

Review

# Removal of Heavy Metal Ions from Wastewaters by Using Chitosan/Poly(Vinyl Alcohol) Adsorbents: A Review

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**Abstract:** Through epistemic efforts in water remediation, numerous sorbents have emerged as either low-cost or more expensive. This review article describes the properties, functions and modifications of cost-effective sorbents based on chitosan and poly(vinyl alcohol) blends for aqueous solutions treatment from heavy metals. Interesting synthesis routes have been reported for the production of membranes, beads, foams and mats, while the kinetic and thermodynamic studies provide spherical knowledge of the system. Tables with the adsorbent's capacity and enthalpy change are included, while indicative images from the synthesis and characterization techniques of the adsorbents are presented.

**Keywords:** chitosan; PVA; synthesis; characterization; adsorption capacity; kinetics



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## 1. Introduction

Heavy metal is one of the most widespread pollutants, with their release into several ecosystems, especially the aquatic one, rising noticeably with industrial development over the last twenty years. Noteworthy is the fact that these notorious toxic metals can end up in ecosystems via several pathways, such as household products, industrial wastewaters, mineral weathering and manufacturing industries such as automobiles, batteries, textiles, dyes and pesticides accompanied by the mismanagement of underground waste disposal, rendering the water bodies as sinks for their accumulation [1]. Even in low concentrations, heavy metals (Cu, Ni, Zn, Pb, Cr, Cd, Co, As, Fe) can provoke several life-threatening effects in animals and human beings (Table 1). Hence, heavy metal contamination has evolved into a severe challenge for both the ecological system and public health, on a global basis. In an attempt to minimize the aforementioned threat, the scientific community has centralized its effort on the removal of heavy metal ions through the application of specified technologies.

**Table 1.** Discharge limits and health effects of heavy metals [2–4].

Heavy Metal	Maximum Industrial Effluent Discharge Standard (mg/L)			Drinking Water (mg/L)	Health Effects	Sources
	EPA	Malaysian (DOE) Standard A	Standard B	WHO		
Lead	0.015	0.1	0.5	0.01	High risk of lower IQ, impaired intellectual ability and behavioral problems such as hyperactivity in children. May cause slow growth, mental retardation, hearing and anemia problems in children. Causes cardiovascular effects, nervous system damage, increased blood pressure and hypertension in adults. Cancer and renal kidney disease.	Metal plating, mining activities, paint-manufacture industries, pesticides, smoking, automobile emissions, burning of coal
Arsenic	0.01	0.05	0.1	0.01	Carcinogenic, dermatological, cardiorenal and gastrointestinal effects. Skin cancers, lungs, bladder and kidney, cancer and other internal tumors. Vascular diseases and diabetes, infant mortality and weight loss of newborn babies. Hearing loss, reproductive toxicity, hematologic disorders, neurological diseases, developmental abnormalities and neurobehavioral disorders.	Mining, smelting of arsenic-bearing minerals, pesticides, fungicides, sedimentary rocks, geothermal water and from weathered volcanic rocks. Human activities such as manufacturing, metallurgy and wood preservation.
Nickel	0.2	0.2	1	0.07	DNA damage, eczema, phytotoxicity, respiratory cancer, dry cough, bone nose, and lung cancer. Cyanosis, rapid respiration, shortness of breath, tightness of the chest, chest pain, nausea, vomiting, dizziness and headache.	Metal plating, mining, fertilizers, tanneries, batteries, paper, pesticides, electronics, petrochemical, textile, production of some alloys, printing and silver refineries.
Chromium	0.05 <sup>a</sup> 0.10 <sup>b</sup>	0.2	0.1	0.05	Lung cancer, dermatitis, severe diarrhea, vomiting, pulmonary congestion, liver and kidney damage.	Plastic, pigment, wood preservative, electroplating, leather tanning, cement, mining, dyeing and fertilizer.
Copper	1.3	0.2	1	2	Abdominal pain, diarrhea, weakness, cramps, increased blood pressure and respiratory rates, kidney and liver damages, convulsions, vomiting or even death.	Mining, refining ores, fertilizer and pesticides industries, tanneries, batteries and paper industries.

Table 1. Cont.

Heavy Metal	Maximum Industrial Effluent Discharge Standard (mg/L)			Drinking Water (mg/L)	Health Effects	Sources
	EPA	Malaysian (DOE) Standard A	Standard B	WHO		
Zinc	5	1	1	3	Abdominal pain, phytotoxic, anemia, nausea, skin irritations, cramps and vomiting.	Pharmaceuticals, galvanizing, paints, pigments, insecticides, cosmetics, brass plating, wood-pulp production, ground and newsprint-paper production, zinc and brass metal works, refineries and plumbing.
Cadmium	0.005	0.01	0.02	0.003	Detrimental effects on kidney, lungs, liver, heart and bones of human being. Cancers, bronchiolitis, emphysema, fibrosis and skeletal damage.	Metal plating, mining activities, paint-manufacture industries, steel and plastics industries, electroplating and coating operations. Nickel–cadmium batteries, Cd-Te thin-film solar cells and pigments. Welding, fertilizers and nuclear emission plants.
Mercury	0.002	0.005	0.05	0.001	Harmful effects on nervous, digestive and immune systems, lungs and kidneys. Corrosive to the skin, eyes and gastrointestinal tract, and may induce kidney toxicity if ingested. Damage to the brain, reproductive, hematologic, cardiovascular and respiratory systems.	Coal-fired power stations, residential coal burning for heating and cooking, industrial processes, waste incinerators, mining for mercury, gold and other metals. Mineral deposits, fossil fuel or ores, pesticides, batteries and paper industry.

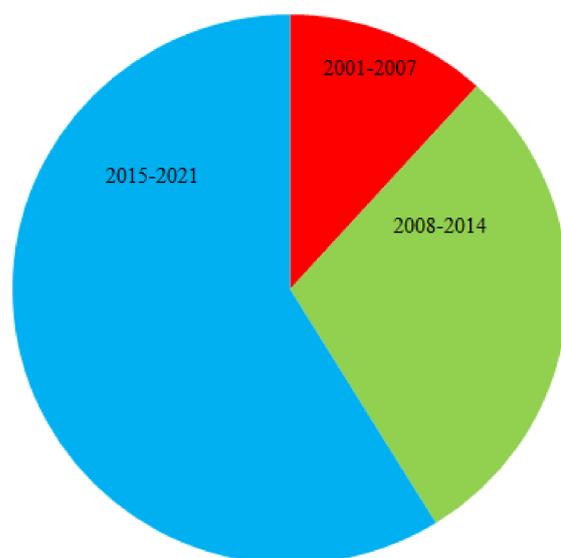
<sup>a</sup> Cr(VI); <sup>b</sup> Cr(III).

To date, a wide spectrum of methodologies has been developed and applied to remove heavy metals from wastewaters, including chemical precipitation, ion exchange, solvent extraction, electrodialysis, adsorption, advanced oxidation processes, and several membrane technologies [5,6]. From both technical and cost-effective points of view, adsorption remains the most applicable choice since it possesses a fast kinetic, costless, manageable, simple, and highly efficient dynamic [1,7,8]. Various adsorbents have been proposed in the literature, such as silica gel, activated carbons, metal-organic frameworks (MOFs), resins, clays, as well as several polymeric types, for the removal of various pollutants from wastewaters and water bodies [7,9–11]. Subsequently, constant research has been comprehensively implemented to develop powerful adsorbents with satisfactory adsorption profiles. Concerning the cost feasibility and sustainable importance, carbohydrate biopolymers, such as cellulose, alginate, and chitosan have been a spot of great attention over the last two decades as highly favorable adsorbents. The latter is attributed to their exceptional inherent merits, involving their natural abundance, biodegradability, easy processing and eco-friendly and low-cost characteristics. Numerous studies have been executed investigating the adsorption propensity of biopolymer-based adsorbents towards several heavy metal types, pharmaceuticals,

dyes and other organic compounds [12,13]. Among these alternatives, chitosan (CS) is the most widespread and environmentally friendly approach in this framework, owing to its remarkable characteristics. CS is synthesized by a deacetylation reaction of chitin, which is a naturally occurring polysaccharide [14]. It possesses an attractive character as a pseudo-natural polymer due to its abundant, nontoxic, biodegradable and biocompatible nature, while its inherent antibacterial and good adsorption-capacity properties should not be omitted [11]. As such, it seems to be a promising candidate for environmental remediation practices.

Nevertheless, since there are two sides to every coin, the rapid disintegration of CS in low pH values and abrupt pH variations limits its applicability as an adsorbent [15,16]. Moreover, CS suffers from a comparatively poor mechanical performance such as low mechanical strength and swelling behavior. Thus, it would be blended with other polymers in order to augment its features. Among them, poly(vinyl alcohol) (PVA) is a nontoxic, biocompatible and biodegradable polymer with good mechanical properties and good fiber and membrane-forming ability. As a matter of the fact, the combination of CS (amino groups) with PVA (hydroxyl groups) can reveal a synergistic effect on the binding and removal of heavy metals from wastewaters [7,15]. A commonly applied practice for the strengthening of CS/PVA-based networks is the crosslinking process, employing agents such as pentasodium tripolyphosphate (TPP), glutaraldehyde (GLA), ethylenediamine, epichlorohydrin (EPI), and ethylene glycol diglycidyl ether (EGDE) reagents.

Since the research within the frame of CS/PVA-based adsorbents is currently blooming, we considered the collection of the most recent and novel literature in the field to be a critical handbook, especially for the new researchers. The present review is intended to offer an overview of the available literature and recent developments of CS/PVA-based adsorbents that displayed superior adsorption activities towards several hazardous and toxic heavy metal ions, including  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$ . Despite the fact that several reviews were published during the last two decades concerning the examination of CS adsorbents as candidates for heavy metal removal, there is an absence of a recent and concentrated effort to gather and present the research progress of such a specialized and promising topic as the CS/PVA-based adsorptive materials, especially in terms of the synthetical pathway, adsorption aptitude, recovery and reusability of the adsorbents. Scheme 1 reveals the ongoing interest of the community for this type of sorbents over the last 21 years. Representative images were selected in order to provide a spherical view to the readers and to simplify the daily routine of the young researchers.



**Scheme 1.** Studies of CS/PVA-based adsorbents for heavy-metal-ion removal over the last 21 years [SCOPUS database].

## 2. Synthesis Routes and Characterization of CS/PVA-Based Adsorbents

The form of adsorbent holds a crucial role in its effectiveness in the removal of heavy-metal-ion pollutants, since any defect in the adsorbent structure could hinder its applicability. More specifically, the form is of much significance in wastewater treatment technologies, since the collection process of the adsorbent material from the aqueous media in practical applications and the adsorption features may be strongly affected. For instance, adsorbents in the shape of flake and powder are not appropriate for such applications, due to the potential dissolution and challenging separation. As far as CS is concerned, raw CS can contain in its polymeric structure crystalline regions, which would make the adsorption of metal ions difficult [17]. CS/PVA hydrogel beads have been extensively explored to ameliorate the adsorption capacity of the polymers by minimizing the crystallinity via the gel-formation procedure and also afford the opportunity of regeneration and reusability after several adsorption cycles. Adsorbents in the form of membranes have been also proposed in the present framework, due to their easy-processing adequate contribution to the removal of heavy metals during wastewater treatment.

In the framework of the above, the several CS/PVA-based adsorbents found in the literature for the remediation of heavy metals have been categorized according to their form (membranes, hydrogels, hydrogel beads, foams) and are discussed for their synthesis route, physicochemical characteristics, adsorption performance, and reusability. Additionally, the most representative and innovative, to our view, works within the field are debated.

### 2.1. Chitosan/Poly(Vinyl Alcohol)-Based Membranes

#### 2.1.1. Solvent Casting

The solvent-casting technique can be considered as the easiest and most widespread synthesis route for the preparation of CS/PVA adsorbents. It is based on the mixing of two polymeric solutions mainly with the aid of magnetic stirring to obtain a homogenous mixture, followed by its deposition into a predefined mold. In a first step, the used solvent is allowed to evaporate, leaving behind a matrix of specific structure and morphology. The formed membrane is then washed with water or any other neutralizing media and dried properly.

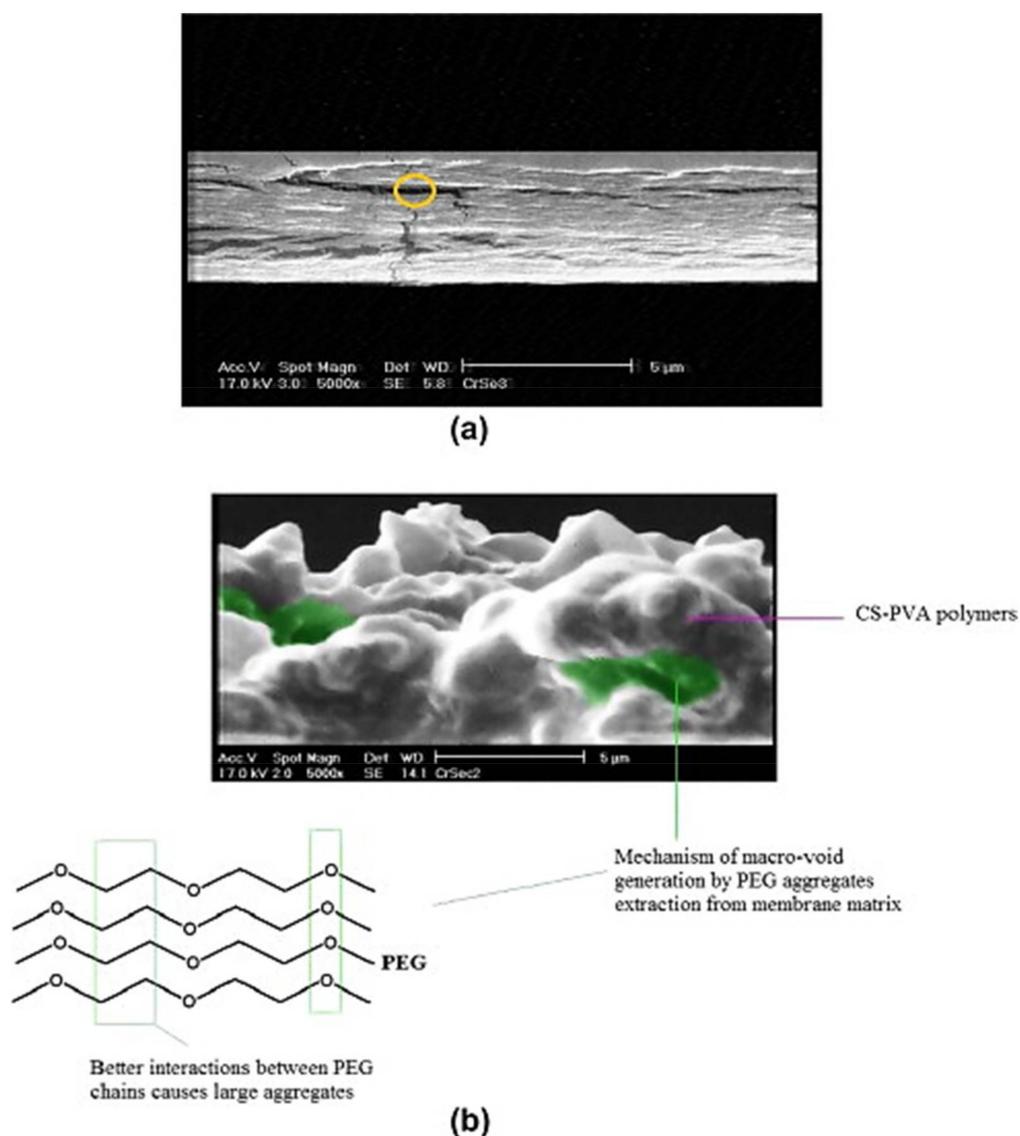
An interesting and first approach utilizing the solvent-casting technique was applied by the team of Anitha et al. [18], who investigated the binding of  $Zn^{2+}$  to CS/PVA membranes. Firstly, CS nanoparticles with a size of 10–60 nm were prepared using the ionotropic gelation technique and employing TPP as the crosslinking agent. Afterward, a CS and a PVA solution were mixed together (1:3 molar ratio) and GLA was used for the crosslinking of the polymeric chains. The two solutions were kept in magnetic stirring, poured into an appropriate mold, and then the formed matrix was dried to prepare the final CS/PVA film. The formed membranes were studied for their morphological and crystallographic properties. Interesting are the findings from the SEM images, implying the adsorption of Zn(II) ions onto the CS/PVA adsorbent's functional groups. The maximum adsorption was observed as 99.45% for an initial zinc-ion concentration of 10 mg/L at pH of 5.0, contact time of 30 min, with 5 g/L of adsorbent dose and agitation rate of 160 rpm. FAAS was used for the determination of zinc-ion concentration. The adsorption kinetics was investigated by fitting the experimental data to pseudo-first-order, pseudo-second-order, Weber and Morris intraparticle diffusion and Boyd kinetic models. Adsorption equilibrium data were analyzed by the Langmuir and Freundlich adsorption isotherm models, and it was found that the Freundlich model best fits the experimental data. The desorption of zinc ions from the CS/PVA blend was carried out with HCl solution. A similar synthetic pathway was applied by the same researchers after two years, aiming this time to be more centered at the removal of lead(II) ions and providing hopeful results for the adsorptive properties of the fabricated membranes for this target pollutant. The maximum adsorption of 96.1% was regarded for an initial concentration of 10 mg/L at pH 5 and contact time 40 min, adsorbent dose of 6 g/L at 30 °C and 150 rpm. The Langmuir, Freundlich and Temkin isotherm models as well as pseudo-first-order, pseudo-second-order, intraparticle diffusion and

Boyd kinetic models fitted the data. The desorption of lead ions was performed effectively using HCl solution reaching a maximum of 91.5%. The system was well-described by the Freundlich and pseudo-second-order models, while the negative value of enthalpy change indicated the exothermic nature of the adsorption [19].

Another common policy in the literature for the improvement of the absorptive properties of CS/PVA-based membranes produced via the solvent-casting technique is the combination with polyionic or other agents. Within this context, Sahebamee et al. [9] fabricated polyethyleneimine (PEI), which is a cationic polymer with plentiful amino groups and a great affinity with various heavy metals. In this study, CS/PVA membranes modified with PEI were prepared for the targeted removal of Cu(II), Cd(II) and Ni(II) ions. The aim was in fact to combine the beneficial adsorptive characteristic of the CS/PVA blend, with the addition of extra adsorption sites after the incorporation of PEI. As for the solvent-casting process, a triple-blend (CS/PVA/PEI) was left for two days to remove the excess air bubbles and facilitate the thermal crosslinking. The solutions were cast on glass plates and the solvent was evaporated at room-temperature (RT) conditions. The variation in this step was that the dried films were immersed in a sodium hydroxide solution to neutralize the acid environment and washed with deionized water. The dried membranes were then characterized by FTIR, SEM, BET, and swelling studies. Results indicated that the composition of PEI in the membranes had a critical point for their adsorptive properties, since it affected the porosity and thus the swelling degrees of the formed materials. The experimental data were fitted to the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The Langmuir equation gave a relatively better fit to the equilibrium data. The low values for  $E$  (below 8 kJ/mol) in the Dubinin–Radushkevich isotherm suggested the physical adsorption nature of the adsorption processes. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to evaluate the kinetics. The negative values of enthalpy change suggested the exothermic nature of the adsorption process. It was found that the affinity of the membrane on the basis of mmol metal ions per g of adsorbent mass was in the order of  $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$  (1.355, 1.286, and 0.998 mmol/g for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$ , respectively) The membrane was regenerated with EDTA and showed less than 5% capacity decrease after four cycles.

Another polymer that was examined for its effect on the porosity of the CS/PVA dense background membranes towards heavy metal removal was poly(ethylene glycol) (PEG). From our perspective, the most critical aspects that an adsorptive membrane should possess are advanced durability between the several regeneration cycles and the high porosity of the membranes, in order to have superior capacity for metal adsorption. According to the study by Salehi et al. [20] CS/PVA/PEG membranes exhibited a promising performance for the removal of  $\text{Cu}^{2+}$  from aqueous solutions, as extracted from the SEM, AFM and wettability studies, proposing PEG as a potential porogen agent for the generation of macrovoids in the compressed matrix of CS/PVA membranes. In an older but more innovative work of the same team, CS/PVA and PEG were combined with amino-modified multiwalled carbon nanotubes (MWCNT-NH<sub>2</sub>) in order to synthesize composite CS/PVA/PEG/MWCNT-NH<sub>2</sub> thin membranes through a simple solvent-casting method, which could contribute to the removal of Cu(II) ions [21]. For the first time, MWCNT-NH<sub>2</sub> nanocomposites were incorporated into the studied matrix in order to enhance the dispersivity, mechanical performance, reusability, stability, and adsorptive properties of the membranes. The thickness of the prepared membranes was approximately 10  $\mu\text{m}$ , while according to SEM and AFM results, the surface of the membranes became rougher after the addition of MWCNT-NH<sub>2</sub>, while the introduction of PEG could ameliorate the adsorption owing to the increased surface area and hydrophilicity of the novel materials, as depicted in Figure 1. The adsorption capacity of copper ions was determined experimentally using 0.4 g/L of adsorbent mass. FAAS was used to determine the Cu(II) concentrations, and the adsorbent capacity was calculated  $\sim 35$  mg/g. The pseudo-second-order kinetic model fitted the experimental data better, while the enthalpy change was about 8.4 kJ/mol. Regeneration of

the membrane was obtained by immersion in EDTA-eluting solution, and showed more than 80% efficiency after three cycles.



**Figure 1.** (a) MWCNT-NH<sub>2</sub> tails pulled out from the fractured matrix of CS/PVA/PEG/MWCNT-NH<sub>2</sub> membrane. (b) Macropores generated by extraction of PEG aggregates from CS/PVA polymeric matrix. Reprinted with permission from [20].

Another group that worked on the incorporation of porogen agents onto CS/PVA-based membranes for advanced adsorptive performance towards heavy metals removal is Habiba et al. [22]. Owing to its porous aluminosilicate architecture, zeolite was effectively enclosed into the CS/PVA matrix, with the aim of hosting several cations and organic compounds, such as methyl orange, Congo red and Cr(VI). The synthesized CS/PVA/zeolite composite membranes were crosslinked employing GLA and were afterward characterized with the aid of a couple of techniques, such as FE-SEM, FTIR, XRD, TGA, while swelling tests were also conducted. Through FTIR and XRD studies, the strong interactions between CS, PVA and the inorganic filler were proved, whereas SEM micrographs depicted the porous and rough surface of the fabricated membranes. The adsorption behavior of the composite for the removal of Cr(VI) was described by using a pseudo-second-order kinetic model. The adsorption capacity of the composite for Cr(VI) was 450 mg/g and a negligible change was observed after five repeated cycles. The effect of the degree of deacetylation on

the property and adsorption capacity of CS/PVA electrospun membranes has also been investigated by Habiba et al. [23].

One more study inspired by the merits of inorganic fillers' incorporation onto the CS/PVA matrix for augmented adsorption performance against heavy metal pollution was successfully reported by Kalantari et al. [24]. This time, talc, with the chemical formula  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$  was combined for the first time with CS and PVA to prepare composite membranes for the removal of Pb(II) and Cr(VI) ions. The adsorbents were prepared once again via a solvent-casting method, while NaOH treatment and drying were applied to obtain the final membranes. The performance of the composites was evaluated through FTIR, FE-SEM, XRD, TGA and solubility tests. The Langmuir isotherm model fitted the data better than the Freundlich isotherm model, and the pseudo-second-order kinetic model fitted the data better than the pseudo-first-order model. The maximum adsorption capacity for Pb(II) and Cr(VI) ions was calculated as 430 and 479 mg/g, respectively. The regeneration studies showed negligible capacity changes after five cycles.

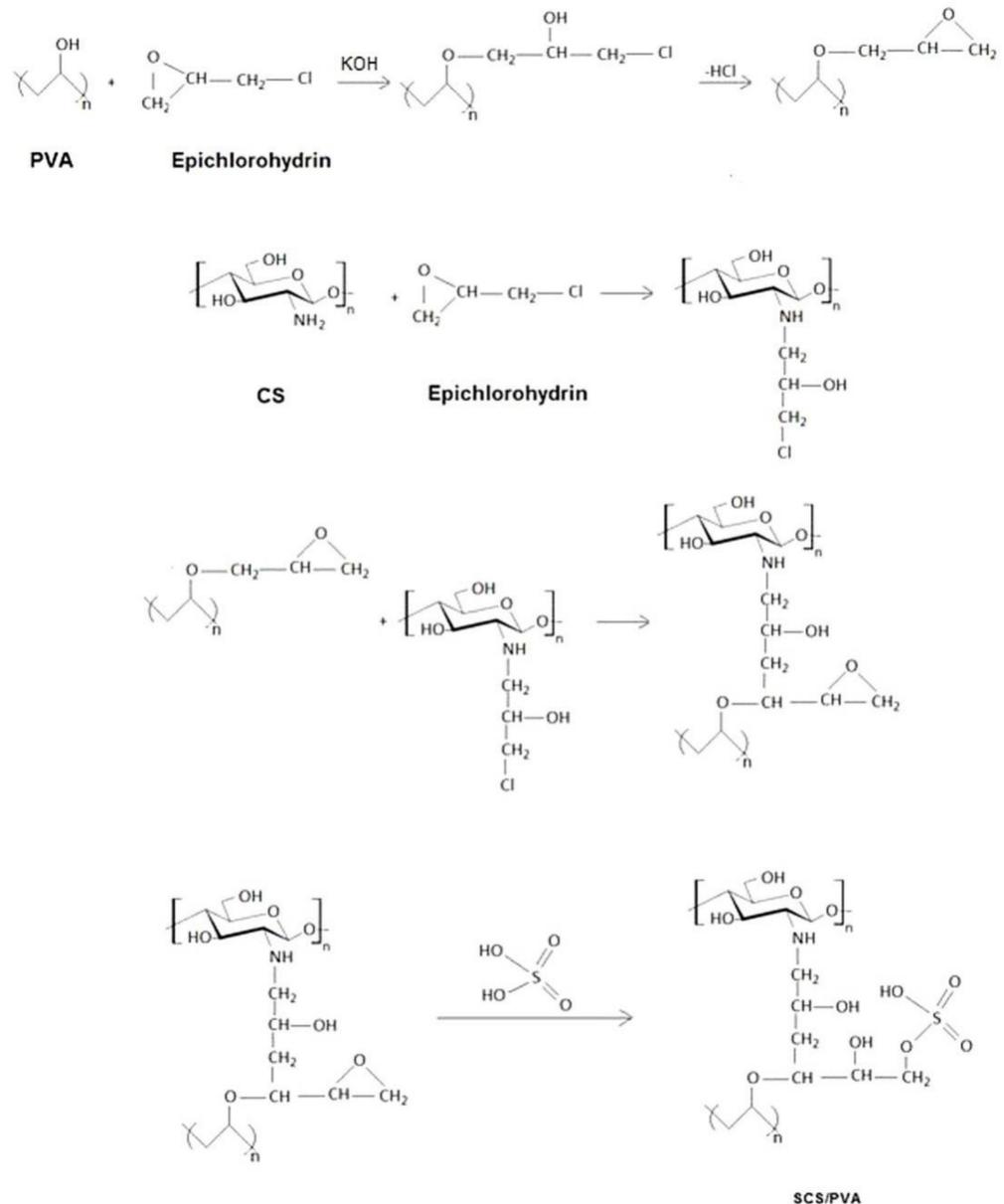
In an attempt to enhance the adsorptive removal of Pb(II) ions from aqueous solutions, Vatanpour et al. modified CS/PVA adsorptive membranes with detonation nanodiamonds (DNDs) [25]. Nanodiamonds have shown an emerging character in the area of adsorption research, due to their outstanding mechanical and thermal performance, accompanied by their large specific surface area and the hydrophilic exterior, attributed to the high number of oxygenated functional groups. As a catholic remark, the addition of 1 wt% DNDs onto the CS/PVA membranes promoted the activity of these materials as heavy metal adsorbents for wastewater-treatment processes, and thus portrayed these materials, to our view, as highly promising. Adsorption capacity for Pb(II) increased from 29.5 mg/g (for the plain membrane) to 121.3 mg/g by the addition of 1.5 wt% DNDs.

An effective and worthwhile approach to mention for boosting the adsorption rate of several polymeric structures is their modification and addition of several new functional groups in the polymeric macromolecular chains. In this context, the team of Abu-Saied had the CS's structure modified with additional sulfonated groups, and then combined the sulfonated product (SCS) with PVA in order to fabricate absorbent membranes via a casting method, for the removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from aqueous media [26]. Epichlorohydrin (ECH) was used to crosslink the polymeric structures, while in Figure 2 the synthesis of sulfonated chitosan/polyvinyl alcohol membrane (SCS/PVA) is depicted. Freundlich and Langmuir adsorption isotherms were fitted to experimental data, and a pseudo-second-order rate equation was employed to model the kinetics of uptake for several copper- and nickel-ion concentrations.

With a similar conceptualization, Ajitha et al. [27] fabricated a chitosan oligosaccharide-graft-maleic anhydride/poly(vinyl alcohol)/silk fibroin (CS/PVA/SF-gMAH) composite membrane for the removal of lead ions from aqueous media. As for the assistance of these components, PVA and silk fibroin supported the polymeric network of CS oligosaccharide, after the formation of hydrogen bonds with the  $-\text{NH}_2$  groups of the oligosaccharide and by adding extra active spots for the adsorption procedure. The efficiency of heavy metal removal of the employed composite membranes could be schematically depicted in Figure 3. The maximum percentage removal of lead ions and the maximum adsorption capacity was found to be 93.75% and 168.93 mg/g, respectively.

Another up-and-coming approach, to our perspective, in the field of adsorptive membranes for organic pollutants removal is ion-imprinting technology. In brief, the ion-imprinting process is a three-step procedure, enclosing: (a) the complexation of metal ions to the polymerizable ligand, which acts as the template; (b) the polymerization of the latter complex; and finally, (c) the removal of the template after the polymerization step [28]. In this way, the designed structures have specified preferences and efficiency towards the target metal ions. In the context of the present literature survey, only two studies were detected applying this kind of methodology to design and prepare CS/PVA-based ion-imprinted membranes (IIM) for heavy metal removal. According to Shawky, a CS/PVA ion-imprinted membrane was prepared, after a crosslinking process with GLA, for the

adsorption of Ag(I) ions in aqueous media. Results showed that the produced IIMs had an adequate performance in terms of reusability and stability, since its operation after five cycles of use was still feasible. The IIM capacity for silver ions was 125 mg/g [28]. Zarghami et al. applied a similar methodology to prepare CS/PVA IIMs for the removal of copper(II) ions, also proving the reusable character of the membranes after the sorption cycles [6].

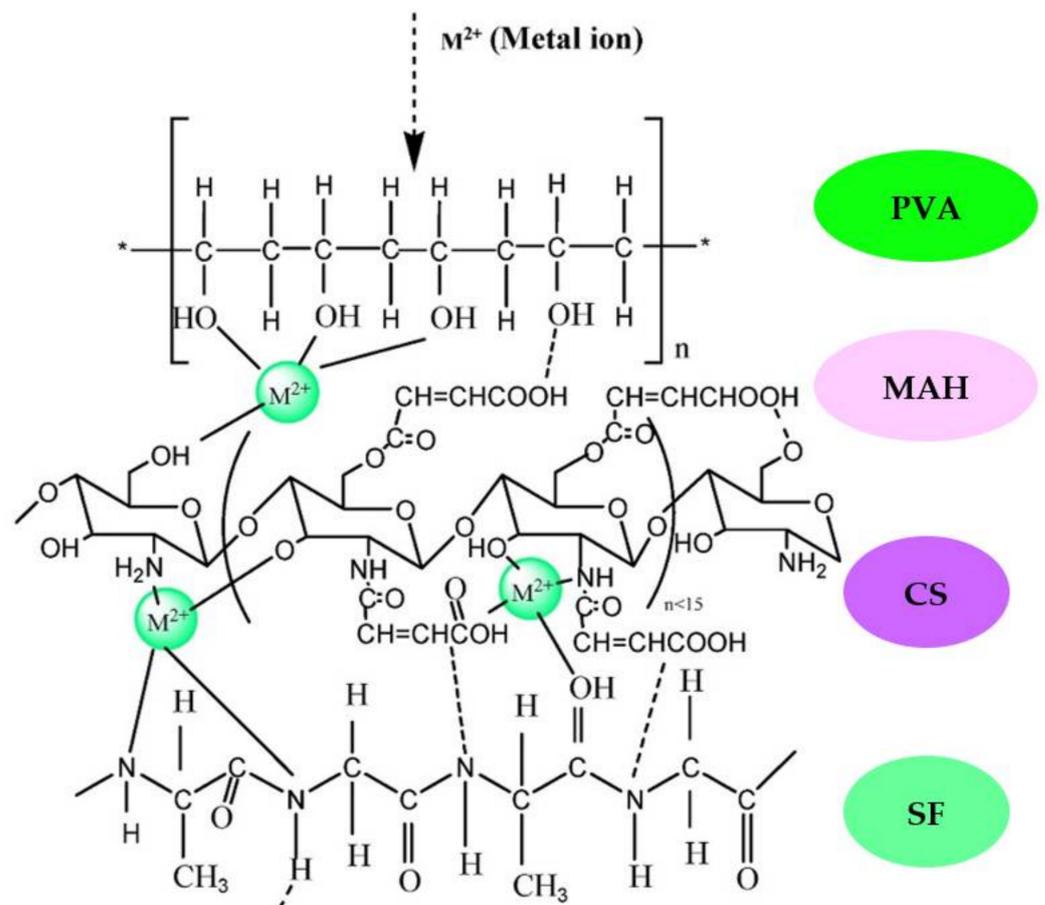


**Figure 2.** Synthetic route for the sulfonated chitosan/polyvinyl alcohol membrane (SCS/PVA). Reprinted from [26].

### 2.1.2. Electrospinning

A highly promising approach for synthesizing absorbent membranes has evolved: the electrospinning technique. By this pathway, electrospun nanofibrous membranes with regulated thickness and composition can be designed, which possess a higher adsorption rate and efficient character for wastewater treatment, due to the nanostructure of the fabricated fibers. As a technique, it requires an easy experimental system, including a high-voltage power supply, one or two needle-topped syringes, and a drum collector [29]. Electrospinning fundamentals are based on electrostatic forces from a viscoelastic polymer

solution to design nanofibers. In more detail, the polyelectrolyte solution is diffused from the tip of the needle and as the electric field is applied, the emitted liquid ink is led to the collector, where it is charge-neutralized [30]. During this path, the organic solvent of the polymeric solution is evaporated, and thus the polymer is solidified, producing a nanofibrous mat, collected at the drum component [29].



**Figure 3.** Structure of chitosan oligosaccharide-graft-maleic anhydride/poly(vinyl alcohol)/silk fibroin (CS/PVA/SF-gMAH)-binding heavy metals. Reprinted from [27].

The electrospinning process is a challenging issue when it comes to chitosan, due to its low solubility, stability, and deficient mechanical performance. To overcome these shortcomings, chitosan is often combined with other polymers, such as poly(vinyl alcohol), in order to ameliorate the mechanical properties of the electrospun fibers [31]. Despite the relatively low number of studies fabricating the electrospinning process, we envision the development of this methodology in the framework of CS/PVA-based absorbents. An interesting study on synthesis and characterization of CS-PVA electrospun nanofibers has been conducted by Talebian et al. [32].

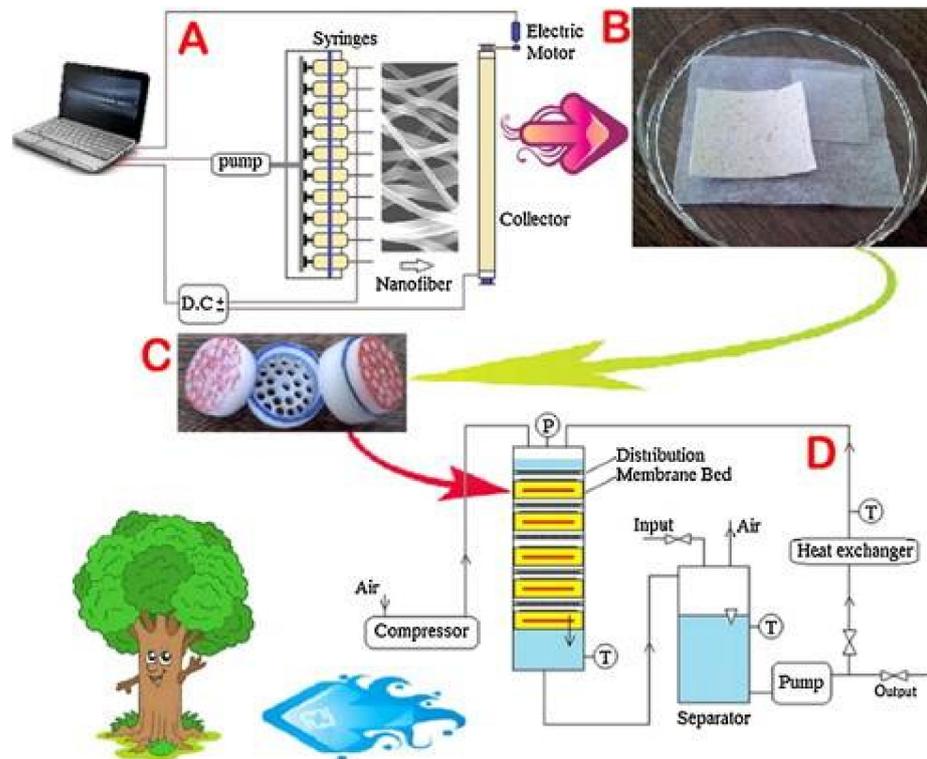
Concerning the CS/PVA adsorbents designed by the electrospinning process for heavy metal removal, there are eight interesting and noteworthy studies that were noticed across the available literature, with the most of them published during the years 2018–2022, aiming for the removal of Pb(II), Zn(II), Ni(II), Co(II), Cd(II), Cr(IV) and Fe(III) ions [33]. In fact, electrospun nanofibrous membranes present a promising character for the adsorption of heavy metal ions, since they possess a high surface area and a highly porous architecture. As far as more technical details are concerned before the electrospinning process, the first step is the preparation of separate CS and PVA solutions in acetic acid and deionized water, respectively, commonly in concentrations of 5 wt% and 10 wt%. Then, the polymeric

solutions are blended in several compositions, mainly in 50/50, 70/30, and 30/70 ratios, and are magnetically stirred under room-temperature or mild heating conditions. The resulting blends are then loaded on the syringes and a high voltage is applied. In fact, the most crucial factors that affect the homogeneous and uniform production of electrospun fibers are the applied voltage, the feeding rate of the polymer solution, and finally the distance between the tip and the sample collector. Across the examined studies, the most applied voltages were of 10, 15, 18, 20, and 23 kV, while feeding rates within the range 0.1–0.6 mL/h were used. The main distance between the tip and collector was the 15 cm.

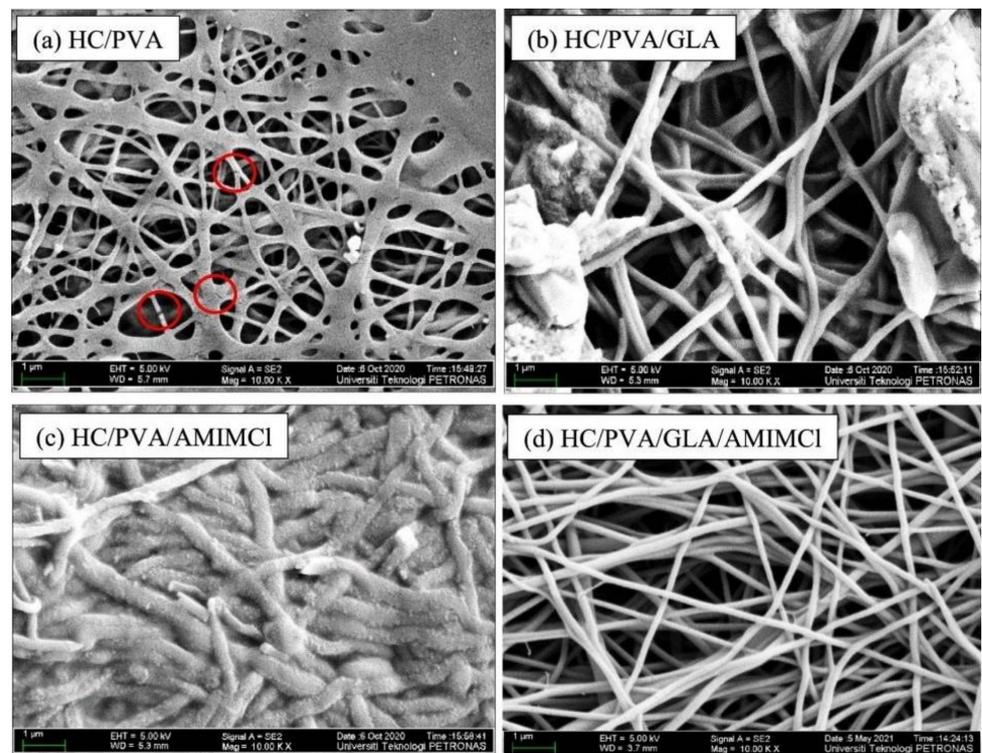
After the completion of the electrospinning process, the electrospun nanofibrous mat can either be dried in an oven at mild temperature in order to remove the excess solvent or crosslinked via chemical and/or thermal ways. In the study of Karim et al. [30], no crosslinking step was applied, and the effective production of the nanomat was confirmed by an FE-SEM microscopic technique, illustrating the uniform nanofibrous membranes with fiber diameters of 50–200 nm. The prepared membranes were further applied as adsorbents for the wastewater treatment by removing Cd(II) and Pb(II) ions. The maximum adsorption capacities of Pb(II) and Cd(II) were 266 and 148 mg/g, respectively. Another study employed a thermal crosslinking step as well on the electrospun fibers in order to prepare more stiff nanostructures. Specifically, Esmaeili et al. [31] heat-crosslinked the formed electrospun CS/PVA membranes, with FTIR, SEM and BET analyses characterizing the designed mesoporous and nanofibrous mats for their perspective towards nickel- and cobalt-ion removal (Figure 4). The kinetic data were better fitted to pseudo-first-order kinetic model, and the Dubinin–Raduskevich isotherm model fitted better than Langmuir and Freundlich. The maximum adsorption capacity was calculated as 54.12 and 13.26 mg/g for nickel and cobalt ions, respectively. The mean adsorption energy was less than 8 kJ/mol, indicating physisorption. The enthalpy change was 16.04 and 25.71 kJ/mol for nickel- and cobalt-ion adsorption, respectively [31].

A perspective similar to our opinion in the present framework was recently published in a work by Rosli et al. [29], in which GLA was used for the crosslinking of the designed nanofibers, whereas the ionic liquid 1-allyl-3-methylimidazolium chloride (AMIMCl) was employed to ameliorate the adsorption capacity of the nanofibrous membranes for Pb<sup>2+</sup> adsorption. FE-SEM-EDX and FTIR techniques were used to characterize the effects of the several applied steps on the performance of the prepared membranes, with the SEM micrographs (Figure 5) illustrating the most superior morphology that the CS/PVA/GTA/AMIMCI nanofibrous adsorbent had for its purpose fulfillment. The highest adsorption capacity of Pb(II) ions removal is 166.34 mg/g and was found to be well-fitted to the Freundlich adsorption isotherm and the pseudo-second-order kinetic model.

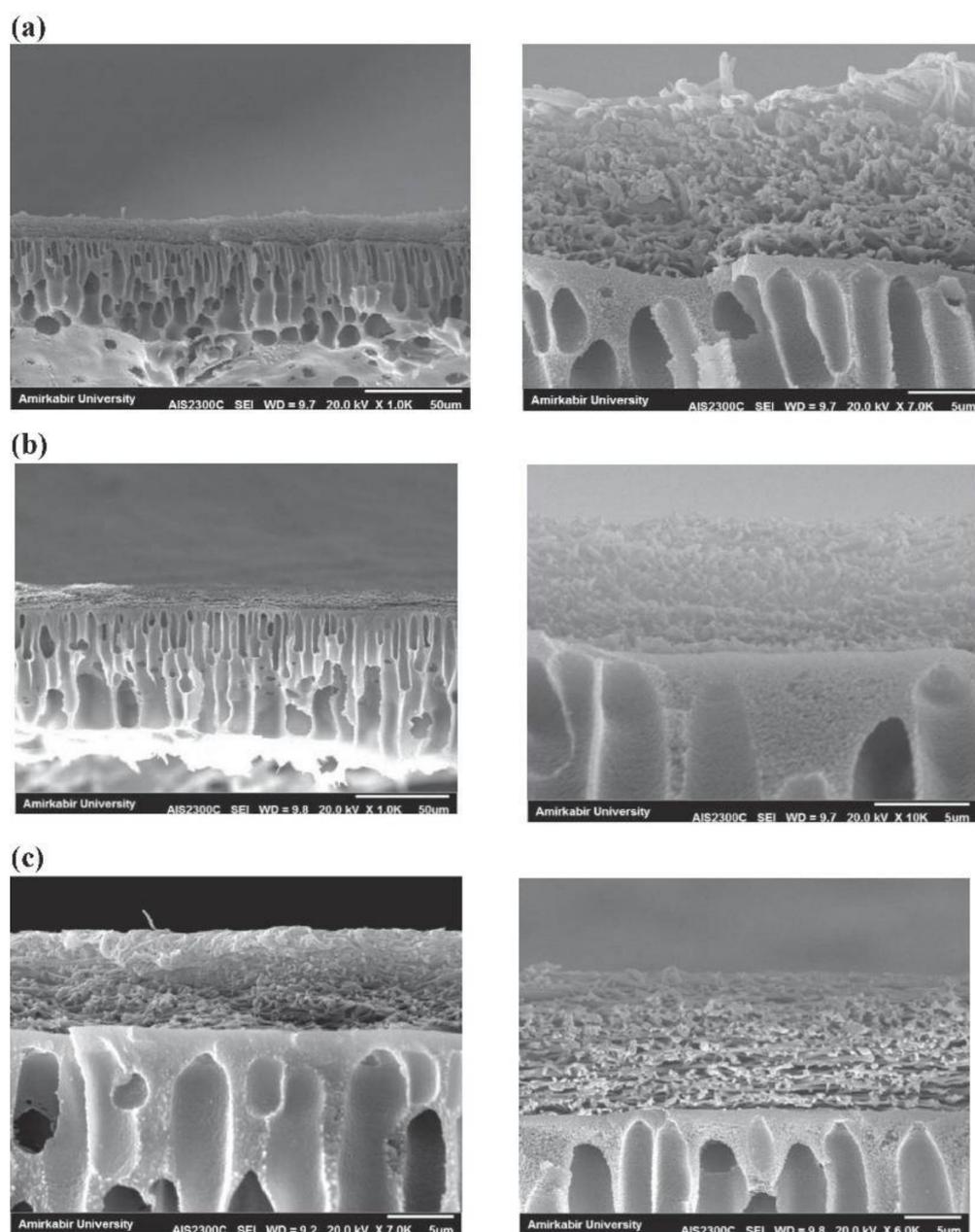
Another option worth mentioning for CS/PVA-based adsorbents is the incorporation of magnetic particles, such as Fe<sub>3</sub>O<sub>4</sub> nanoparticles, into the nanofibers produced by the electrospinning technique, in order to separate and remove metal ions and microparticles from the treated wastewaters [33,34]. According to Koushkbaghy et al.'s study, dual-layered membranes were prepared for the removal of Cr<sup>6+</sup> and Pb<sup>2+</sup> from aqueous samples [34]. In brief, aminated Fe<sub>3</sub>O<sub>4</sub> (A-Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were synthesized using a typical hydrothermal method, and were then blended with a CS/PVA mixture, which was further electrospun to form a CS/PVA/A-Fe<sub>3</sub>O<sub>4</sub> nanofibrous adsorptive coating. GLA solution was employed to crosslink the nanofibers. The latter layer was successfully deposited on a polyethersulfone (PES) film, produced via a simple solvent-casting process. The two-layered membranes were characterized by SEM (Figure 6), TEM and AFM analysis from a morphological point of view. The maximum adsorption capacities of Cr(VI) and Pb(II) ions were found to be 509.7 and 525.8 mg/g, respectively, at optimum pH of 3 in a binary system. The adsorbent showed good reusability for three cycles.



**Figure 4.** Schematic of the electrospinning process (A); nonwoven polyester web before electrospinning process and chitosan/PVA nanofiber membrane produced on the nonwoven polyester web after electrospinning process (B); membrane module (C); schematic of adsorption process (D). Reprinted with permission by [31].



**Figure 5.** FESEM images of the original and modified HC/PVA nanofibers. Reprinted with permission by [29].



**Figure 6.** Cross-section images of (a) PES/PVA/chitosan, (b) PES/PVA/chitosan/A-Fe<sub>3</sub>O<sub>4</sub>-2 and (c) crosslinked PES/PVA/chitosan/A-Fe<sub>3</sub>O<sub>4</sub>-2 nanofibrous membranes. Reprinted with permission by [34].

With the aim to overcome the slow heavy-metal-adsorption speed of electrospun CS/PVA nanofibers, Habiba et al. [7] reported on the fabrication and incorporation of zeolite as a nanofiller into the electrospun membrane. In fact, the porous architecture of zeolite can receive and host toxic heavy metals, accompanied by the beneficial properties of the functional CS/PVA matrix, and thus provide, in our view, highly efficient absorbents. Herein, the composite electrospun nanofibrous membranes were crosslinked with GLA and afterward characterized for their morphological and physicochemical properties, and finally, adsorption tests were executed for Cr(VI), Fe(III), and Ni(II) ions. We believe that among the most crucial and promising features of the synthesized CS/PVA/zeolite membranes were the rigidity, the weight stability in various pH and the effective reusability of the studied composite absorbent. Cr(VI) adsorption was better described by the pseudo-second-order kinetic model, while Fe(III) and Ni(II) were better described by the pseudo-first-order

model. The capacities of the membranes were 8.84, 6.14 and 1.76 mg/g for chromium, iron and nickel ions, respectively. Desorption studies were performed with distilled water and the membrane showed good performance after five cycles.

Last but not least for the CS/PVA electrospun membranes, the study by Fan et al. [35], functionalizing  $\beta$ -cyclodextrin for organic pollutants removal, could not be omitted from the current review. Because of its unique truncated conical structure (hydrophilic outer surface and a lipophilic central cavity),  $\beta$ -cyclodextrin is a favorable candidate for the accommodation of organic pollutants and heavy metals by the formation of noncovalent inclusion complexes. Moreover,  $\beta$ -cyclodextrin is a nontoxic and stable compound, boosting by this means its further exploration within this context. According to the aforementioned study,  $\beta$ -CD/CS/PVA electrospun nanofibrous membranes were prepared with epichlorohydrin (ECH) employed as crosslinking agent. The optimal conditions were selected after a multiobjective response-surface method. Lead ions and bisphenol-A were used as model compounds for the adsorption tests. The adsorption of Pb(II) reached equilibrium in 10 min, while the Freundlich and pseudo-second-order models better described the system. The adsorbent capacity for lead ions was  $\sim 13$  mg/g. The adsorption–desorption cycles showed good results after five times. Table 2 summarizes the chitosan/poly(vinyl alcohol)-based membranes used for heavy metal ions removal with all the appropriate synthesis, adsorption and characterization information.

## 2.2. Chitosan/Poly(Vinyl Alcohol) Hydrogels

### 2.2.1. Hydrogels

Another class of CS/PVA-based adsorbents that should be included, in our perspective, in the present review is hydrogels. There exist only four research articles in the enclosed bibliography that are generally related to hydrogels, while the remaining seventeen studies are reporting on hydrogels specifically in the shape of beads. The term “hydrogel” refers to three-dimensional structures that are able to swell into liquids, including water, saline buffers, and biological fluids up to 1000 times their own weight, due to natural or chemical crosslinking, without being dissolved [15]. In this research area, hydrogels own their success in their ability to absorb a large amount of water, and thus raise the possibility for metal ions’ restraint and transfer through the binding on the surface of hydrogel pores.

A research group from Thailand employed a microwave-assisted irradiation methodology in order to prepare chitosan/polyvinyl alcohol/polyvinylpyrrolidone (CS/PVA/PVP) hydrogel for the removal of four toxic heavy metals from aqueous media, including  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  [36]. This microwave-assisted approach was applied in order to initiate and hasten the polymeric network’s formation. The authors proposed the optimal ratio of CS:PVA:PVP, while ECH was used as a crosslinker. The formed hydrogels were studied through FTIR, SEM-XPS, and XAS techniques, while the swelling and gel fraction values were also calculated. Among the most significant outcomes of the study, the new hydrogel displayed an ability to adsorb and remove metal ions for the range pH = 4–8, whereas the use of a mild desorbing agent, such as 0.1M ethylenediaminetetraacetic acid (EDTA), could provide the recovery and reusability of the hydrogel, proposing its sustainable nature. The Langmuir and pseudo-second-order models better fitted the results. The maximum capacities of Pb(II), Cu(II), Ni(II) and Cd(II) ions were 80.02, 33.07, 15.13 and 8.36  $\text{mg g}^{-1}$ , respectively.

Aiming at the selective removal through adsorption of uranyl ions, Liu et al. [37] fabricated and succeeded on an ion-imprinted hydrogel (IIH) using the target ions as template and ethylene glycol diglycidyl ether (EGDE) as a crosslinking agent in order to form the interpenetration network (IPN). For the removal of the template ions, the hydrogel was cut into small pieces and immersed in a 0.1 M  $\text{HNO}_3$  solution. A nonimprinting hydrogel was also synthesized without the presence of templates in order to compare their performance. According to the conducted studies, the imprinted hydrogels displayed enhanced activity towards the targeted ions. The maximum adsorption value for uranyl ions onto the IIH was 132 mg/g.

**Table 2.** Chitosan/poly(vinyl alcohol)-based membranes for heavy metal ions removal.

Adsorbent	Crosslinker	Synthetical Pathway	Characterization Techniques	Target Heavy Metal Ions	Isotherms and Kinetics	$\Delta H^\circ$ (kJ/mol)	$Q_{\max}$ (mg/g)
CS/PVA [29]	GLA	Electrospinning technique	FESEM-EDX, FTIR	Pb <sup>2+</sup>	L, F*, T Ps1, Ps2*, Intra	-	166.34
$\beta$ -CD/CS/PVA [35]	ECH	Electrospinning process—crosslinking	FTIR, SEM	Pb <sup>2+</sup>	L, F* Ps1, Ps2*, Intra	-	13.44
CS/PVA [30]	n.r.	Electrospinning technique	FE-SEM	Pb <sup>2+</sup> , Cd <sup>2+</sup>	L*, F Ps1, Ps2*, Intra	-	266.12 148.79
CS/PVA/ Zeolite [7]	GLA	Electrospinning technique	FE-SEM, XRD, FTIR, swelling test	Cr <sup>6+</sup> , Fe <sup>3+</sup> , Ni <sup>2+</sup>	L Ps1*, Ps2*, Intra	-	8.84 6.14 1.76
CS/PVA [31]	-	Electrospinning technique—thermal crosslinking	BET, SEM, FTIR	Ni <sup>2+</sup> , Co <sup>2+</sup>	L, F, D-R* Ps1*, Ps2	16.05 25.72	54.12 13.26
Cs/PVA [23]	GLA	Electrospinning technique	FE-SEM, FTIR, XRD, TGA, tensile and weight loss testing	Fe <sup>3+</sup> Cr <sup>6+</sup>	L*, F	-	11.3 117
PVA/CS/ A-Fe <sub>3</sub> O <sub>4</sub> [34]	GLA	-PES membranes: solvent casting -PVA/CS/A-Fe <sub>3</sub> O <sub>4</sub> membrane: electrospinning process	SEM, TEM and AFM analysis	Cr <sup>6+</sup> , Pb <sup>2+</sup>	L*, F, D-R Ps1*, Ps2, Intra	-	509.7 525.8
CS/PVA/ DNDs [25]	NaOH	Crosslinking and solvent casting	SEM, FTIR	Pb <sup>2+</sup>	L*, F -	3.77	92
CS/PVA/PEI [9]	Thermal crosslinking (50 °C for 48 h) and NaOH	Solvent casting	FTIR, SEM, swelling degree and BET	Cu <sup>2+</sup> , Cd <sup>2+</sup> , Ni <sup>2+</sup>	L*, F, D-R, T Ps1, Ps2*, Intra	-6.15 -7.31 -10.07	86.08 112.13 75.5
CS/PVA/ Talc [24]	NaOH	Solvent casting	FTIR, FE- SEM, XRD, TGA, weight-loss experiments	Pb <sup>2+</sup> Cr <sup>6+</sup>	L*, F Ps1, Ps2*	-	430 479
(COS-g- MAH)/PVA/ SF [27]	-	Solvent casting	FTIR, XRD	Pb <sup>2+</sup>	L*, F Ps1, Ps2*, Intra	-	168.93
CS/PVA/ Zeolite [22]	Thermal crosslinking (70 °C for 2h) and NaOH	Solvent casting	FE-SEM, FTIR, XRD, TGA, water loss	Cr <sup>6+</sup>	L, F* Ps1, Ps2*, Intra	-	450
SCS/PVA [26]	ECH	Solvent casting	FTIR, SEM, XRD and TGA analyses	Cu <sup>2+</sup> Ni <sup>2+</sup>	L, F* Ps2*	-	80.6 35.5
CS/PVA [19]	GLA	Solvent casting	SEM	Pb <sup>2+</sup>	L, F*, T Ps1, Ps2*, Intra, Boyd	-8.54	14.24
CS/PVA [6]	GLA	Crosslinking of blended CS/PVA	SEM	Cu <sup>2+</sup>	L, F* Ps1, Ps2*, Intra	-	55.55
CS/PVA/PEG [21]	NaOH	Solvent casting	SEM, AFM, and wettability analyses	Cu <sup>2+</sup>	-	9.12	26
CS/PVA [18]	GLA	Blending and solvent casting	SEM, TEM, XRD	Zn <sup>2+</sup>	L, F* Ps1, Ps2*, Intra, Boyd	-	2.19
CS/PVA/PEG/ MWCNT-NH <sub>2</sub> [20]	Thermal (48 h at 50 °C)	Solvent casting	Water content, AFM, SEM	Cu <sup>2+</sup>	Ps1, Ps2*	8.40	35
CS/PVA [28]	GLA	Solution casting	FTIR	Ag <sup>+</sup>	-	-	125

\* The asterisk represents the best fitted model.

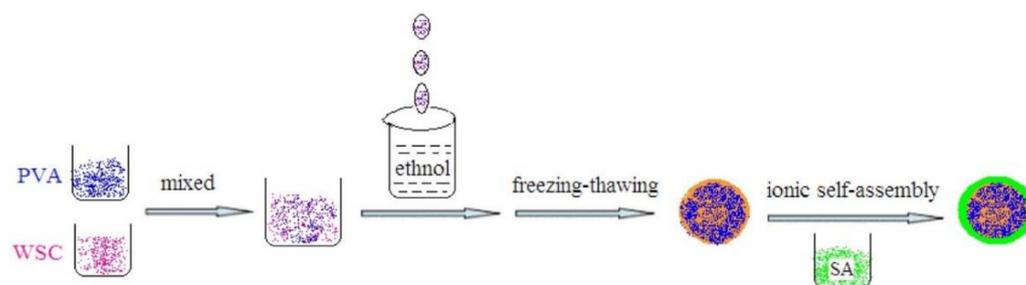
A sophisticated and easy approach for the fabrication of CS/PVA-based hydrogels was reported by Cao et al. [38], who worked on the development of dual self-healing and adsorptive hydrogels for the removal of chromium ions. Hydroxypropyl chitosan (HPCS), polyacrylamide (PAM) and polyvinyl alcohol (PVA) were employed to design the polymeric network, using oxidized sodium alginate (OSA) and boric acid as double crosslinking agents, which could not only improve the stability of the formed 3D structures, but also attained a dual self-healing ability. As outlined from the performed measurements, the final hydrogels exhibited adequate thermal stability, adaptable mechanical performance, and good adsorptive efficiency towards Cr(VI) binding. The adsorption capacity of Cr<sup>6+</sup> reached 95.31 mg/g and could be described by the pseudo-first-order kinetic model and Langmuir adsorption isotherm model.

### 2.2.2. Beads

As mentioned above, the most common morphology of hydrogel-like CS/PVA adsorbents is the spherical one. As for the synthesis of adsorbing hydrogel beads, the most widespread policy is the precipitation of a polymeric solution droplet into an antisolvent and/or gelation bath for the formation of spherical structures. Commonly, a NaOH solution is used as a precipitation bath for the gelation process and the formation of spherical

beads [39,40]. Another crosslinking agent used frequently in the gelation processes of CS/PVA-based hydrogel beads found during the present review is GLA [41,42], while a  $\text{CaCl}_2$ -saturated boric solution was also employed in two different studies preparing crosslinked spherical hydrogels [43,44].

A study reporting on the formation and performance of physically crosslinked core-shell water-soluble CS (WSC), PVA and sodium alginate (SA) including hydrogel beads, was published by Dong et al. [45], and presents to our view a representative first example. According to the applied protocol, dual-strengthened beads were formed throughout three freezing/thawing/crosslinking cycles. Briefly, the CS/SA networking complex was developed on the outer surface of the CS/PVA hydrogel particles, which were additionally crosslinked with calcium ions. A brief description of the applied formation methodology is depicted in Figure 7. The final beads exhibited superior thermal stability, and mechanical and adsorption behavior for the removal of copper and lead ions. The adsorption capacities of dry particles toward Pb(II) and Cu(II) could reach 39.28 and 26.03 mg/g, respectively.



**Figure 7.** Formation of physically crosslinked dual-strengthened Ca-SA-WSC@WSC/PVA particles. Reprinted with permission from [45].

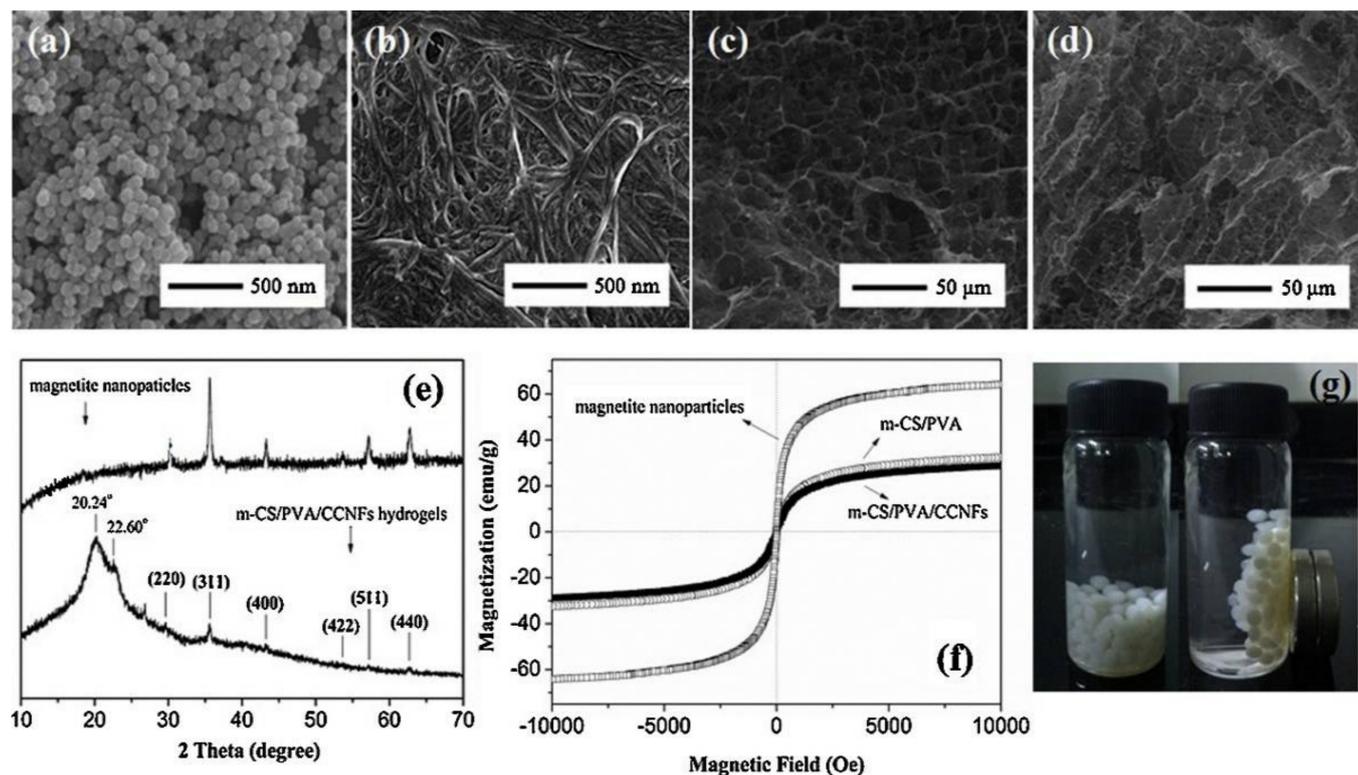
As referred above for the CS/PVA-based adsorptive membranes, several porogen agents can be also employed in order to facilitate the enhanced porous architecture for the manufactured hydrogel bead adsorbents. Across the enclosed literature, ZnO nanoparticles, CuO nanorods and activated carbon (AC) were justifiably used to boost the porosity of the formed hydrogel beads [1,46,47].

An exceptional and pioneering role—to our belief—in this type of adsorbents is held by the inclusion of magnetic nanoparticles into the CS/PVA polymeric matrix. In fact, the use of magnetic separation technologies can easily facilitate the quick separation and recovery of bead adsorbents. Specifically, magnetite ( $\text{Fe}_3\text{O}_4$ ) has been extensively combined with CS as a magnetic component, due to its large surface area, superior magnetic performance and chemical inertness, accompanied by its biocompatible character [48]. Chitosan adsorbents with magnetic properties have been investigated as contributors to the removal of heavy metals from polluted wastewaters, while to our vision, the exploration of these materials will flourish to a greater extent in the upcoming years.

From the technical point of view, magnetite nanoparticles can be dispersed into the CS/PVA mixture, vigorously stirred in an ultrasonic bath and then instantaneously dropped with the aid of a syringe needle and precipitated into a NaOH bath [5,12,49]. The formed beads can be further treated thermally for their drying.

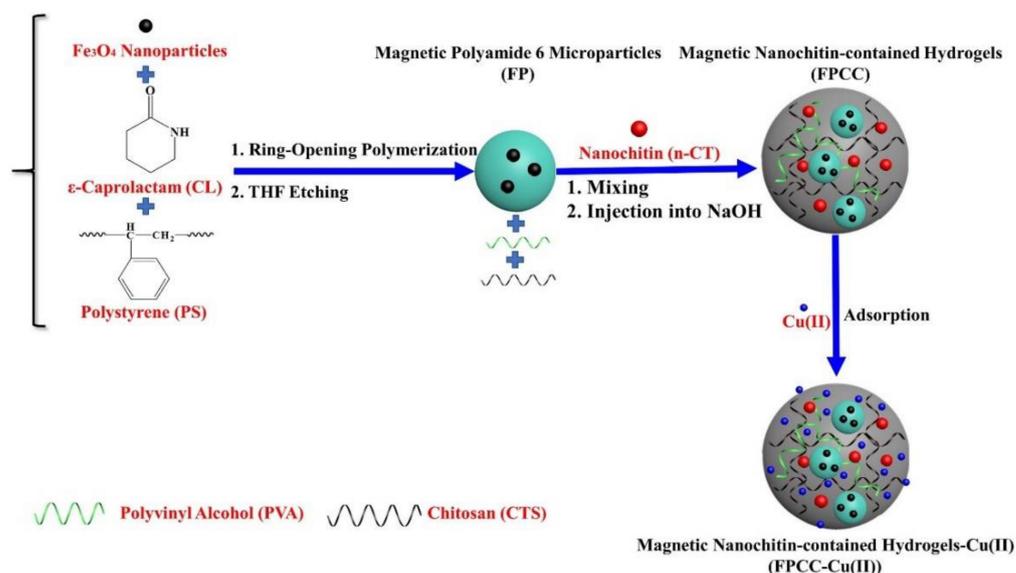
With the aim of improving the interaction between CS and heavy metals in liquid media, Lv et al. [48] modified CS with xanthate, increasing by this means the adsorption capacity of the CS/PVA system. After an instantaneous gelation step, the wet magnetic beads were immersed into a GLA solution in order to obtain gelated magnetic CS/PVA beads. The adsorbent capacity was about 35 mg/g and remained high after three cycles. HCl was used for the regeneration process. In addition, a magnetic xanthate-modified polyvinyl alcohol and chitosan composite (XMPC) for the efficient removal and recovery of heavy metal ions from aqueous solutions was synthesized by Wang et al. [50].

Another successful approach for the synthesis of chemically and mechanically reinforced magnetic CS/PVA absorbent beads was published by Zhou et al. [51]. According to the authors, a combination of carboxylated cellulose nanofibrils (CCNFs), amine-functionalized magnetite nanoparticles and poly(vinyl alcohol) (PVA) blended with chitosan (CS), was functionalized with the aim of preparing spherical-shaped absorbents, applying an instantaneous gelation methodology. The formed beads were proposed for the removal of Pb(II) ions, possessing adequate effectiveness concerning their reusability. The SEM, XRD and magnetization measurements are altogether depicted in Figure 8.



**Figure 8.** SEM images of magnetite nanoparticles (a), CCNFs (b), m-CS/PVA hydrogels (c), and m-CS/PVA/CCNFs hydrogels (d), XRD patterns of magnetite nanoparticles and m-CS/PVA/CCNFs hydrogels (e), magnetization curves of magnetite nanoparticles and hydrogels at room temperature (f) and photographs of m-CS/PVA/CCNFs hydrogels in Pb(II) solution before and after magnetic separation by an external magnetic field (g). Reprinted from [51].

Wu and his coworkers [14] designed magnetic CS/PVA hydrogel beads modified with nanochitin (CS/PVA/CT/Fe<sub>3</sub>O<sub>4</sub>) for Cu<sup>2+</sup> adsorption from aqueous media, facilitating a complex synthetic route (Figure 9). The intended aim of nanochitin's use was the effective metal-ion-chelating function through its higher surface area and more functional groups, a perception we believe to really promising. The final hydrogel beads exhibited an exceptional adsorption capacity to Cu<sup>2+</sup> in an aqueous solution, while its ease in separation implied the high dynamic of these materials in antipollution practices. The Langmuir isotherm model and pseudo-second-order kinetic model better fitted the experimental data, and the adsorption capacity was calculated as ~100.9 mg/g, with equilibrium being achieved within 10 min. Table 3 summarizes the chitosan/poly(vinyl alcohol)-based hydrogels/beads used for heavy metal ions removal with all the appropriate synthesis, adsorption and characterization information.



**Figure 9.** Schematic representation of preparation of the magnetic nanochitin-contained hydrogels (FPCC) and their adsorption ability to metal cations. Reprinted from [14].

### 2.3. Other CS/PVA Composites (The Case of Foams and Fixed-Bed Columns)

As referred above, the form of each adsorbent destined for wastewater remediation, and especially heavy metal removal, is of great importance, since it can affect the separation process of the adsorbent materials from treated media in practical applications. Due to its high microporosity and specific surface area, easy processing, and separation, the foam form is a promising kind of adsorbent, which is nevertheless hardly explored in the area of CS/PVA-based materials for heavy metal removal.

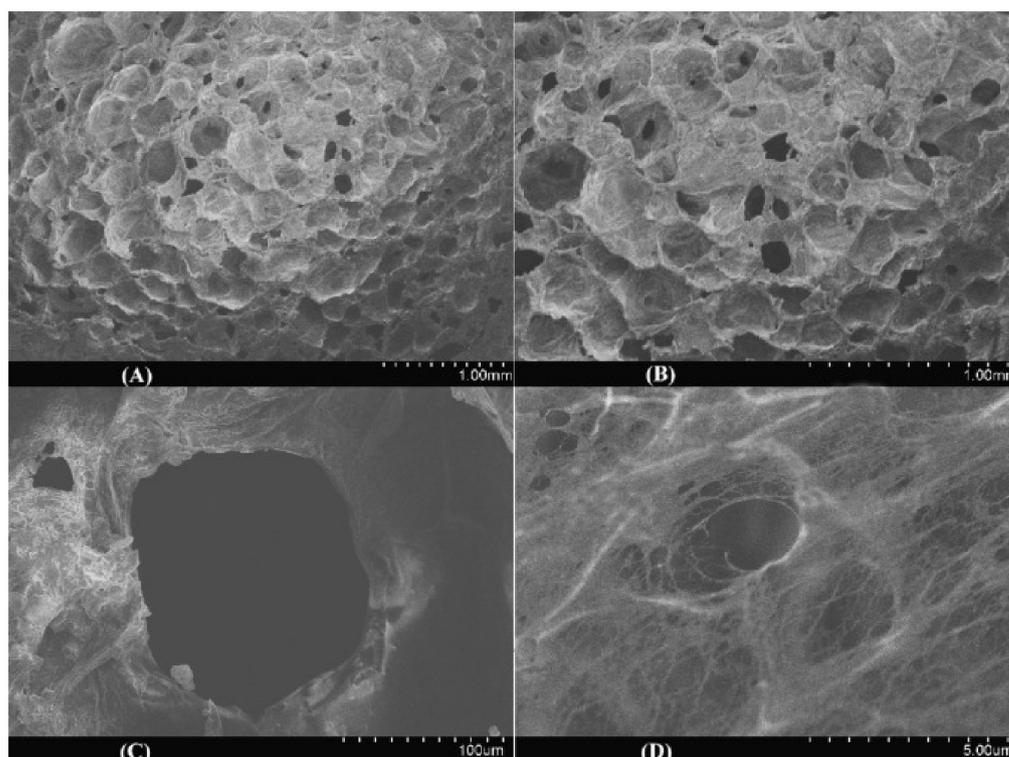
One study that, in our opinion, stands out as the most novel research work within this context, was reported by Li et al. [11], fabricating CS and PVA to prepare composite foam adsorbents for the removal of malachite green (MG) and  $\text{Cu(II)}$  ions. As for the synthetical route, a homogeneous mixture of CS, PVA and  $\text{CaCO}_3$  was prepared and shaken for 6 h at  $80^\circ\text{C}$ . After the cooling of the mixture, the appropriate amount—from a stoichiometric point of view—of HCl was added, in order to facilitate the dissolution of  $\text{CaCO}_3$  and liberate  $\text{CO}_2$  bubbles. The foam was subsequently formed after the application of three freezing/thawing cycles. The prepared CS/PVA foams were studied for their morphological and thermal properties, exhibiting good processing characteristics accompanied by an adequate thermal/chemical stability. In more detail, the newly introduced foams displayed high and well-developed porosity, as depicted in SEM images (Figure 10), stiffer structure and inertness in an acidic and alkaline environment, as well as good mechanical strength. The adsorption capacity of copper ions was  $193.39\text{ mg/g}$ . Interestingly, the foam showed better desorption by using EDTA, while more than 77% of copper ions removed after six cycles, thus outlining this combo as an auspicious aspect for such applications.

Facilitating a “starch expansion process”, Wang et al. [17], also prepared CS/PVA foams investigated for copper(II)-ion removal. For the preparation of foam-like adsorbents, the authors used two types of CS/PVA blends, one with water-soluble and the other with insoluble CS, which were mixed with the dispersion of corn starch. Afterward, HCl and HCHO were also added, and these samples were dried in an oven. In order to minimize any potential release of CS, GLA was used as a crosslinker after the addition of the acid; and the two types of foams, with and without the presence of a crosslinker, were compared in terms of porosity and adsorption. Table 4 summarizes the chitosan/poly(vinyl alcohol)-based foams used for heavy metal ions removal with all the appropriate synthesis, adsorption and characterization information.

**Table 3.** Chitosan/poly(vinyl alcohol)-based hydrogels/beads for heavy metal ions removal.

Absorbent Composition	Crosslinker	Synthetical Pathway	Characterization Techniques	Target Heavy Metal Ions	Isotherms and Kinetics	$\Delta H^\circ$ (kJ/mol)	$Q_{max}$ (mg/g)
Hydrogel HPSCS/PAM/PVA [38]	Crosslinking agent (OSA, H <sub>3</sub> BO <sub>3</sub> ) and NaOH	Polymerization and crosslinking process	FTIR, TGA, SEM, swelling test	Cu <sup>6+</sup>	L *, F Ps1 *, Ps2	-	95.31
Hydrogel CS/PVA/PVP [36]	ECH	Microwave-assisted irradiation	Swelling tests, gel fraction measurements, FTIR, SEM-XPS, XAS	Pb <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Cd <sup>2+</sup>	L *, F Ps1, Ps2 *	-	80.02 33.07 15.13 8.36
Hydrogel CS/PVA [37]	EGDE	Gelation process	BET, FTIR	UO <sup>2+</sup>	L *, F Ps2	-	132
Beads CS/PVA [42]	GLA	Precipitation into an antisolvent using a prototype instrumentation	FTIR, SEM-EDX, swelling testing	Cu <sup>2+</sup>	Ps1, Ps2 *, Intra	-	41
Beads CS/AC/PVA [47]	NaOH	Crosslinking	FE-SEM, EDS, XRD, BET	Pb <sup>2+</sup>	L, F *, T Ps1, Ps2 *	-	9.51
Beads Fe <sub>3</sub> O <sub>4</sub> -NPs-contained polyamide 6 (PA 6) microparticles (FP) encapsulated into PVA-CS hybrids (PVA/CTS) [14]	NaOH	In situ encapsulation of FP microparticles and n-CT nanoparticles into PVA-enhanced CTS hydrogels	SEM, TEM, FTIR, EDS, DLS, compression testing	Cu <sup>2+</sup>	L *, F, D-R Ps1, Ps2 *, Intra	-	100.9
Beads CS/SA/PVA particles [45]	SA	Precipitation into an antisolvent	FTIR, TGA, DMTA, SEM/EDS	Pb <sup>2+</sup> , Cu <sup>2+</sup>	-	-	39.28 26.03
Beads XMMCP/PVA [48]	GLA	Instantaneous gelation method	FTIR, XRD, SEM, BET, swelling tests	Pb <sup>2+</sup>	-	-	35
Beads XMPc [50]	GLA	Instantaneous gelation method	FTIR, Raman, SEM, TGA, DSC, BET, XRD	Pb <sup>2+</sup> , Cu <sup>2+</sup> , Cd <sup>2+</sup>	L *, F Ps1, Ps2 *, Intra	6.56 1.13 0.44	67 100 307
Beads CS/PVA/ZnO [46]	NaOH	Precipitation into antisolvent	XRD, FTIR, SEM, TEM, antibacterial properties	Cu <sup>2+</sup>	L *, F Ps1, Ps2 *, Intra	27.75	90.90
Beads CS/PVA/CuO [1]	Thermal (320 K for 12 h), NaOH	Precipitation into antisolvent	XRD, FTIR, SEM-EDS, TEM	Pb <sup>2+</sup>	L *, F, D-R Ps1, Ps2 *, Intra	11.62	116.84
Beads CS/PVA-Fe <sub>3</sub> O <sub>4</sub> [12]	Thermal (24h at 40 °C), NaOH	Instantaneous gelation method	FTIR, SEM-EDX, TEM, BET, DLS, TGA, DSC, swelling tests	Cu <sup>2+</sup>	L *, F Ps1, Ps2 *, Intra, Arrhenius	65	143.39
Beads Magnetic CS/PVA [5]	NaOH	Fe <sub>3</sub> O <sub>4</sub> nanoparticles: coprecipitation method CS/PVA beads: precipitation into an antisolvent	XRD, SEM, FTIR, TGA, BET	Cu <sup>2+</sup>	L *, F, D-R, BET Ps1, Ps2 *, Intra, Elovich	127.4	502.5
Beads PVA/CS/GO [44]	CaCl <sub>2</sub> -saturated boric acid solution	Instantaneous gelation method	SEM, TGA, BET, XRD	Cu <sup>2+</sup>	L *, F Ps1, Ps2 *, Intra	26.56	162
Beads Magnetic CS/PVA [49]	NaOH	Gelation method	FTIR, SEM-EDX	Co <sup>2+</sup>	L, F* Ps1, Ps2 *, Intra	8.5	14.39
Beads m-CS/PVA/CCNFs [51]	NaOH	Instantaneous gelation method	SEM, XRD, TGA	Pb <sup>2+</sup>	L *, F Ps1, Ps2 *, Intra	-	171
Beads CS/PVA [43]	CaCl <sub>2</sub> -saturated boric acid solution	Precipitation into an antisolvent/Crosslinking	BET, EDS, XRD, SEM, swelling tests	Cu <sup>2+</sup> , Pb <sup>2+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup>	L *, F Ps1, Ps2 *	187.94 101.57 88.6 91.98	238.45 166.44 74.18 126.06
Beads CS/PVA [41]	GLA	Suspension into an antisolvent	FTIR, XRD, SEM	Cd <sup>2+</sup>	L *, F Ps1, Ps2 *	40.32	142.9
Beads CS/PVA [39]	NaOH	Precipitation into an antisolvent	Swelling freeze-thaw cycles	Cu <sup>2+</sup>	L *, F Ps1, Ps2 *	-	47.85
Beads CS/PVA [40]	NaOH	Precipitation in antisolvent	SEM, FTIR, XPS	Pb <sup>2+</sup>	-	-	0.9

\* The asterisk represents the best fitted model.



**Figure 10.** SEM micrographs of PVA/CS foam with different magnification: (A) 30 $\times$ , (B) 50 $\times$ , (C) 400 $\times$  and (D) 10,000 $\times$ . Reprinted from [11].

**Table 4.** CS/PVA-based foams adsorbents for heavy metal ions removal.

Absorbent Composition	Crosslinker	Synthetical Pathway	Characterization Techniques	Target Heavy Metal Ions	Isotherms and Kinetics	$\Delta H^\circ$ (kJ/mol)	$Q_{\max}$ (mg/g)
CS/PVA [11]	HCl	Blending and application of multiple freeze–thaw cycles	BET, EDS, TGA, SEM, swelling tests	$\text{Cu}^{2+}$	L *, F Ps1, Ps2 *, Intra	64.52	193.39
CS/PVA [17]	GLA	Blending, addition of HCl, HCHO and drying	Swelling tests, SEM	$\text{Cu}^{2+}$	-	-	27.38

\* The asterisk represents the best fitted model.

### 3. Conclusions

The effective removal of heavy metals from wastewater has witnessed vast developments in recent years. Adsorption processes possess superior advantages, such as simple design and low initial cost, over other methods such as membrane filtration and photocatalysis. The synergetic effect of chitosan and PVA shows great potential for heavy metal removal from aqueous solutions, especially when combined with a suitable third chelator. Referring to Richard Feynman, we state that there is plenty of room at this scientific corner for developing highly efficient sorbents for heavy metal and organic pollutants.

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## Abbreviations

AC, activated carbon; AFM, atomic force microscopy; AMIMCl, 1-allyl-3-methylimidazolium chloride; BET, Brunauer–Emmett–Teller; CCNFs, carboxylated cellulose nanofibrils; COS-g-MAH, chitosan oligosaccharide-graft-maleic anhydride; CS, chitosan; DMTA, dynamic mechanical thermal analysis; DNDs, detonation nanodiamonds; D-R, Dubinin–Radushkevich model; DSC, differential scanning calorimetry; ECH, epichlorohydrin; EDS, energy-dispersive X-ray spectrometer; EGDE, ethylene glycol diglycidyl ether; F, Freundlich; FE-SEM, field-emission scanning electron microscopy; FTIR, Fourier transform infrared spectroscopy; GO, graphene oxide; GLA, glutaraldehyde; HPCS, hydroxypropyl chitosan; IIM, ionic imprinted membrane; Intra, intraparticle diffusion model; L, Langmuir; MWCNT-NH<sub>2</sub>, multiwalled carbon nanotubes; NPs, nanoparticles; OSA, oxidized sodium alginate; PAM, polyacrylamide; PEG, polyethylene glycol; PEI, polyethyleneimine; PS1, pseudo-first-order model; PS2, pseudo-second-order model; PVA, poly(vinyl alcohol); PVP, polyvinylpyrrolidone; SA, sodium alginate; SCS, sulfated chitosan; SEM, scanning electron microscopy; SF, silk fibroin; SLS, sodium lauryl sulphate; T, Temkin; TEM, transmission electron microscopy; TGA, thermogravimetric analysis; XAS, X-ray absorption spectroscopy; XMMCP, xanthate-modified magnetic chitosan; XMPC, magnetic xanthate-modified polyvinyl alcohol and chitosan composite; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; β-CD, β-cyclodextrin.

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