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Chitosan Aerogels as an Alternative to Desalination

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ABSTRACT

Water scarcity is an emerging problem in the world. Despite water covering 71% of the Earth, up to two billion people lack access to clean water globally. Conventional desalination methods are readily available, but consume large amounts of energy; consequently, they are substantially more expensive than naturally sourced freshwater. Aerogels are an emerging material that poses as a potential alternative to conventional desalination methods. This material is lightweight, porous, and has low density, allowing it to exhibit exceptional absorption qualities. This study explores the use of chitosan aerogels as an alternative to desalination.

Introduction

Water scarcity is an emerging issue in certain developing areas of the world. 71% of the Earth is covered by water, yet there are around two billion people in the world, of which 73% live in Asia and the Middle East, without access to clean water (Dolan, 2021). In recent years, efforts have been made to tap into this water reserve. The current status quo of desalination methods – reverse osmosis and electrodialysis – uses membrane separation. However, they leave a residue waste substance called brine that is detrimental to waterways, and large amounts of energy are consumed (Darre, 2018).

Reverse Osmosis

Reverse osmosis takes advantage of a naturally occurring phenomenon known as osmosis — water passes through a membrane into a salty solution until the concentration of water is equal on both sides (Darre, 2018). Reverse osmosis inverses this mechanism, pushing the water from the salty side into the side with the fresh water until all the salt is filtered out (Darre, 2018). However, because this goes against natural processes, it consumes large amounts of energy (Darre, 2018). The cost of operating desalination equipment is often prohibitive; the lowest price for desalinated seawater obtained from reverse osmosis is around $750 per 325,851 gallons — more than double the average cost of groundwater (Darre, 2018).

Electrodialysis

Similarly, this process also consumes large amounts of energy, as it primarily relies on sending an electric charge through aqueous solutions to separate the cationic and anionic substances on each anode (Darre, 2018). Membranes line the water at every interval to allow only one specific ion to go through. As the final product, this method leaves concentrated ions clumped together at each anode (Darre, 2018). Disposal costs significantly affect total treatment cost, providing a cost ranging from $\$0.38/m^3$ to $\$6.38/m^3$, depending on residue waste disposal cost and water recovery (Darre, 2018). Both methods are not economically feasible, as conventional freshwater is significantly cheaper than desalinated water (Darre, 2018).

Aerogels

To combat this issue, aerogels have emerged as a potential alternative. Aerogels are a material that is composed of 99.8% air, with extremely low densities running from 0.0011 to 0.5 g/cm 3, a high porosity of > 85%, and small pores around twenty to forty nanometers; it is one of the lightest solids in the world (Hajar, 2016). Although brittle, aerogels can withstand up to four thousand times their weight. Its small pores trap heat effectively, allowing the material to act as an efficient thermal insulator; it's often seen on the interior of buildings to keep rooms warm (Hajar, 2016). Perhaps the most famous application is NASA's use of aerogels to capture comet dust in space. However, most importantly, aerogels are natural absorbents. They have already been used to absorb anionic dyes in industrial waste, with cellulose nanofibrils and chitosan aerogel composites exhibiting absorption capacities of 1400 mg g^{-1} towards anionic dyes (Esmaeili, 2021).

Other notable absorbents have been identified as potential alternatives alongside aerogels. However, they lack the efficiency and cost to compete with conventional methods of desalination. For instance, in one study, silica beads were used to desalinate salt water (Kyaw, 2013). In this study, salt water was evaporated at 100°C to vaporize the water molecules (Kyaw, 2013). Once in the gaseous phase, these water vapors were condensed and trapped within a bed of silica beads, allowing for liquid water to be collected afterward (Kyaw, 2013). Despite its technical success, this study was unable to address the problem of energy consumption that conventional desalination processes are struggling with; a large amount of energy is necessary to vaporize large amounts of water (Kyaw, 2013).

Another prominent absorbent in the market is ion exchange resins. These plastic beads are charged with a specific type of cation and anion and placed in a continuous tube (Alexandratos, 2009). As water is poured through the tube, it flows and interacts with the plastic resins; the salt ions present in the water undergo an ion exchange for the cation or anion that the ionization resins were originally charged with (Alexandratos, 2009). Once the water reaches the end of the tube, all its salt ions are removed. However, these resins cost two thousand dollars per cubic foot to manufacture. As a result, it is only utilized in niche applications, specifically to create deionized water for laboratory experiments (Alexandratos, 2009). As such, the lack of efficiency and cost-effectiveness of current absorbents increases the need for a solution that will address both issues in desalination.

Aerogels, specifically organic ones, are natural absorbents. They absorb ions through a process known as chemisorption (Ihsanullah, 2022). In this process, various functional groups outlining the surface of the gel attract different ions to the material with dipole-dipole interactions (Ihsanullah, 2022). To maximize the absorption capacity of the gel, the primary precursor must possess a diverse range of functional groups. Chitosan, a natural biopolymer, possesses hydroxyl and amine functional groups, positioning itself as a material that can absorb both the cationic sodium and anionic chloride ions.

Methods

Although chitosan can absorb both negatively and positively charged ions, synthesizing two different types of aerogels will yield a higher absorption capacity. During the development process, various additives are added to magnify certain functional groups while diminishing the intensity of others. The various synthesis methods below were compiled with inspiration from existing source material concerning the absorption of industrial dyes. After manufacturing the gels, the aerogels were molded into beads no more than four millimeters in diameter. This maximized the surface area of the gel, thereby increasing the absorption capacity.

Absorbing Chloride Ions

To synthesize aerogels that absorb anions, 3 grams of chitosan powder was blended in 100 mL of NaOH/urea/H2O solution with the ratios of 5:6:89% (w/w %), respectively. This gel was frozen at −20 °C for 12 hours and then thawed at room temperature; this cycle was repeated three times (Zahra, 2021). Afterward, cellulose nanofibers were mixed with the chitosan solution at a mass ratio of 1:1, in addition to 20 mL of citric acid solution (Zahra, 2021). This effectively formed a solid gel. After this gel was washed several times with distilled water, it was placed into circular molds and stored in the freezer at 80 °C for 24 hours. The pre-frozen samples were dried using a vacuum freeze dryer (Christ, Alpha 2–4 LDplus, Germany) at a temperature of −50 °C for 24 hours (Zahra, 2021).

Absorbing Sodium Ions

To obtain aerogels suited for absorbing cations, 1.0 grams of chitosan was dissolved in 90 mL 0.2 mol/L acetic acid solution. This mixture was continuously stirred at room temperature for 2 hours (Li, 2016). As a part of the sol-gel process, this formed the solution that will eventually coagulate into the gel after chemical and physical modification. 10 mL glutaraldehyde (3–7% w/w) was then added to the chitosan solution and consistently stirred for 30 minutes (Li, 2016). This solution was then poured into circular molds; the cross-linked hydrogel was obtained after being kept for another 24 hours at room temperature for gelation. After separation from the molds, the hydrogel was frozen at −60 ◦C for 2 hours; it was then thawed at room temperature for another 6 hours, after which a solvent exchange was performed with deionized water several times until the solution was purified. Finally, the chitosan aerogel monolith was obtained after freeze-drying for 48 hours under a vacuum of fewer than 20 pascals (Li, 2016).

Aerogel Beads

After manufacturing the gels, the aerogels were crushed into beads no more than four millimeters in diameter. This maximized the surface area of the gel, thereby increasing the absorption capacity. To reuse the aerogel beads, one must submerge them in a bath of hydrochloric acid for the cationic ions, and sodium hydroxide for the anionic ions, to perform an ion exchange – the sodium and chloride ions are exchanged for hydrogen ions and hydroxide ions respectively. This consequently forms NaCl.

The absorption capacity was determined by calculating the change in mass of the salt water for every one gram of aerogel bead used after 90 minutes.

Results

These beads exhibited absorption capacities of 1428.7 mg g^{-1} towards the salt ions. Additionally, these aerogels can be manufactured for about 65 cents per cubic centimeter and cost 0.1 cents to desalinate one liter of salt water. Unfortunately, the beads fall short of beating the current desalination price.

Discussion

To utilize these aerogel beads for desalination, they must be placed in a water-absorbing bag. This bag of aerogel beads can be submerged in salt water for approximately 60-90 minutes. Afterward, the water is desalinated, and the beads can be reused up to fifteen times. Despite their technical success in absorbing sodium and chloride ions, chitosan aerogels are not economically feasible to implement in the desalination industry – it is more expensive than conventional methods by about one order of magnitude. However, despite not being financially feasible to implement in the desalination industry, this material shows promise as a sustainable absorbent that can readily absorb cations and anions. Their versatility warrants consideration for absorbing complex compounds.

Technical success was achievable with precise production processes. The first step of the production process is known as the sol-gel process – where various aggregates coagulate into a solution that ultimately forms a gel. Once this gel was frozen in the physical crosslinking process, the chitosan polymer chains were physically pulled closer together by freezing and thawing the gel solution, effectively cross-linking the mixture (Sirajudheen, 2021). The chemical crosslinking process introduced citric acid; in this context, citric acid acted as a chemical cross-linker; it bonded to the hydroxyl groups present in the chitosan chains. More citric acid thereby meant stronger bonds. Glutaraldehyde is another common chemical cross-linker of chitosan used in various other applications (Lei, 2021).

After the gel was formed, the solution underwent rigorous purification. The drying process of aerogels is very delicate. Any imperfections in the mixture compromise the success of the drying process. This purification was necessary to ensure the success of the drying process; any impurities present in the gel would compromise its success (Zhang, 2020).

To obtain an aerogel, all the moisture present in hydrogels must be eliminated. This can't be accomplished simply by evaporating the water in the hydrogel with heat. As the water vapor is drawn out, it binds to the hydroxyl groups present in the gel structure and pulls the gel in on itself (Sánchez, 2022). This is a process known as capillary action. Thus, to avoid structural collapse, the industry uses supercritical and subcritical drying. Subcritical drying uses low temperatures to initiate sublimation: the water vapor freezes into ice, and turns immediately from solid to gas, bypassing the liquid phase, and thus capillary action, altogether (Sánchez, 2022). Supercritical drying utilizes high temperatures and pressures to reach the supercritical point of the water. In this phase, water exists both as a liquid and as a gas (Sánchez, 2022). As a result, it acts as a middle ground to facilitate a smooth transition from liquid to gas phases. Because the process is volatile, stable solvents such as liquid carbon dioxide are favorable in the industry today.

Because of the delicate drying process, vigorous purification with distilled water was necessary to ensure any residue contaminants were removed before the gel moved to the drying phase.

Chitosan Aerogels

Chitosan was a favorable compound to work with due to its versatile range of functional groups; this is ultimately what allowed the biopolymer to absorb both kinds of ions, and this versatility can extend beyond desalination. The goal of this research was to provide a cheap desalination method while also making sure the environment stays unharmed and unpolluted. This restricted the type of aerogels that could be used to be that of biopolymers such as cellulose and chitosan. Most of the biopolymers in the world are anionic, meaning their overall charge, as well as most of their functional groups, is negative. This makes it problematic to absorb the anionic chloride ions from the salt – the same charges would repel each other.

On the other hand, chitosan, the second most abundant biopolymer behind cellulose, can absorb and remove the anionic chloride ions. Chitosan is a linear polysaccharide composed of randomly distributed β — linked D-glucosamine and N-acetyl-D-glucosamine (Songlin, 2021). It is synthesized by treating the chitin shells of shrimp and other crustaceans with an alkaline substance, such as sodium hydroxide (Songlin, 2021).

It has cationic amine groups on its surface suitable for chloride absorption. Additionally, it has strong mechanical properties, easy access, and biodegradability (Kyzas, 2021). Because it also possesses anionic hydroxyl groups on its surface, it can also absorb the cationic sodium ions. Biopolymers such as chitosan have a variety of functional groups – both cationic amine groups and anionic hydroxyl groups. This positions chitosan in a unique situation, where it has the potential to absorb both the cationic sodium ions and anionic chloride ions in salt or any other complex material. In a process known as chemisorption, charged ions are attracted to functional groups of the opposite charge in a dipole-dipole interaction. This is what allowed the chitosan aerogel beads to be successful. Along these lines, chitosan is well known for its ability to form gels, making it favorable as an aerogel precursor, and amplifying its versatility for future applications (Kyzas, 2021).

Overall, chitosan aerogels are not compatible financially with desalination. However, its versatility in its ability to absorb both cations and anions warrants further investigation for other absorption applications. Such applications include cleaning up oil spills, creating deionized water, and removing harmful contaminates from wastewater in treatment plants.

Conclusion

With water scarcity increasing in recent years, cheaper alternatives to desalination become crucial. Aerogels have emerged as a promising absorbent that exhibits high porosity, low density, and micropores. To extend the versatility of aerogels, chitosan was selected as the primary precursor to synthesize as the absorbent. These chitosan aerogels were arranged into microbeads to maximize surface area and can be reused upon submersion in a strong acid or base bath. While chitosan aerogels can successfully desalinate salt water, it is still not able to compete financially with the status quo of desalination; thus, it requires additional research before it can enter the market.

Limitations

The main limitation is the reusability of the beads. After submerging in a strong acid or base bath, the beads can only be reused up to fifteen times. This is primarily because, with every ion exchange, residue contaminations remain present in the aerogel. As a result, the efficiency of the absorption diminishes with every use. With every submersion, the purity of the acids and bases is also diminished; the NaCl that forms from the reaction between the aerogel and the acids/bases contaminates the solution. With the notion that the beads are already more expensive than conventional desalination methods, the limited reusability of the chitosan aerogel beads restricts widespread use.

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References

Al-Azmi, Amal, and Sajjad Keshipour. (2019). “Cross-Linked Chitosan Aerogel Modified with Pd(Ii)/Phthalocyanine: Synthesis, Characterization, and Catalytic Application.” *Nature News*, www.nature.com/articles/s41598-019-50021-6

Hajar Maleki, et al. “Recent Advances in Aerogels for Environmental Remediation Applications: A Review.” *Chemical Engineering Journal*, 21 Apr. 2016, www.sciencedirect.com/science/article/abs/pii/S1385894716305484.

Ihsanullah Ihsanullah, et al. (2022). “Aerogel-Based Adsorbents as Emerging Materials for the Removal of Heavy Metals from Water: Progress, Challenges, and Prospects.” *Separation and Purification Technology*, www.sciencedirect.com/science/article/abs/pii/S1383586622004804.
Songlin Fan, et al. (2021). “Fabrication of a CO2-Responsive Chitosan Aerogel as an Effective Adsorbent for the Adsorption and Desorption of Heavy Metal Ions.” *Journal of Hazardous Materials*, www.sciencedirect.com/science/article/abs/pii/S0304389421011894.

Esmaeili, Zahra, et al. (2021). “Preparation and Characterization of Highly Porous Cellulose Nanofibrils/Chitosan Aerogel for Acid Blue 93 Adsorption: Kinetics, Isotherms, and Thermodynamics Analysis.” *Journal of Chemical & Engineering Data*, vol. 66, no. 2, pp. 1068–1080, https://doi.org/10.1021/acs.jced.0c00872.

Franco, Paola, et al. (2021). “Porous Aerogels and Adsorption of Pollutants from Water and Air: A Review.” *Molecules (Basel, Switzerland)*, www.ncbi.nlm.nih.gov/pmc/articles/PMC8347855/.

Kyzas, George Z, et al. (2017). “Chitosan Adsorbents for Dye Removal: A Review.” *Polymer International*, vol. 66, no. 12, pp. 1800–1811, https://doi.org/10.1002/pi.5467.

Lei, Chunyan, et al. (2021). “Mussel-Inspired Synthesis of Magnetic Carboxymethyl Chitosan Aerogel for Removal Cationic and Anionic Dyes from Aqueous Solution.” *Polymer*, vol. 213, p. 123316, https://doi.org/10.1016/j.polymer.2020.123316.

Li, Ang, et al. (2016). “An Environment-Friendly and Multi-Functional Absorbent from Chitosan for Organic Pollutants and Heavy Metal Ion.” *Carbohydrate Polymers*, vol. 148, pp. 272–280, https://doi.org/10.1016/j.carbpol.2016.04.070.

Sánchez, Carlos Manuel Jarquín. (2022). “Aquaperla: Proposal for Cost-Effective & Biodegradable Water Filters.” *Medium*, 31 Dec. cjarquin.medium.com/aquaperla-proposal-for-cost-effective-biodegradable-water-filters-569f75023def.

Sirajudheen, Palliyalil, et al. (2021). “Applications of Chitin and Chitosan Based Biomaterials for the Adsorptive Removal of Textile Dyes from Water — a Comprehensive Review.” *Carbohydrate Polymers*, vol. 273, p. 118604, https://doi.org/10.1016/j.carbpol.2021.118604.

Zhang, Enshuang, et al. (2020). “High-Capacity Reusable Chitosan Absorbent with a Hydrogel-Coated/Aerogel-Core Structure and Superhydrophilicity under Oil for Water Removal from Oil.” *ACS Applied Bio Materials*, vol. 3, no. 9, pp. 5872–5879, https://doi.org/10.1021/acsabm.0c00585.

Dolan F, Lamontagne J, Link R, Hejazi M, Reed P, Edmonds J. (2021). “Evaluating the economic impact of water scarcity in a changing world.” *Nat Commun* ;12(1):1915. doi: 10.1038/s41467-021-22194-0. PMID: 33772023; PMCID: PMC7997906.

Darre, N.C., Toor, G.S. (2018). “Desalination of Water: a Review.” *Curr Pollution Rep* 4, 104–111 https://doi.org/10.1007/s40726-018-0085-9

Kyaw Thu, Anutosh Chakraborty, Bidyut Baran Saha, Kim Choon Ng, (2013). "Thermo-physical properties of silica gel for adsorption desalination cycle," *Applied Thermal Engineering*, Volume 50, Issue 2, Pages 1596-1602, ISSN 1359-4311, https://doi.org/10.1016/j.applthermaleng.2011.09.038.

Alexandratos, Spiro. (2009). "Ion-Exchange Resins: A Retrospective from Industrial and Engineering Chemistry Research," *Ind. Eng. Chem*. Res. 48, 1, 388–398 Publication Date: November 26, 2008 https://doi.org/10.1021/ie801242v