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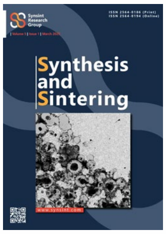

Review article

Recent developments in chitosan-based adsorbents for tetracycline removal: A mini-review

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ABSTRACT

Tetracyclines (TCs) are widely used antibiotics that have raised concerns due to their presence in the environment, posing risks to human health and ecosystems. This mini-review explores recent advancements in utilizing chitosan-based adsorbents to remove TCs from wastewater efficiently. Our review reveals that adsorption performance is highly influenced by temperature and pH, with most studies reporting effective TC removal between 25–45 °C and pH values of 2–12. The Langmuir and Freundlich isotherm models are both applicable, depending on the specific adsorbent, indicating both monolayer and heterogeneous adsorption behavior, with maximum adsorption capacities ranging from 19.32 mg/g to 940 mg/g, with the highest capacity shown for bacterial cellulose microfibers (BCM) char/chitosan (CS)/polyethyleneimine (PEI). Kinetic studies predominantly followed the pseudo-second-order model, suggesting chemisorption as a rate-limiting step, while some followed a pseudo-first-order model. High removal rates (≈ 90–99%) were reported for materials like zeolitic imidazolate framework (ZIF-8)-chitosan, BCM char/CS/PEI, and carboxymethyl-chitosan (CMC)-modified Na-Mt (montmorillonite). This review highlights the significant potential of chitosan-based adsorbents. At the same time, further research is needed to optimize adsorption conditions, understand the mechanisms involved, and address the diverse sources of TC pollution. Given the global impact of TCs, a comprehensive approach encompassing enhanced monitoring, stricter regulations, the development of advanced treatment technologies like chitosan-based adsorbents, and public awareness campaigns is imperative to mitigate their environmental risks effectively.

KEYWORDS

Tetracyclines
Chitosan-based adsorbents
Wastewater treatment
Antibiotic removal
Environmental pollution

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1. Introduction

Antibacterial medications rank among the most frequently prescribed treatments globally. Antibiotics, a type of antibacterial agent, consist of intricate molecular structures capable of killing or inhibiting the proliferation of bacteria [1–4]. Antibiotic medications are categorized based on their mode of action, range of effectiveness, chemical composition, and routes of administration. Antibacterial agents serve therapeutic roles and are also utilized as growth enhancers in animal agriculture. A study by Scaria and colleagues in 2021 highlighted this

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alarming trend. Their findings revealed that global antibiotic consumption surged dramatically, rising from 21 billion daily doses in 2000 to an estimated 35 billion daily doses in 2015, representing a substantial increase of almost 65 percent. This data emphasizes the escalating reliance on antibiotics globally [5–8].

Furthermore, according to Klein and colleagues (2018), it has been projected that the consumption of antimicrobial medications will experience a twofold increase by the year 2030. Excessive usage of antibiotics can lead to the emergence of antibiotic-resistance genes (ARGs), which can have detrimental effects on human health. These genes are produced through natural mutations in microorganisms and are favored by antibiotics. As a result, the effectiveness of a drug's ability to eliminate bacteria is compromised [9–11]. Horizontal transfer enables ARGs to move to different bacteria, impacting bacterial populations and enhancing antibiotic resistance. Multidrug-resistant Mycobacterium Tuberculosis, Methicillin-resistant Staphylococcus aureus, and Clostridium difficile are some strains that have inflicted significant damage [12, 13].

TC, a widely used class of antibiotics, was first discovered in the late 1940s from Streptomyces species. Since then, TC antibiotics have been developed and marketed for their effectiveness in the medical field. The latest iteration, the third generation, exhibits enhanced strength and effectiveness. TC's mechanism of action applies binding to the 30S ribosomal subunit of bacteria, thereby hindering bacterial protein synthesis, a crucial step in their growth and proliferation [14]. As Fuoco (2012) notes, this antibiotic's comprehensive efficacy hinders the growth of a diverse range of microorganisms, including both gram-negative and gram-positive bacteria, as well as protozoan parasites like mycoplasma, rickettsia, and chlamydia [15]. TC's widespread use as an antibiotic is attributed to its low cost and strong effectiveness.

The extreme usage of antibiotics like TC in human and animal medical treatment and farming practices poses a significant risk to human well-being and the environment. Recently, traces of TC have been detected in various locations, such as sediments, surface water, soil, marine habitats, and samples of living organisms. TC presents adverse impacts on ecosystems, as it can gather throughout the food chain, leading to toxicity in the microbial population and promoting the emergence and propagation of antibiotic opposition. Furthermore, TC risks the quality of drinking and irrigation water systems, leading to disturbances in the microbial balance within the human gut. Such negative impacts highlight significant apprehensions regarding TC pollution, introducing a growing public health challenge [16–18].

Over the past ten years, numerous technologies have been assessed for eliminating TC pollutants. These methods encompass biological approaches [19], electrochemical degradation [20], photodegradation processes [21], adsorption mechanisms [22], ozonation methods [23], advanced oxidation techniques [24], and more. Most of these approaches come with disadvantages like exorbitant expenses, elevated energy demands, substantial sludge or by-product generation, sluggish procedures, and a brief lifespan. In contrast, the adsorption method has gained widespread attention in water and wastewater treatment due to its cost-effectiveness, ease of use, rapid responsiveness, suitability for online operation, absence of sludge formation, and potential for reuse. This research focuses on adsorption as a promising approach for removing TC contaminants. Recent studies have highlighted the use of polymeric and biopolymeric materials as effective adsorbents, with chitosan and its modified forms receiving considerable attention due to their efficacy as biosorbents in eliminating pharmaceutical contaminants. Chitosan possesses several advantageous characteristics, including biodegradability, biocompatibility, hydrophilicity, non-toxicity, antimicrobial properties, low immunogenicity, affordability, and availability [25–28].

Recently, a growing interest has been in developing chitosan-based adsorbents for removing TC from various environments. Studies have highlighted the potential of chitosan due to its unique properties and sustainable sourcing. This mini-review aims to delve into recent advancements in chitosan-based adsorbents and their performance in TC removal, shedding light on the significance of these developments in addressing the environmental impact of TC contamination. Exploring the effectiveness of chitosan in TC absorption and its implications on the global environment, a critical examination of the current research landscape sets the stage for future directions in this crucial area of environmental remediation.

2. Chitosan source and properties

Chitin, the second most abundant natural polysaccharide after cellulose, was first identified in 1823 [29]. Its deacetylated derivative, chitosan, possesses unique properties making it an effective tetracycline adsorbent. Crucially, amino groups and a high surface area contribute significantly to its adsorption capacity [30, 31]. This combination allows chitosan to effectively bind tetracycline molecules, making it a promising material for wastewater treatment applications.

Chitosan is a biopolymer derived from chitin, typically sourced from natural materials like shrimp, lobster shells, crab, fungal mycelia, and green algae. Additionally, it can be found in the exoskeletons of insects and the cell walls of fungi. The chitin concentration in fungi ranges from 19% to 42%, whereas it can be as high as 75% in exoskeletons. However, not all shellfish byproducts are suitable for chitin extraction. For instance, blue crabs (Callinectes) contain only 14% chitin, while clam shells and oysters have a chitin content between 4% and 6% [32, 33]. The amount of chitin present can differ based on the levels of minerals, proteins, and carotenoids, which are influenced by factors such as species, phase of the nutritional condition, reproductive cycle, age, and the methods used during peeling in the processing stage. Chitosan is constructed by the deacetylation of chitin, which can occur through either enzymatic or alkaline methods. However, the enzymatic approach has primarily been restricted to laboratory settings. At the same time, the alkaline method is more prevalent in industrial applications due to its efficiency, cost-effectiveness, and ease of use [31, 34].

Chitosan is a biopolymer derived from chitin through partial deacetylation, consisting of β–(1–4)–d–glucosamine, as illustrated in Fig. 1. This biopolymer falls under the category of glycosaminoglycans and is made up of two primary sugars: β–(1–4)–2–amino–d–glucose and β–(1–4)–2–acetamido–d–glucose, along with N–acetylglucosamine and glucosamine. The ratio of these components varies based on the alkaline treatment used, often leading to unequal proportions. Structurally, chitosan resembles cellulose, where the hydroxyl group found in cellulose is substituted by amino groups or acetamido at the carbon-2 position in chitosan [35]. Consequently, unlike many other polysaccharides mainly consisting of carbon, hydrogen, and oxygen, chitosan and chitin incorporate nitrogen (6.89%), enhancing their commercial appeal [36]. The molecular chain arrangement and orderly packing significantly influence the physicochemical characteristics of chitosan and chitin. Chitosan and its N-acetyl variant contain highly

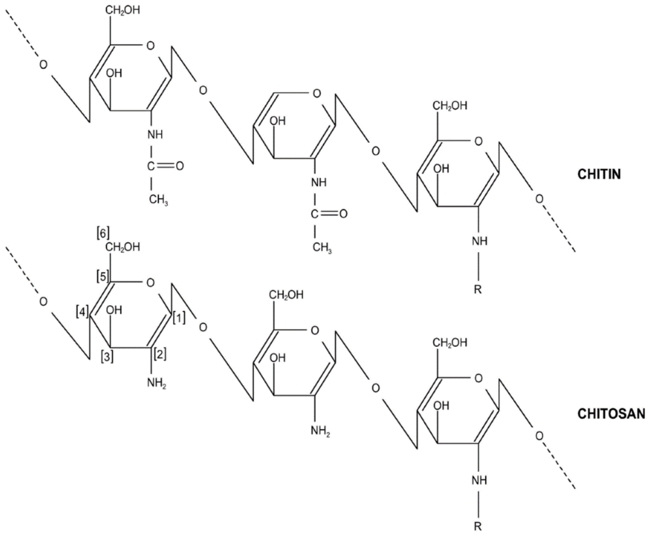

Fig. 1. Structure of chitin and chitosan [30].

reactive amino groups and numerous hydroxyl groups. This composition leads to a pronounced propensity for inter- and intra-molecular hydrogen bonding, contributing to stable crystalline structures and the development of linear aggregates. Chitosan generally exhibits lower crystallinity than chitin, which likely enhances its reactivity with various reagents and improves solubility. While most aqueous acids can dissolve chitosan, chitin is only soluble in limited solvents. The protonation of the amino groups along the chitosan polymer results in numerous cationic sites, boosting its solubility through increased polarity. This distinctive characteristic broadens the range of potential uses for chitosan, particularly its capacity to adsorb various pollutants [37].

Table 1 presents an overview of the critical characteristics of chitosan. Its inherent features, including its polycationic nature in acidic environments, capacity to establish hydrogen bonds, and engagement in electrostatic and van der Waals interactions, contribute to its effectiveness as an adsorbent. Additionally, factors such as degree of deacetylation (DD), molecular weight (MW), solubility, crystallinity, particle size, and surface area significantly affect the properties of the resulting chitosan-based material and its adsorption capabilities [38]. Thus, understanding and optimizing these characteristics are crucial for developing efficient adsorbent materials.

Table 1. Key characteristics of chitosan.

Physicochemical properties	- Conducts ions - A linear amino-polysaccharide rich in nitrogen - A cationic biopolymer characterized by a significant charge density - Presence of functional groups that allow for chemical activation and cross-linking - Capable of complexing and chelating - Exhibits adsorption characteristics - Can create intermolecular hydrogen bonds - pKa ranges between 6.5 and 6.7 (pKa is a number that describes the acidity of a particular molecule.) - Acts as a flocculant
Biological properties	- Adhesion to biological tissues - Properties that combat acidity, ulcers, and tumors - Safe for use without toxicity - Ability to inhibit microbial growth - Capable of breaking down naturally - Biological effectiveness - Activity that reduces lipid levels - Capable of adsorption - Substances that prevent blood clotting

3. Current developments in chitosan-based adsorbents for TC removal

The antibiotic TC ranks as the world's second most extensively utilized drug. It undergoes inadequate absorption in metabolism, potentially presenting an ecological hazard due to a notable portion remaining unmetabolized [39, 40]. In research investigations, the focus has been on the absorption of TC when it comes to antibiotics. TC's adsorption has been analyzed in various academic papers, as detailed in Table 2.

A research team led by Caroni [41] explored how TC interacts with chitosan particles. Their findings suggested a two-step process: First, the TC hydrochloride molecule loses a proton, becoming negatively charged. Second, the chitosan molecule gains a proton becoming positively charged, allowing it to attract and bind the negatively charged TC molecules. The research conducted by Caroni and colleagues [42] focused on investigating the adsorption of protonated TC on chitosan through the solution depletion technique. The study revealed that the sorption of TC is associated with the surface protonation of chitosan, which is directly correlated with the concentration of its continuous phase. A rise in TC levels appeared to disturb the chitosan surface, leading to the chitosan framework's disturbance at approximately 1.2 $g.l^{-1}$ evidenced by an uptick in TC adsorption levels [41, 42].

Examining adsorption rates before surface disturbance indicated the presence of two different kinetics for protonated and non-protonated TC, wherein non-protonated TC appeared to be the primary driver in TC adsorption. It was uncovered that the rate of protonated TC was comparable to the speed at which the surface becomes charged, with a notable disparity observed for the non-protonated variant. This difference primarily stems from the repulsive forces between chitosan and the protonated TC sites that carry a positive charge.

Zhang and colleagues [43] developed a range of composite adsorbents with magnetic core-brush structures by conducting co-polymerization grafting on the chitosan/Fe_3O_4 composite (CS-MCP) surface. According to Zhang et al., this was proposed as an economical adsorbent for eliminating TC from both individual and combined solutions with diclofenac sodium. The authors also showed that enhancing MCP with methylmethacrylate (CM-MCP), acrylic acid (CA-MCP), and 2-methyl acryloyloxyethyl trimethyl ammonium chloride (CD-MCP) can enhance its efficiency in adsorbing TC [43].

Of the altered MCPs, CD-MCP demonstrated the most significant capability for this application, owing to its positively charged surface that strongly attracted anionic entities via electrostatic interactions between the anionic species and the polymer. In a separate research project, Oladoja and colleagues showcased the exceptional adsorption capabilities of magnetic macro-reticulated cross-linked chitosan (MRC) produced with a gastropod shell serving as a pore-generating element. The adsorption energy reached up to 100 kJ/mol, highlighting the prevalence of chemisorption. It was demonstrated that the adsorption of TC was predominantly governed by kinetics rather than diffusion control, further emphasizing the impressive capabilities of MRC. Research conducted by Oladoja and colleagues in 2014 found that organic substances like humic acid hindered the effectiveness of eliminating total coliforms [44].

Abdolmaleki and colleagues employed a novel adsorbent for TC, which consisted of electrospun nanofibers of poly(vinyl alcohol) and chitosan crosslinked with glutaraldehyde. The production of chitosan/PVA electrospun nanofibers involved using a 75:25 volume ratio of chitosan to PVA, resulting in diameters ranging from 3 to 11 nm and 6 to 18 nm pre- and post-crosslinking with glutaraldehyde. They utilized the response surface method to assess how various factors impact the adsorption capacity, indicating the significance of the initial TC concentration, volumetric ratio of PVA to chitosan, pH level, and adsorbent dosage. They managed to reach a peak adsorption ability of 102 mg/g [45].

In many industrial wastewater sources, there is commonly a blend of pharmaceutical substances and metal ions. This occurrence is illustrated in animal waste, where high levels of TC (TC) and copper ions can lead to environmental contamination in water bodies [46]. Certain studies have utilized chitosan derivatives as flocculants for Cu(II) ions and TC. One example is the application of carboxyethyl chitosan in the flocculation of a solution containing TC and Cu(II) ions, as proposed by Zhang et al. [47].

The flocculation mechanism for the removal of Cu(II) ions is believed to involve charge neutralization, whereas TC is effectively removed through incorporation into Cu(II) hydroxides in a synergistic manner. Our collaborative work with Jia and colleagues has led to significant advancements in the field. By incorporating aromatic ring-containing [2,4-bis(dimethyl amino)-6-chloro-(1,3,5)-triazine (BDAT) functional groups into chitosan flocculant, we have improved the elimination efficacy of TC and Cu(II). This was achieved by fostering strong interactions between BDAT-chitosan, TC, and Cu(II). The enhancement was attributed to mechanisms such as electrostatic coordination and attraction between BDAT-chitosan and Cu(II), coordination between Cu(II) and TC, and π stacking involving the negatively assessed aromatic rings in TC and the positively assessed triazine rings in BDAT-chitosan [48].

Huang and colleagues conducted research on the elimination of TC by employing a nanocomposite known as MSCG, comprising magnetic $Fe_3O_4@SiO_2$, graphene oxide, and chitosan, which demonstrated effective adsorption likely due to pi interactions and electrostatic forces. The findings indicated that the existence of Cu(II) had a substantial enhancing influence on the adsorption of TC. It was achieved by connecting the substance being analyzed and the material that absorbs it, resulting in a rise in the maximum adsorption capacity of TC from 67.57 to 183.47 mmol/kg [49]. Their research showed that (i) the attraction of positively charged nitrogens in the TC and MSCG through electrostatic forces and (ii) the considerable π interactions between the rings of benzene in TC molecules and the extensive pi systems present on the surface of graphene oxide may play a critical role in driving the mechanism of adsorption. The introduction of TC into the solution led to a notable attraction between certain oxygen-containing functional groups (such as –OH and C=O) on Cu(II) and TC, which resulted in a significant growth in the amount of TC adsorption as the concentration of Cu(II) increased. Compared to TC adsorption alone, the proportion of C=O decreased following TC/Cu adsorption. Research conducted by Huang et al. [49] explored how the presence of Mg^{2+}, Ca^{2+}, K^+, and Na^+ cations affected the adsorption of TC on magnetic $Fe_3O_4@SiO_2$-chitosan/graphene oxide. Their findings indicated that introducing these cation electrolytes did not notably impact adsorption efficiency [49].

Liu and colleagues conducted a separate investigation, creating a biochar modified with chitosan-Fe/S (BCFe/S) to adsorb TC from water sources effectively. The adsorption efficiency of BCFe/S was significantly higher than that of pristine chitosan, biochar, and Fe/S. The performance showed remarkable variability across different mass ratios of biochar: chitosan: $FeSO_4$. The adsorption capabilities of the composite were significantly boosted by increasing the concentration of $FeSO_4$ and the proportion of biochar within its composition, a feat sure to impress. Liu and colleagues delved into a comprehensive comparison of the adsorption characteristics of biochar and BCFe/S, meticulously examining their similarities and distinct differences across all facets of their adsorption behavior. Illustrating this point, the maximum adsorption capacity reached 75.36 mg/g for biochar at a pH of 9, while BCFe/S achieved a significantly higher capacity of 180.39 mg/g at a pH of 5 [50].

Additionally, research demonstrated that the presence of Ca^{2+}, NH^{4+}, K^+, and Na^+ had a contrasting impact on the adsorption of TC onto BCFe/S, which was ascribed to processes such as ion exchange, chelation, hydrogen bonding, and hydrated radius. Nevertheless, the presence of Ca^{2+} ions did not have a notable impact on biochar adsorption of total carbon. In addition to electrostatic attraction, π-π stacking, filling pores, bonding with silicates, and forming hydrogen bonds, chelation, and ion exchange were recognized as crucial adsorption processes for eliminating TC with biochar, specifically with BCFe/S. The SED research showed that elevated temperatures led to a uniform biochar surface, whereas BCFe/S exhibited a heterogeneous surface. Moreover, the BCFe/S surface exhibited fewer adsorption sites, lacking adsorption energy. The unreactive adsorption sites showed little response to temperature changes, with only a limited number of sites becoming active when the solution's temperature was raised. The process of TC adsorption on BCFe/S was classified as chemisorption, while on biochar, it was identified as physisorption [50].

In their study conducted in 2019, Ma and colleagues established that by using carboxymethyl-chitosan, the spacing between the layers of Na-montmorillonite was increased, leading to enhanced absorption capabilities for chlortetracycline (CTC) and TC. The equilibrium for eliminating TC and CTC was quickly reached within 2 hours. At pH levels between 4 and 7, simultaneous adsorption was promoted by electrostatic interactions between the positively charged carboxymethyl-chitosan and the negatively charged antibiotic anions, alongside cation exchange [51]. In their research, Li and colleagues explored the integration of covalent organic frameworks (COF) and chitosan in a film composed of magnetic $NiFe_2O_4$-COF-chitosan-terephthalaldehyde nanocomposites (NCCT) for adsorbing cefotaxime (CTX) and TC. The collaborative action of the amino and hydroxyl groups in chitosan, along with the phenyl group of terephthalaldehyde and COF, greatly enhanced the absorption of antibiotics into NCCT [52].

Chitosan's significant contribution involved its chemical bonding with terephthalaldehyde, which effectively limited the degradation of NCCT in acidic environments. At pH 8, TC demonstrated a peak adsorption capacity of 388.52 mg/g, whereas at pH 4 CTX reached 309.26 mg/g. The mechanisms of TC adsorption on NCCT involved a range of processes, such as complexation, ion exchange, attraction based on electric charge, hydrogen bond formation, and interaction with π-π. On the other hand, the processes for the absorption of CTX included electrostatic affinity, condensation responses, π-π interaction, and hydrogen connection [52].

Recently, there has been a notable interest in using metal-organic frameworks (MOFs) for adsorption. A study by Zhao and colleagues involved integrating common MOFs such as Fe-BTC (1,3,5-benzenetricarboxylate), ZIF-8, HKUST-1 (Hong Kong University of Science and Technology, which is also called MOF-199), and ZIF-67 into a chitosan framework for TC adsorption. The composite beads made of ZIF-8 and chitosan demonstrated outstanding adsorption characteristics, showing great potential for multiple reuse while achieving a maximum adsorption capacity of 495.04 mg/g. The bonding interactions in ZIF-8-chitosan adsorption included electrostatic forces, hydrogen bonds, and π-π stacking relationships [53]. A study led by Ahamad et al. [54] unveiled a novel composite material known as CTM (chitosan, thiobarbituric acid, malondialdehyde)@Fe_3O_4, malondialdehyde, and thiobarbituric acid, combining mesoporous magnetic chitosan and Fe_3O_4. With its substantial surface area measuring 376 $m^2.g^{-1}$, this nanocomposite demonstrated exceptional adsorption capabilities for TC, achieving a maximum adsorption capacity of 215.31 mg/g. The potential adsorption process was characterized by the interaction of carbonyl groups and phenyl rings in TC, which tended to cluster with the hydrophobic regions of the nanocomposite. It led to creating π-π conjugation effects and hydrophobic bonds [54]. In a study by Ranjbari and colleagues [55], it was shown that incorporating tricaprylmethylammonium chloride (known as Aliquat-336) ionic liquid into chitosan notably enhanced the adsorption performance of chitosan towards TC. Using chitosan hydrogel beads and tricaprylmethylammonium chloride (CS-TCMA), a removal efficiency of 90% was attained within a time frame of under 45 minutes over a broad pH spectrum from 5 to 11. The rise in TCMA quantity boosted the enhancement of hydrogel beads' adsorption efficiency. The primary binding mechanisms observed in the adsorption process of TC onto the CS-TCMA surface involved XH (an attractive interaction between a X–H antibonding orbital and a π orbital (X = C, N, and O))/π, ion-π interactions, and hydrogen bonds [55].

Several studies have underscored the significant potential of modified chitosan materials for enhanced TC removal. For instance, Turan et al. [56] delved into the use of zirconium-loaded chitosan modified with perlite (Zr/CS/Pt) and zirconium-loaded chitosan (Zr/CS) composites. These materials exhibited superior adsorption capacities compared to raw chitosan, indicating that the incorporation of zirconium and perlite significantly enhanced TC uptake [56]. Similarly, Bruckmann et al. [57] explored the use of magnetic chitosan ($CS{\cdot}Fe_3O_4$) for TC removal. Their findings revealed a high adsorption capacity of 211.21 $mg.g^{-1}$ at pH 7.0, underscoring the effectiveness of this magnetic adsorbent for antibiotic removal [57].

Further enhancing the adsorption capacity and reusability of chitosan-based adsorbents has been a critical focus of recent research. Liu et al. [58] demonstrated the effectiveness of ethylenediamine-modified magnetic chitosan (EMMCS-G) for TC removal, achieving a removal rate of 94% under optimized conditions. This modification significantly improved the adsorption capacity compared to unmodified magnetic chitosan. The adsorption process was consistent with the pseudo-second-order kinetic and Freundlich isotherm models, indicating a multi-layer adsorption mechanism driven by hydrogen bonding, π-π interactions, and electrostatic attraction [58].

Researchers are enhancing existing chitosan-based adsorbents, exploring novel material designs, and understanding the underlying adsorption mechanisms. Guo et al. [59] examined the adsorption efficacy of chitosan-modified bentonite for the removal of TC, and their findings suggest that the composite material could serve as a cost-effective adsorbent for TC removal, given its enhanced adsorption capacity compared to unmodified bentonite [59].

Mosaffa et al. [60] explored bacterial cellulose microfibers (BCM) biochar incorporated into chitosan/polyethyleneimine beads as a bio-based adsorbent for TC and metronidazole (MET) removal. The study underscored the crucial role of the porous bead structure in contributing to the adsorbent's exceptional capacity and reusability over multiple cycles, as the composite material demonstrated high removal efficiencies, reaching 90% and 99.13% removal for MET and TC, respectively [60].

Zheng et al. [61] developed a functionalized magnetic chitosan-based adsorbent (Fe_3O_4@CAA (chitosan-based adsorbent) with enhanced adsorption capacity for TC removal. This core-shell structured material, synthesized via ultrasound-initiated radical grafting copolymerization and cross-linking, exhibited a remarkable adsorption capacity of 325.04 mg/g. The abundant functional groups, including amino, hydroxyl, and sulfonic acid, contributed to the increased adsorption sites. The adsorbent demonstrated excellent reusability over five adsorption-desorption cycles, highlighting its potential for efficient and sustainable TC removal. The adsorption mechanism primarily involved electrostatic interactions and hydrogen bonding, while the presence of Cu(II) further enhanced TC removal through the formation of a strong Cu(II)-TC complex [61].

Table 2. Chitosan-based adsorbents for TC removal.

Adsorbent	Adsorption condition	Adsorption isotherm	Adsorption kinetic	Adsorption capacity (mg/g)	Removal efficiency (%)	Ref.
GC/MGO (genipin-crosslinked chitosan/graphene oxide)-SO_3H	25–40 °C pH = 2–12	Freundlich	Pseudo-second order	556.28	-	[62]
CMC modified Na-Mt	25–45 °C pH = 4–7	Freundlich	Pseudo-second order	271.74	≈ 96	[51]
BCFe/S	25–45 °C pH = 2–12	Langmuir	Pseudo-second order	183.01	-	[50]
Chitosan-olive pomace	5–25 °C pH = 2–12	Langmuir	Pseudo-first order	16	≈ 75	[63]
CDF (chitosan, diphenylurea and formaldehyde)@MF	25–65 °C pH = 2–10	Langmuir	Pseudo-first order	168.24	-	[64]
ZIF-8-chitosan	20–80 °C pH = 1–11	Langmuir	Pseudo-second order	495.04	≈ 90	[53]
CS-TCMA	25–45 °C pH = 5–11	Langmuir	Pseudo-second order	22.42	≈ 90	[55]
CTM@Fe_3O_4	25–65 °C pH = 2–10	Langmuir	Pseudo-second order	215.31	-	[54]
Alginate microbeads/CS/TiO_2	25–60 °C pH = 2–12	Langmuir & Freundlich	Pseudo-second order	0.96	≈ 100	[65]
$NiFe_2O_4$-COF-chitosan-terephthalaldehyde	20–40 °C pH = 3–11	Freundlich	Pseudo-second order	388.52	≈ 95	[52]
NDMCMs (nitrilotriacetic acid-modified magnetic chitosan microspheres)	25–45 °C pH = 2–10	Freundlich	Pseudo-second order	373.5	-	[66]
Zn-CSNW (chitosan nonwoven fabric)	pH = 3–10	Langmuir and Freundlich	Pseudo-second order	195.9	≈ 90	[67]
Halloysite/chitosan	pH = 2.8–8.5	Freundlich	Pseudo-second order	19.4	≈ 73	[68]
LCBW (leached carbon black waste)-chitosan	pH = 7.5–8.5	Langmuir	Pseudo-second order	205	≈ 92	[69]
Zr/CS/Pt	pH = 2–10	Langmuir	Pseudo-second order	104.17	≈ 95	[56]
Chitosan-based hydrogel	15–45 °C pH = 2–10	Langmuir	Pseudo-second order	541.3	-	[70]
$CuCoFe_2O_4$@chitosan	25–40 °C pH = 3.5–11.5	Freundlich	Pseudo-second order	4.04	≈ 93	[71]
CS-modified bentonite	20–40 °C pH = 2–10	Freundlich	Pseudo-second order	19.32	-	[59]
EMMCS-G (ethylenediamine-modified magnetic chitosan)	pH = 3–11	Freundlich	Pseudo-second order	84	≈ 94	[58]

Table 2. Continued.

Adsorbent	Adsorption condition	Adsorption isotherm	Adsorption kinetic	Adsorption capacity (mg/g)	Removal efficiency (%)	Ref.
CS/Fe_3O_4	pH = 4–10	Elovich	Sips	211.21	≈ 74	[57]
ZNF/CS-CRD (zinc ferrite/chitosan-curdlan)	25–45 °C pH = 2–11	Langmuir	Pseudo-second order	371.42		[72]
BCM Char/CS/PEI	25–40 °C pH = 2–10	Temkin	Pseudo-second order	940	≈ 99	[60]
Fe_3O_4@CAA	pH = 2–10	Langmuir	Pseudo-second order	325.04	-	[61]
DCPD (brushite)-CS	25–45 °C pH = 3–11	Langmuir	Pseudo-second order	223.84	-	[73]
DCPA (monetite)-CS	25–45 °C pH = 3–11	Langmuir	Pseudo-second order	205.92	-	[73]

These recent studies showcase the versatility and potential of chitosan-based adsorbents for TC removal from contaminated water sources. Continued research focused on developing novel chitosan-based materials with enhanced adsorption capacity and reusability and an improved understanding of adsorption mechanisms will pave the way for more effective and sustainable water treatment technologies.

4. Performance evaluation of the effects of chitosan on TC absorption

The performance of chitosan-based adsorbents in removing TC from wastewater has been evaluated through various adsorption conditions, isotherm models, kinetic studies, adsorption capacities, and removal efficiencies, as summarized in Table 2.

The adsorption performance of chitosan varies significantly with temperature and pH. Most studies reported effective adsorption at temperatures ranging from 25 to 45 °C, with some materials showing efficacy at temperatures as high as 80 °C. The pH range for optimal TC removal was generally between 2 and 12, indicating the broad applicability of chitosan-based adsorbents in diverse wastewater conditions. Notably, the chitosan-olive pomace adsorbent was effectively removed at lower temperatures (5–25 °C), suggesting its potential for energy-efficient applications.

Different isotherm models were applied to describe the adsorption behavior. The Langmuir model was frequently observed, indicating monolayer adsorption on a surface with a finite number of identical sites. It was evident in materials such as ZIF-8-chitosan and CTM@Fe_3O_4, which exhibited high adsorption capacities (495.04 mg/g and 215.31 mg/g, respectively). In contrast, the Freundlich model applied to several adsorbents, including CMC-modified Na-Mt and $NiFe_2O_4$-COF-chitosan-terephthalaldehyde, suggesting heterogeneous adsorption sites.

Kinetic studies predominantly followed the pseudo-second-order model, indicating that the rate-limiting step may involve chemisorption. This was particularly evident in adsorbents such as GC/MGO-SO_3H and ZIF-8-chitosan, which also exhibited high adsorption capacities. Conversely, some materials like Chitosan-olive pomace followed a pseudo-first-order model, reflecting different mechanisms of interaction between TC and the adsorbent.

The adsorption capacity of chitosan-based adsorbents for TC varied significantly across different materials. The highest reported capacity was observed for BCM char/CS/PEI at 940 mg/g, which highlights the potential of composite materials in enhancing adsorption performance. Other notable capacities included GC/MGO-SO_3H (556.28 mg/g) and $NiFe_2O_4$-COF-chitosan-terephthalaldehyde (388.52 mg/g). In contrast, simpler chitosan formulations like halloysite/chitosan and CS-modified bentonite showed much lower capacities (19.4 mg/g and 19.32 mg/g, respectively), emphasizing the importance of material design in optimizing performance.

The various adsorbents varied widely in removal efficiencies for TC. High removal rates were achieved with CMC-modified Na-Mt (≈ 96%), BCM char/CS/PEI (≈ 99%), and ZIF-8-chitosan (≈ 90%). These results indicate that chitosan-based adsorbents can effectively reduce TC concentrations in wastewater, making them viable options for pharmaceutical wastewater treatment. However, some materials did not report removal efficiency, highlighting areas for further investigation.

In conclusion, the performance evaluation of chitosan-based adsorbents reveals their promising potential in TC absorption from wastewater. The choice of adsorbent, along with optimizing adsorption conditions and understanding the underlying mechanisms, plays a crucial role in enhancing removal efficiencies and capacities. Further research into composite materials and novel formulations may lead to even more effective solutions for pharmaceutical wastewater treatment.

5. Exploring the impact of TCs on the global environment

The widespread environmental contamination by tetracyclines (TCs) poses a significant global threat. A seven-year investigation (2017–2023), encompassing 16 countries and resulting in 41 detailed reports, has revealed the pervasive presence of various TCs, including doxycycline, chlortetracycline, oxytetracycline, and tetracycline itself, across diverse geographical regions [74]. This extensive research, primarily focused on Europe, South America, Africa, and Asia, underscores the urgent need to address the escalating issue of TC pollution and its far-reaching ecological consequences.

China emerges as a significant focal point, accounting for approximately 49% of all reported occurrences of TCs in the environment. This statistic underscores the pressing issue of TC contamination in the country, which reflects broader antibiotic consumption trends. Notably, around 70% of the world's antibiotic usage occurs in Asia, with China responsible for a substantial portion of this consumption. The environmental impact of TCs is further illustrated by the detection of elevated concentrations across various regions. Reports indicate that maximum concentrations of commonly reported TCs exceed 5 µg/l. For example, DC has been identified as a major environmental pollutant in Argentina and Kenya, reaching 28.43 and 32.2 µg/l, respectively. CTC levels were notably high in China, detected at 10.02 µg/l, primarily from surface water bodies. Additionally, Iran reported significant TC concentrations linked to hospital wastewater discharges [74].

The richness of TC types detected in Spain and China reveals complex pollution sources. In Spain, high levels of TC and oxytetracycline were predominantly traced back to poultry farming, indicating a relatively singular source of contamination. In contrast, China exhibited a more diverse profile with all TC types showing high detection concentrations from varied and non-representative origins. This diversity highlights the need for further investigation into the multifaceted sources of these pollutants, promising potential discoveries that could significantly advance our understanding of TC pollution.

In summary, the global occurrence and impact of TCs present significant environmental challenges that warrant urgent attention. The findings from recent studies call for enhanced monitoring and regulatory measures to mitigate the risks associated with TC contamination in ecosystems worldwide, underscoring the global nature of this issue and the need for a coordinated, international response.

6. Conclusions and outlook

The widespread presence of TC compounds in the environment necessitates continued efforts to develop efficient removal strategies, and this mini-review has highlighted the promising advancements in chitosan-based adsorbents for this purpose. While these adsorbents, particularly those with composite or novel formulations, show considerable potential, several key areas require further exploration and development. Beyond optimizing adsorption conditions and elucidating mechanisms, future research should focus on enhancing the selectivity of chitosan-based adsorbents to target specific TC compounds in complex matrices, exploring the potential of functionalizing chitosan with tailored ligands, investigating the reuse and regeneration potential of these materials through innovative desorption techniques, assessing the stability of these materials under diverse environmental conditions (e.g., variable pH, ionic strength, presence of other pollutants), and developing scalable, cost-effective synthesis and manufacturing processes for large-scale application. Moreover, lifecycle assessments (LCA) should be conducted to ensure these materials' sustainability and environmental friendliness. Addressing the technical, economic, and environmental aspects is essential to translate lab-scale results into large-scale applications. The long-term performance of these materials in real-world scenarios should be evaluated, and studies should assess their impact on ecological systems. Finally, interdisciplinary collaboration, including material scientists, chemical engineers, and environmental experts, will be crucial to accelerate innovation and address challenges of TC pollution through a comprehensive approach combining enhanced monitoring and stricter regulations, as well as public education and awareness campaigns. By thoroughly exploring these aspects, we can unlock the full potential of chitosan-based adsorbents and create a more sustainable approach to mitigating TC pollution and safeguarding ecosystems.

CRediT authorship contribution statement

Alireza Pishevar: Writing – original draft, Investigation.
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Gity Behbudi: Supervision, Project administration.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

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