.

(146) Wang, Q.; Shao, J.; Xu, J.; Dong, F.; Xiong, Y.; Chen, Q. In-situ formed Cyclodextrin-functionalized graphene oxide/poly (N-isopropylacrylamide) nanocomposite hydrogel as an recovery adsorbent for phenol and microfluidic valve. *J. Colloid Interface Sci.* **2022**, *607*, 253−268.

(147) Acevedo-García, V.; Rosales, E.; Puga, A.; Pazos, M.; Sanromán, M. A. Synthesis and use of efficient adsorbents under the principles of circular economy: Waste valorisation and electro-advanced oxidation process regeneration. *Sep. Purif. Technol.* **2020**, *242*, 116796.

(148) Liu, S. X.; Sun, C. L.; Zhang, S. R. Photocatalytic Regeneration of Exhausted Activated Carbon Saturated with Phenol. *Bull. Environ. Contam. Toxicol.* **2004**, *73* (6), 1017−1024.

(149) Myint, K. T. T.; Liu, Y.; Niu, H.; Chen, J.; Jiao, Z. Photodegradation of Organic Pollutants Via Carbon Nitride/Graphene-Oxide Nanocomposite Loaded on Polyacrylic Acid Hydrogel with Free Separation. *Catalysis Surveys from Asia* **2021**, *25* (2), 159−167.

(150) Xing, Y.; Liu, D.; Zhang, L.-P. Enhanced adsorption of Methylene Blue by EDTAD-modified sugarcane bagasse and photocatalytic regeneration of the adsorbent. *Desalination* **2010**, *259* (1), 187−191.

(151) Lin, L.; Jiang, W.; Bechelany, M.; Nasr, M.; Jarvis, J.; Schaub, T.; Sapkota, R. R.; Miele, P.; Wang, H.; Xu, P. Adsorption and photocatalytic oxidation of ibuprofen using nanocomposites of TiO_2 nanofibers combined with BN nanosheets: Degradation products and mechanisms. *Chemosphere* **2019**, *220*, 921−929.

(152) Piao, M.; Du, H.; Sun, Y.; Teng, H. Self-regeneration hybrid hydrogel for bisphenol a adsorption in water. *Environmental Science and Pollution Research* **2022**, *29* (28), 43169−43178.

(153) ChemAnalyst. *Hydrochloric Acid Price and Forecast.* https://www.chemanalyst.com/Pricing-data/hydrochloric-acid-61 (accessed 2023/08/21).

(154) ChemAnalyst *Titanium Dioxide Price and Forecast.* https://www.chemanalyst.com/Pricing-data/titanium-dioxide-52 (accessed 2023/08/21).

(155) Plaza, J.; Arencibia, A.; López-Muñoz, M. J. Optimization of thermal exfoliation of graphitic carbon nitride for methylparaben photocatalytic degradation under simulated solar radiation. *Journal of Materials Chemistry A* **2023**, *11* (18), 9922−9930.

(156) Oladipo, H.; Yusuf, A.; Al-Ali, K.; Palmisano, G. Techno-Economic Evaluation of Photocatalytic H 2 S Splitting. *Energy Technology* **2021**, *9*, 2100163.

(157) de Lasa, H.; Serrano, B.; Salaices, M. The Irradiation Field in Photocatalytic Reactors. In *Photocatalytic Reaction Engineering*; de Lasa, H., Serrano, B., Salaices, M., Eds.; Springer US: Boston, MA, 2005; pp 63−100.

(158) Muthukumar, C.; Changmai, M.; Vincent, S.; Raju, K.; Mathai, J.; Damale, S.; B G, P. K. Process optimization, characterization and economic evaluation of nanoparticles derived from galvanic sludge for photodegradation of 4-nitrophenol under natural sunlight. *Journal of Cleaner Production* **2022**, *371*, 133616.

(159) Eskandari, P.; Roghani-Mamaqani, H.; Salami-Kalajahi, M.; Abousalman-Rezvani, Z. Modification of cellulose nanocrystal with dual temperature- and CO_2-responsive block copolymers for ion adsorption applications. *J. Mol. Liq.* **2020**, *310*, 113234.

(160) Bai, Y.; Liang, Y. N.; Hu, X. An eco-friendly approach for heavy metal adsorbent regeneration using CO_2-responsive molecular octopus. *Chemosphere* **2017**, *185*, 1157−1163.

(161) Han, D.; Tong, X.; Boissière, O.; Zhao, Y. General Strategy for Making CO_2-Switchable Polymers. *ACS Macro Lett.* **2012**, *1* (1), 57−61.

(162) Wang, Q.; Xiong, Y.; Xu, J.; Dong, F.; Xiong, Y. Oxidation-Resistant Cyclodextrin-Encapsulated-MXene/Poly (N-isopropylacrylamide) composite hydrogel as a thermosensitive adsorbent for phenols. *Sep. Purif. Technol.* **2022**, *286*, 120506.

(163) Yang, B.; Xu, D.; Wu, X.; Li, Z.; Lei, L.; Zhang, X. Efficient removal of pentachlorophenol from wastewater by novel hydrophobically modified thermo-sensitive hydrogels. *Journal of Industrial and Engineering Chemistry* **2015**, *25*, 67−72.

(164) Yao, Y.; Liu, S. *Ultrasonic Technology for Desiccant Regeneration*, 1st ed.; Wiley: Hoboken, NJ, 2014; p 334.

(165) Breitbach, M.; Bathen, D. Influence of ultrasound on adsorption processes. *Ultrasonics Sonochemistry* **2001**, *8* (3), 277−283.

(166) Girard, M.; Vidal, D.; Bertrand, F.; Tavares, J. R.; Heuzey, M.-C. Evidence-based guidelines for the ultrasonic dispersion of cellulose nanocrystals. *Ultrasonics sonochemistry* **2021**, *71*, 105378.

(167) Gkika, D. A.; Mitropoulos, A. C.; Kyzas, G. Z. Why reuse spent adsorbents? The latest challenges and limitations. *Science of The Total Environment* **2022**, *822*, 153612.