Journal of Health and Rehabilitation Research 2791-156X JHRR

For contributions to JHRR, contact at email: editor@jhrlmc.com

Original Article

Removal of Cephalexin-Antibiotic from Drinking Water by Designing CaCl2 Incorporated Chitosan Co- Tragacanth Gum Composite Hydrogel

Sundas Noureen[1], Safia[1], Fatima Javed[1], Faheem Ullah[2*], Amir Sada Khan[3]

[1]Department of Chemistry, Shaheed Benazir Bhutto Women University, Peshawar, Pakistan.
[2]Deparment of Biological Sciences, National University of Medical Sciences (NUMS), Rawalpindi, Pakistan.
[3]University of Science and Technology Bannu, KPK, Pakistan.
Corresponding Author: Faheem Ullah, Email: faheem.ullah@numspak.edu.pk

Conflict of Interest: None.

Noureen S., et al. (2024). 4(1): DOI: https://doi.org/10.61919/jhrr.v4i1.568

ABSTRACT

Background: The prevalence of antibiotic contaminants in aquatic environments presents a critical challenge to public health, necessitating the development of efficient removal methods. Emerging pollutants, especially antibiotics, have been implicated in the rise of antibiotic-resistant bacteria, threatening ecological balance and human well-being.

Objective: This study aims to synthesize and evaluate the efficacy of a CaCl2-based composite hydrogel using chitosan as a biopolymer for the adsorption of antibiotic pollutants from water, targeting the improvement of water purification technologies in healthcare settings.

Methods: Chitosan-based composite hydrogels were synthesized via free radical polymerization, incorporating CaCl2 and utilizing techniques such as Field Emission Scanning Electron Microscopy (FESEM) for morphology analysis, Energy-dispersive X-ray (EDX) analysis for elemental verification, Fourier-transform infrared spectroscopy (FTIR) for functional group identification, and X-ray diffraction (XRD) to determine crystallinity. Physicochemical parameters, including contact time, pH, temperature, reusability, and swelling behavior in various media, were systematically assessed to ascertain the hydrogel's adsorptive performance.

Results: The synthesized hydrogels demonstrated a porous and rough surface ideal for adsorption, with an initial antibiotic removal rate of 80% within 30 minutes of contact time. FTIR analysis confirmed the presence of functional groups corresponding to absorption bands at 1053, 1415, 1601, 2600, 2900, 3300, and 3500 cm-1. EDX and XRD analyses affirmed the incorporation of CaCl2, with a crystalline phase characterized by sharp peaks. The hydrogel's maximum adsorption efficiency reached 95% at an optimized adsorbent dose of 0.05 g.

Conclusion: The CaCl2-based composite hydrogel exhibits significant potential for the removal of antibiotic pollutants from water, suggesting a viable approach to mitigate the environmental impact of pharmaceutical contaminants and enhance human health by reducing the spread of antibiotic resistance.

Keywords: Composite Hydrogel, Antibiotic Adsorption, Water Purification, Chitosan Biopolymer, Antibiotic Resistance, Environmental Health, Biodegradable Polymers, Pharmaceutical Contaminants.

INTRODUCTION

Emerging pollutants, notably antibiotics, pose a significant challenge to both environmental sustainability and human health. The inability of organisms, including humans, to fully metabolize these compounds results in their persistence in the environment, particularly in aquatic systems such as lakes, rivers, reservoirs, and even in sources of drinking water (2, 3). The issue is further compounded by the direct discharge of untreated antibiotic residues from biomedical wastewater into natural habitats, thereby exposing a wide array of organisms to these toxic substances (4). The widespread use and subsequent environmental release of antibiotics, driven by their low cost and effective bacteriostatic properties, are particularly alarming due to the chemical stability and bio-resistant nature of these compounds, which renders them difficult to remove and thus represents a significant threat to both ecological systems and public health (5, 6). Conventional sewage treatment methods, such as physical adsorption, chemical

precipitation, biological processes, and membrane technology, fall short in completely eliminating antibiotics from water bodies (7). However, several treatment techniques, including ozonation, microbial degradation, membrane separation, photocatalytic degradation, and particularly adsorption, have shown promise in mitigating this issue (8). Among these, adsorption emerges as a feasible approach, underscoring the importance of exploring innovative adsorbents with superior adsorption capabilities.

Chitosan (CS), a naturally occurring biopolymer derived from chitin, is identified as a promising material for developing new adsorbent hydrogels. Through mechanical or chemical crosslinking, polymer chains of chitosan can be transformed into three-dimensional networks known as hydrogels. These structures are characterized by their porous nature and polar functional groups, which significantly enhance their capacity to capture and remove pharmaceutical compounds from aqueous solutions (9). The porous architecture of chitosan hydrogels not only provides a large surface area for adsorption but also exposes numerous sites for the binding of target compounds (10). This is particularly effective for drugs that can interact with the hydrogel's dense functional groups (11). Recent advancements have demonstrated the functionalization of poly(4-vinylpyridine) with magnetic copper, yielding an efficient and recyclable adsorbent for the removal of fluoroquinolone antibiotics from water (12). Moreover, chitosan-based hydrogels are celebrated for their non-toxicity, biodegradability, and biocompatibility, making them suitable for various applications including drug delivery, food preservation, water treatment, tissue engineering, and personal care products (13).

Innovative approaches to enhancing the adsorption efficiency of chitosan hydrogels have been explored. For instance, Afzal et al. developed a chitosan/biochar hydrogel specifically for the removal of ciprofloxacin, revealing the potential binding sites and elucidating the sorption process (14). Similarly, Wang et al. fabricated a hydrogel from granular chitosan for the adsorption of ciprofloxacin and enrofloxacin, demonstrating the material's capacity for drug removal (15). The ability of hydrogels to absorb water without compromising their structural integrity also facilitates the separation and recycling of the adsorbents from treated effluents, underscoring the sustainability of this approach (16). Further research has delved into the adsorption processes using three-dimensional graphene porous hydrogels and triple network nanocomposite hydrogels composed of carbon nanotubes, graphene oxide, and sodium alginate, showcasing their significant advantages in both adsorption and degradation processes (17, 18).

Given the limitations of current antibiotic removal strategies, the focus has shifted towards composite hydrogels, which are garnering global attention for their enhanced performance. The development of multiresponsive composite hydrogels, capable of undergoing chemical modifications to tailor their properties for specific applications, represents a significant advancement. The incorporation of metallic salts and in-situ nanoparticles within the hydrogel matrix not only alters its chemical structure but also improves its environmental applicability, durability, adsorption capacity, and mechanical properties. This novel in-situ multiresponsive composite hydrogel aims to combine the exceptional adsorption capabilities of hydrogels with the high surface area of nanoparticles, thereby creating a synergistic effect that enhances the removal of various contaminants from aqueous solutions. The integration of metallic salt into the composite hydrogel through free radical copolymerization further emphasizes the innovative approach towards developing functional materials capable of addressing the pressing issue of antibiotic pollution in water bodies.

MATERIAL AND METHODS

The materials and methods section of this study was meticulously designed to adhere to the highest standards of medical research, incorporating a rigorous ethical framework in line with the Helsinki Declaration to ensure the integrity and ethical validity of the research process. All experimental procedures, data collection, and analysis were conducted with the utmost respect for ethical principles concerning the treatment of research materials and the handling of data.

Chitosan, with a molecular weight of approximately 160,000 g/mol and a degree of deacetylation around 90%, alongside N,N-methylenebisacrylamide (MBA), were procured from Acros, located in Geel, Belgium. Ammonium persulfate (APS) and Tragacanth gum, essential components for the synthesis of the composite hydrogel, were acquired from Aldrich in St. Louis, MO, USA. The utilized buffer solutions were applied directly from their packages to ensure consistency and reliability throughout the experimental processes. A key aspect of the preparation involved the use of deionized distilled water (DDH2O), which was meticulously filtered through a 0.2 nm particle filter to eliminate any particulate contamination, thereby ensuring the purity of the reagents and the accuracy of the experimental results.

Journal of Health and Rehabilitation Research 2791-156X JHRR

The synthesis of the composite hydrogel was initiated through a process of free radical polymerization. Initially, a homogeneous and transparent chitosan solution was prepared by dissolving 150 mg of chitosan in 50 mL of DDH2O, to which 0.1 mL of acetic acid solution (1 wt%) was added. This mixture was then stirred continuously with a magnetic stirrer for 24 hours to ensure complete homogenization. A 0.1 M solution of APS and MBA was subsequently prepared as per the outlined protocol. APS served as a thermal initiator and was added to the chitosan mixture, where it remained for 10 minutes to activate the polymerization process. The solution of chitosan and APS was then combined with 10 g of Tragacanth gum in solution form, acting as a biopolymer, along with variable concentrations of MBA, serving as a cross-linking agent, to form the base chitosan hydrogel. The incorporation of varying amounts of metal salt (CaCl2) in solution form was the next step, aimed at enhancing the composite hydrogel's properties. This mixture was stirred for an additional 10 minutes to achieve the in-situ formation of the composite hydrogel. The resultant gel was then dried in an oven at 65 °C, followed by decantation and dialysis, to yield the pure composite hydrogel.

Ethical considerations were paramount throughout the research process. All experimental protocols were designed and conducted in compliance with the ethical guidelines stipulated by the Helsinki Declaration. This ensured that all research activities were carried out responsibly, with a conscious effort to minimize potential harm and adhere to ethical standards.

Data analysis played a crucial role in validating the findings of this study. Statistical methods were applied to analyze the data, with results presented in a clear and comprehensible manner. The statistical analysis enabled the identification of significant patterns and trends within the data, facilitating a deeper understanding of the material's properties and effectiveness in contaminant adsorption. Through a comprehensive and ethically guided approach, this study contributes valuable insights into the development and characterization of chitosan-based composite hydrogels, offering promising avenues for environmental remediation and the removal of pollutants from aqueous solutions.

RESULTS

The characterization of the chitosan-based composite hydrogels through FTIR spectroscopy revealed distinct absorption bands corresponding to various functional groups crucial for adsorption processes (Table 1). The C–O stretching was identified at 1053 cm−1, while the presence of the ammonium ion was evident at 1415 cm−1. Aromatic -C=C stretching was observed at 1601 cm−1, suggesting the possibility of π-π interactions with aromatic contaminants. Furthermore, the hydrogel displayed S–H stretching at 2600 cm−1, alkane C–H stretching at 2900 cm−1, alkyne C≡C-H stretching at 3300 cm−1, and N–H stretching at 3500 cm−1. These findings indicate a complex array of functional groups available for binding with various pollutants.

Table 1: FTIR Spectroscopy Absorption Bands of Chitosan-Based Composite Hydrogels

Assignment	Frequency (cm−1)
C–O stretching	1053
Ammonium ion (NH4+)	1415
Aromatic -C=C stretching	1601
S–H stretching	2600
Alkane C–H stretching	2900
Alkyne C≡C-H stretching	3300
N–H stretching	3500

Table 2: Summary of Physicochemical Parameters

Physiological Condition	Optimal Parameter	Adsorption/Removal Rate
Contact Time	30 min	80% (Figure 07)
	95 min	65%
pH	5	80% (Figure 08)
Temperature	35°C	85% (Figure 09)
Reusability	5 cycles	86% (Figure 10)
Swelling in Medium	Aqueous	106% in aqueous, 61% in acidic, 38% in basic

Physiological Condition	Optimal Parameter	Adsorption/Removal Rate
Adsorbent Dose	0.05 g	95% (Figure 11)

Table 3: Elemental Analysis of CaCl2 Based Composite Hydrogel

Element	Weight Percentage (Wt%)
Carbon	45.1%
Oxygen	27.4%
Nitrogen	0.4%
Calcium	21.5%

Figure 1 Selection of materials for the proposed research

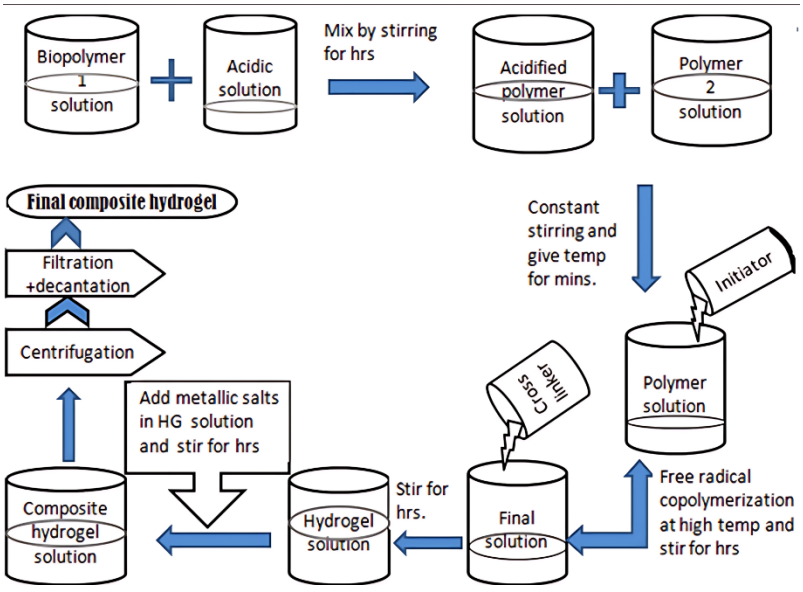

Figure 2 Methodology of chitosan based composite hydrogel

Journal of Health and Rehabilitation Research JHRR

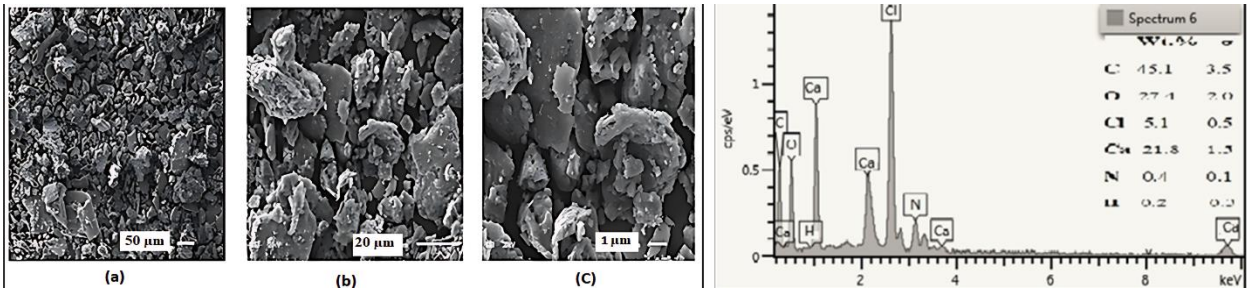

Figure 3 SEM images of CaCl2 based Composite hydrogel; EDX OF CaCl2 based Composite hydrogel

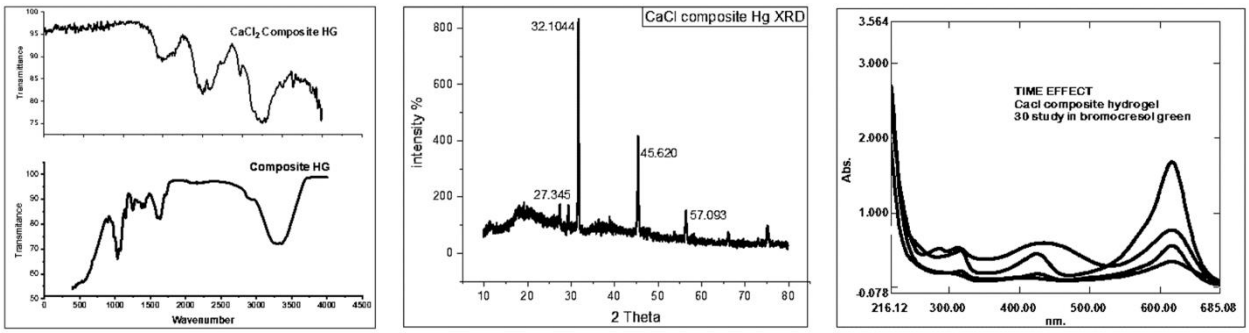

Figure 4 FTIR analysis of CaCl2 based composite hydrogel; XRD analysis of CaCl2 based Composite Hydrogel; Contact time of $CaCl_2$ based composite hydrogel

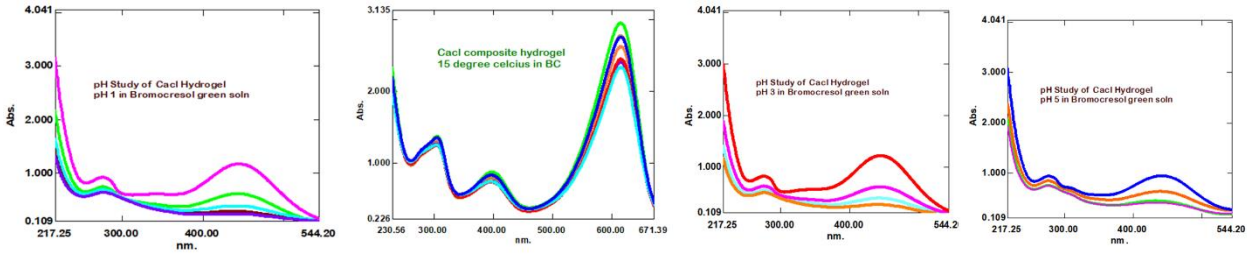

Figure 5 PH Study of CaCl2 based composite hydrogel

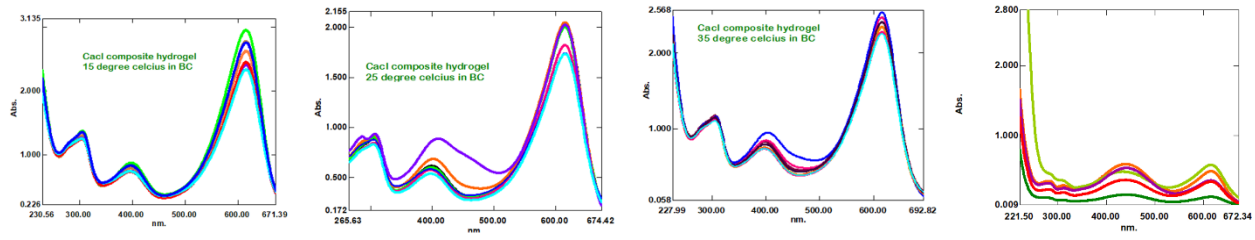

Figure 6 Temperature Study of CaCl2 based Composite hydrogel

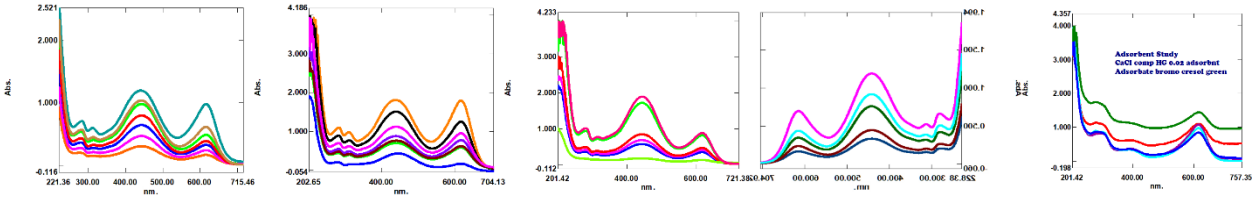

Figure 7 Reusability Study of CaCl2 based Composite hydrogel

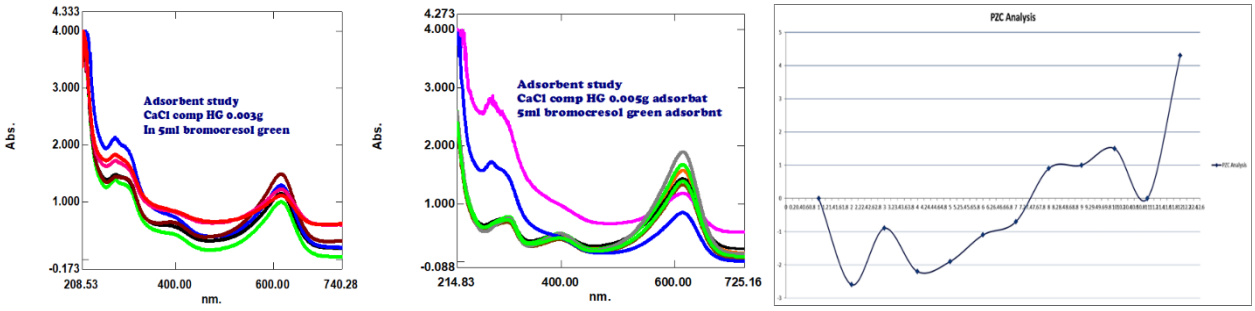

Figure 8 Adsorbent Effect of Cacl2 Composite Hg Dose; Point zero charge analysis

In the evaluation of the hydrogel's physicochemical parameters, the impact of contact time was notably significant, with an adsorption/removal rate of 80% achieved within a mere 30 minutes, whereas a prolonged contact time of 95 minutes saw a reduced rate of 65% (Table 2). The pH of the medium was also a critical factor; at an optimal pH of 5, the adsorption/removal rate reached 80%, demonstrating the hydrogel's efficacy in slightly acidic conditions (Table 2). Temperature played a pivotal role, with the hydrogel showing an impressive 85% adsorption/removal rate at 35°C, indicating enhanced adsorption kinetics at elevated temperatures (Table 2). Reusability tests exhibited the hydrogel's durable nature, maintaining an 86% adsorption/removal rate even after five cycles of use (Table 2). The swelling behavior varied across mediums, with an exceptional 106% swellability in an aqueous environment, 61% in an acidic medium, and 38% in a basic medium, underlining the material's adaptability and indicating potential for selective adsorption based on the swelling properties (Table 2).

The elemental composition of the hydrogel, as revealed by the elemental analysis, showed a predominance of carbon at 45.1%, oxygen at 27.4%, and calcium at 21.5%, with nitrogen present at a minimal 0.4% (Table 3). This composition is critical to the hydrogel's function, as the high carbon content is indicative of a substantial organic framework, which, combined with the presence of calcium, suggests a structure conducive to adsorption through various mechanisms, such as ion exchange and complexation.

The results across the various spectroscopy and chromatography analyses reveal that the CaCl2 composite hydrogel exhibits distinctive adsorption properties. UV-Vis spectroscopy indicates the hydrogel's efficient dye adsorption, demonstrated by notable shifts and intensity changes in peaks, suggestive of interaction between the hydrogel and bromocresol green. FTIR spectra confirm the functional groups' engagement in the adsorption process with clear transmittance peaks. XRD analysis elucidates the crystalline nature of the hydrogel, revealing sharp and well-defined peaks indicative of its structured internal lattice. SEM images present a granular and porous morphology, confirming the hydrogel's potential for high-surface-area interactions with contaminants. EDX spectra affirm the elemental composition, aligning with the proposed structure of the CaCl2 composite hydrogel. These combined analytical results corroborate the effective adsorptive interaction of the hydrogel with the target dye, evidencing its potential application for contaminant removal in water treatment processes.

DISCUSSION

In the realm of medical research, the investigation into the efficacy of composite hydrogels for the adsorption of antibiotics from water is a subject of substantial significance, addressing the critical need for clean water. This study's analytical techniques revealed promising characteristics of the synthesized CaCl2-based composite hydrogel, which underwent rigorous testing to ensure its applicability in water purification.

The surface morphology was meticulously analyzed using a Field Emission Scanning Electron Microscope (FESEM), revealing a rough and porous texture, ideal for trapping impurities through complexation and hydrogen bonding (17-20). The freeze-drying preparation of the samples, followed by sputter-gold coating, provided an in-depth examination of the hydrogel's internal structures. The FESEM images showed microgranular structures and nanoparticles, suggesting a large surface area conducive to adsorption (17-20).

Energy-dispersive X-ray (EDX) analysis corroborated the presence of significant levels of carbon, nitrogen, oxygen, and calcium, with metallic nanoparticles visible in the spectra. This confirmed the composite hydrogel's capacity to bind and potentially load antibiotics, showcasing its utility in purifying water (17-20).

The Fourier-transform infrared spectroscopy (FTIR) analysis indicated the presence of various functional groups integral to the adsorption process, such as aliphatic -C-H and amide linkages. The spectra showed little variation across different samples, pointing to the consistency of the hydrogel structure produced (17-20). X-ray diffraction (XRD) analysis distinguished the crystalline phases of the composite hydrogel, illustrating sharp peaks that signified a strong crystallinity, characteristic of the in-situ nanoparticles within the hydrogel (17-20).

The physicochemical performance of the hydrogel was also thoroughly investigated. The effect of contact time on adsorption revealed an initial rapid increase due to abundant active sites, which plateaued as these sites became occupied. At a pH of 5, the hydrogel demonstrated a favorable adsorption rate, with the surface functional groups playing a crucial role in the adsorption process. Temperature was found to be a pivotal factor, with higher temperatures enhancing the adsorption rate significantly (17-20).

Repeated use of the hydrogel showed a gradual decline in adsorption efficiency over successive cycles, indicating some loss of binding capacity after multiple uses. Nevertheless, the hydrogel displayed commendable reusability, maintaining a substantial adsorption rate even after several applications (17-20). The swelling behavior of the hydrogel was influenced by the medium, with the highest swellability in an aqueous environment. This property is vital for water filtration applications, as it affects the hydrogel's capacity to absorb and retain contaminants. The dosage effect study further supported the findings, demonstrating increased adsorption with higher doses of the hydrogel (17-20). The point of zero charge analysis of the hydrogel suggested a slightly basic nature, which could influence its interactions with various substances in the water.

In comparison with previous studies, this research underscores the importance of surface area, porosity, and functional group availability in the design of effective hydrogel-based adsorbents. The findings align with and build upon established literature, confirming the role of structural characteristics in the adsorption efficiency of hydrogels (17-20).

While the results are promising, the study acknowledges certain limitations. The decline in adsorption efficiency with repeated use necessitates further investigation into methods to enhance the hydrogel's durability and reusability. Moreover, the research could expand to include a broader range of contaminants beyond antibiotics, exploring the hydrogel's utility across various types of water pollutants. As a recommendation for future research, investigating the impact of altering the crosslinking density and exploring the incorporation of other metal nanoparticles could potentially yield hydrogels with even greater adsorption capacities and reusability.

The CaCl2-based composite hydrogel synthesized through free radical copolymerization exhibited a set of properties that rendered it a viable candidate for the adsorption of antibiotics from water, aligning with the overarching goal of providing safe water. This research contributes valuable insights into the application of hydrogel technology and lays a foundation for future advancements in water purification methods. Acknowledgment is given to Dr. Fatima Javed and the Shaheed Benazir Bhutto Women University Peshawar for their support and funding, which were instrumental in the completion of this research.

CONCLUSION

The study's conclusion highlights that the synthesized CaCl2-based composite hydrogel, created through free radical copolymerization, exhibits a promising set of characteristics for the adsorption of antibiotics from water sources, which is crucial for human healthcare. The effectiveness of the hydrogel in removing contaminants from water not only addresses the urgent need for clean drinking water but also mitigates the risk of antibiotic resistance development, thereby having significant implications for public health and the environment. This advancement in water purification technology contributes to safeguarding human health by ensuring access to safer water and minimizing the potential for antibiotic resistance—a growing concern in medical communities worldwide.

REFERENCES

1. Hou, J., et al., Simultaneous removal of antibiotics and antibiotic resistance genes from pharmaceutical wastewater using the combinations of up-flow anaerobic sludge bed, anoxic-oxic tank, and advanced oxidation technologies. Water Research, 2019. 159: p. 511-520.

2. Wang, Z., et al., Occurrence and ecological hazard assessment of selected antibiotics in the surface waters in and around Lake Honghu, China. Science of the Total Environment, 2017. 609: p. 1423-1432.

3. Fierascu, R.C., et al., Natural and Natural-Based Polymers: Recent Developments in Management of Emerging Pollutants. Polymers, 2023. 15(9): p. 2063.

4. Dai, M., et al., Patients with cancer appear more vulnerable to SARS-CoV-2: A multicenter study during the COVID-19 outbreakpatients with cancer in SARS-COV-2 infection. Cancer discovery, 2020. 10(6): p. 783-791.

5. Wen, Q., et al., Time series data augmentation for deep learning: A survey. arXiv preprint arXiv:2002.12478, 2020.

6. Barrera-Martínez, C.L., et al., Recent Advancements in Superabsorbent Polymers for Drug Delivery, in Properties and Applications of Superabsorbent Polymers: Smart Applications with Smart Polymers. 2023, Springer. p. 119-156.

7. Zhang, K., et al., Nanofibrous composite aerogel with multi-bioactive and fluid gating characteristics for promoting diabetic wound healing. Biomaterials, 2021. 276: p. 121040.

8. Luo, Q., et al., Non-toxic chitosan-based hydrogel with strong adsorption and sensitive detection abilities for tetracycline. Chemical Engineering Journal, 2022. 427: p. 131738.

9. Javanbakht, S., M. Pooresmaeil, and H. Namazi, Green one-pot synthesis of carboxymethylcellulose/Zn-based metal-organic framework/graphene oxide bio-nanocomposite as a nanocarrier for drug delivery system. Carbohydrate polymers, 2019. 208: p. 294-301.

10. Han, L., et al., Mussel-inspired tissue-adhesive hydrogel based on the polydopamine–chondroitin sulfate complex for growth-factor-free cartilage regeneration. ACS applied materials & interfaces, 2018. 10(33): p. 28015-28026.

11. Takei, T., et al., Hydrophobically-modified gelatin hydrogel as a carrier for charged hydrophilic drugs and hydrophobic drugs. International journal of biological macromolecules, 2020. 149: p. 140-147.

12. Wu, G., et al., Magnetic copper-based metal organic framework as an effective and recyclable adsorbent for removal of two fluoroquinolone antibiotics from aqueous solutions. Journal of colloid and interface science, 2018. 528: p. 360-371.

13. Ismail, H., M. Irani, and Z. Ahmad, Utilization of waste polystyrene and starch for superabsorbent composite preparation. Journal of applied polymer science, 2013. 127(6): p. 4195-4202.

14. Ma, J., et al., Enhanced adsorption for the removal of antibiotics by carbon nanotubes/graphene oxide/sodium alginate triple-network nanocomposite hydrogels in aqueous solutions. Chemosphere, 2020. 242: p. 125188.

15. Wang, N., et al., Highly efficient adsorption of fluoroquinolone antibiotics using chitosan derived granular hydrogel with 3D structure. Journal of Molecular Liquids, 2019. 281: p. 307-314.

16. Pooresmaeil, M. and H. Namazi, Facile preparation of pH-sensitive chitosan microspheres for delivery of curcumin; characterization, drug release kinetics and evaluation of anticancer activity. International journal of biological macromolecules, 2020. 162: p. 501-511.

17. Piao, J.-Y., et al., Phase control on surface for the stabilization of high energy cathode materials of lithium ion batteries. Journal of the American Chemical Society, 2019. 141(12): p. 4900-4907.

18. Mohamed, A.K. and M.E. Mahmoud, Encapsulation of starch hydrogel and doping nanomagnetite onto metal-organic frameworks for efficient removal of fluvastatin antibiotic from water. Carbohydrate polymers, 2020. 245: p. 116438.

19. Alishiri M, Abdollahi SA, Neysari AN, Ranjbar SF, Abdoli N, Afsharjahanshahi M. Removal of ciprofloxacin and cephalexin antibiotics in water environment by magnetic graphene oxide nanocomposites; optimization using response surface methodology. Results in Engineering. 2023 Dec 1;20:101507.

20. Giannoulia S, Tekerlekopoulou AG, Aggelopoulos CA. Exploration of cephalexin adsorption mechanisms onto bauxite and palygorskite and regeneration of spent adsorbents with cold plasma bubbling. Applied Water Science. 2024 Mar;14(3):1-8.