Adsorption of cefixime and amoxicillin from aqueous media employing MWCNTs and Clinoptilolite

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ABSTRACT

In the present study, the adsorption mechanism was systematically examined for the removal of cefixime and amoxicillin, two antibiotic compounds, utilizing MWCNTs and clinoptilolite as organic and inorganic adsorbents, respectively. Optimal conditions for maximal cefixime adsorption were identified at a pH of 8.7, utilizing an MWCNTs and clinoptilolite concentration of 3.65 and 2.5 mg/L respectively. The peak adsorption percentage for amoxicillin was observed at a pH of 7.5 with an MWCNTs concentration of 3.5 mg/L. Based on the findings, it was determined that MWCNTs effectively adsorbed both cefixime and amoxicillin; conversely, clinoptilolite demonstrated an inability to adsorb amoxicillin while exhibiting significant cefixime adsorption capabilities. In this investigation, MWCNTs and clinoptilolite were employed to facilitate the absorption of the two antibiotics, cefixime and amoxicillin, from aqueous solutions under both batch and continuous operational conditions. The merits of this methodology include the utilization of cost-effective adsorbents, elevated efficiency, and a straightforward procedural approach.

1. Introduction

The study of pollution removal from the environment is essential due to its significant implications for both environmental sustainability and public health [1,2]. Antibiotic residues present in aquatic environments, predominantly originating from veterinary and human pharmaceutical applications, represent a significant environmental concern [1, 2]. The residual quantity of the pharmacological agent retained within the biological systems of humans or animals typically ranges from 30-90% of the administered dosage, with a substantial portion often expelled as an active compound [3,4]. The clinical manifestations associated with multidrug-resistant bacterial infections are particularly noteworthy, as the therapeutic regimens appear to be fraught with complexity, exorbitant costs, and, ultimately, a lack of efficacy [5-9]. Preventive measures are frequently regarded as a pressing medical challenge, given that the

utilization of antibiotics transcends the boundaries of clinical environments. It is estimated that no less than fifty percent of all pesticides are utilized within the domains of agriculture and farming [10]. Consequently, the mitigation of antibiotic deposition within natural ecosystems are of paramount importance and serves as a compelling subject for investigation [11–13]. Amoxicillin and cefixime, which are classified within the penicillin and cephalosporin families, are extensively employed in the treatment of various bacterial diseases [14] caused by pathogens such as Staphylococcus aureus, Streptococcus pneumoniae, Escherichia coli, among others [15, 16]. Due to the widespread application of cefixime in the therapeutic management of diverse diseases in both humans and animals, it occupies a prominent role in environmental pollution and may contribute to the persistence of pathogenic bacteria in ecological settings, even at minimal concentrations [17]. Amoxicillin,

characterized as a broad-spectrum β-lactam antibiotic within the penicillin class, is utilized as a veterinary therapeutic agent for the management of bacterial infections, particularly in the context of gastrointestinal and systemic disorders [18, 19]. Its frequent application in prescription medications (targeting bacterial infections) and as a therapeutic intervention is attributed to its expansive efficacy against a variety of bacterial strains [20]. Furthermore, amoxicillin has been demonstrated to exhibit minimal degradability, remaining in urine and feces in its active form [21, 22]. The capacity for absorption, even at exceedingly low concentrations (below 1 mg/L), is highly advantageous for the removal of contaminants from water or wastewater matrices. To this point, only a limited number of studies have been published that concentrate on the removal of antibiotics from wastewater utilizing alternative sorbents [23-26]. The presence of active antibiotic residues in environmental matrices such as surface water, groundwater, and soil are attributable to the runoff generated from domestic, agricultural, and industrial effluents. Certain antibiotics that are frequently utilized have demonstrated persistence characterized by extended half-lives. Consequently, these substances may exert deleterious effects on water quality and aquatic organisms. The extensive application of antibiotics leads to modifications in microbial ecosystems, imposing selective pressures on susceptible bacterial populations, thereby facilitating the survival of resistant strains and fostering the emergence of antimicrobial resistance, which undermines the efficacy of existing antibiotics against newly emerging infectious diseases. In addition to their long-term implications, antibiotics have the potential to provoke allergic responses in specific individuals and disrupt the indigenous microbial communities upon entering the human body through the food chain and drinking water sources [27-32]. Traditional treatment methods may prove inadequate in sufficiently removing antibiotic concentrations from water and wastewater [33-38]. Therefore, a variety of alternative techniques have been effectively implemented to achieve the significant elimination of these pollutants from aqueous environments, encompassing advanced oxidation processes, electrochemical techniques, membrane filtration, and adsorption technologies.
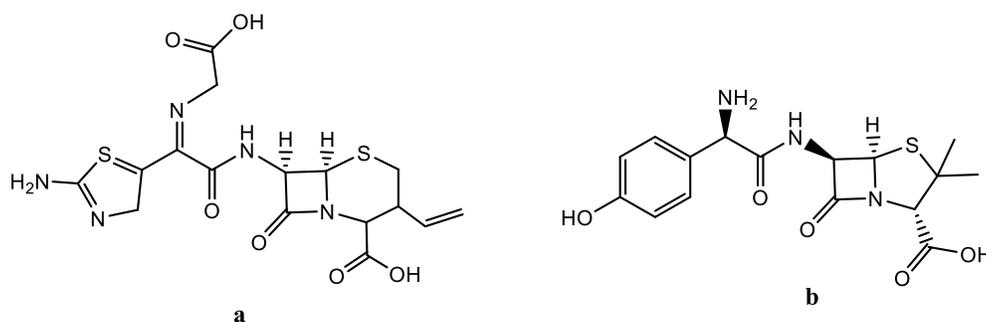

Fig. 1. The structure of a) cefixime and b) amoxicillin

In contemporary discourse, local media characterized by minimal financial investment and substantial support has garnered significant scholarly interest. The adsorption phenomena on MWCNTs represent a viable methodology for the extraction of antibiotics from aqueous matrices, attributable to its elevated adsorption potential, operational simplicity, reduced energy demands, augmented surface area, inherent surface reactivity, minimal water loss, and ecological sustainability [27, 28]. Consequently, investigations have been undertaken to synthesize MWCNTs utilizing cost-effective and renewable substrates, including bark and root systems of various plants [29-30]. Among the conventional adsorbent materials, clinoptilolites emerge as superior micro- and nanoporous substances, possessing critical relevance in the realms of separation processes and ion exchange applications [31-38]. Furthermore, an additional line of inquiry involves the examination of clinoptilolite and MWCNTs derived from coconut peel as a cost-efficient and economically viable novel adsorbent for the removal of the aromatic heterocyclic antibiotics cefixime and amoxicillin (Figure 1). The main aim of this study was to use MWCNT to remove amoxicillin and cefixim using a batch process.

2. Results and discussion

The occurrence of antibiotic pharmaceuticals within the aquatic environment represents a significant and emergent area of inquiry, attributed to the discharges from pharmaceutical manufacturing facilities and the administration of veterinary and human medications. In the present investigation, MWCNTs and clinoptilolite

were employed as adsorbents to extract two specific antibiotics, cefixime and amoxicillin, from aqueous solutions utilizing both batch and continuous processing methodologies.

2.1. Batch adsorption study

Initially, extensive investigations similar to community studies were conducted to ascertain optimal performance across varying pH levels, diverse drug concentrations, different durations of contact, and requisite volumes of adsorbent, as well as to determine the equilibration period and the most appropriate type of isotherm. An adsorption isotherm elucidates the correlation between the quantity of adsorbate present on an adsorbent and the concentration of the adsorbate at equilibrium. The examination of equilibrium concerning antibiotic adsorption provides substantial insights into the adsorption capacities of

MWCNTs and clinoptilolite, which serve as two distinct adsorbents. The characteristics of the adsorbents' surfaces and their dependencies are represented by an adsorption isotherm defined by specific constant quantities.

Furthermore, it enables a comparative analysis of the adsorption capacities of MWCNTs and clinoptilolite as adsorbents for various antibiotics. Adsorption isotherms are employed to characterize the distribution of adsorbate species between the liquid and solid phases under equilibrium conditions. In the present research manuscript, both Langmuir and Freundlich isotherms were utilized to scrutinize the conditions of adsorption reactions. The experimental findings indicated that the adsorption of cefixime and amoxicillin onto MWCNTs aligns with the Freundlich and Langmuir isotherm models. Based on the results obtained, MWCNTs exhibited the capability to adsorb both cefixime and amoxicillin (Figure 2).
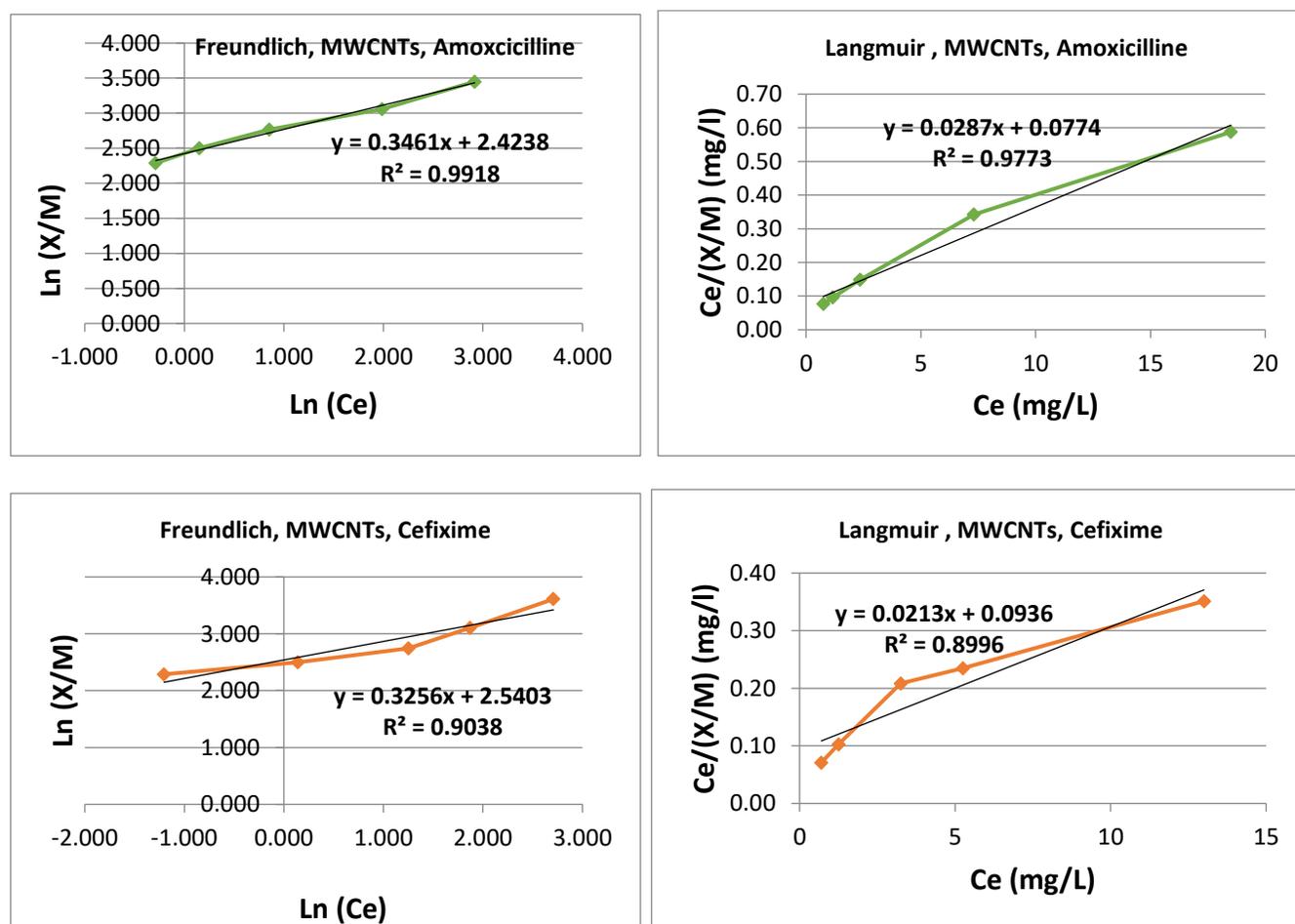

Fig. 2. The Freundlich and Langmuir isotherms of Cefixime and Amoxicillin onto MWCNTs.

Also, the experimental findings indicated that the adsorption of cefixime and amoxicillin onto clinoptilolite line up with the Freundlich and Langmuir isotherm models. Based on the results obtained, clinoptilolite failed to adsorb amoxicillin but successfully adsorb a significant
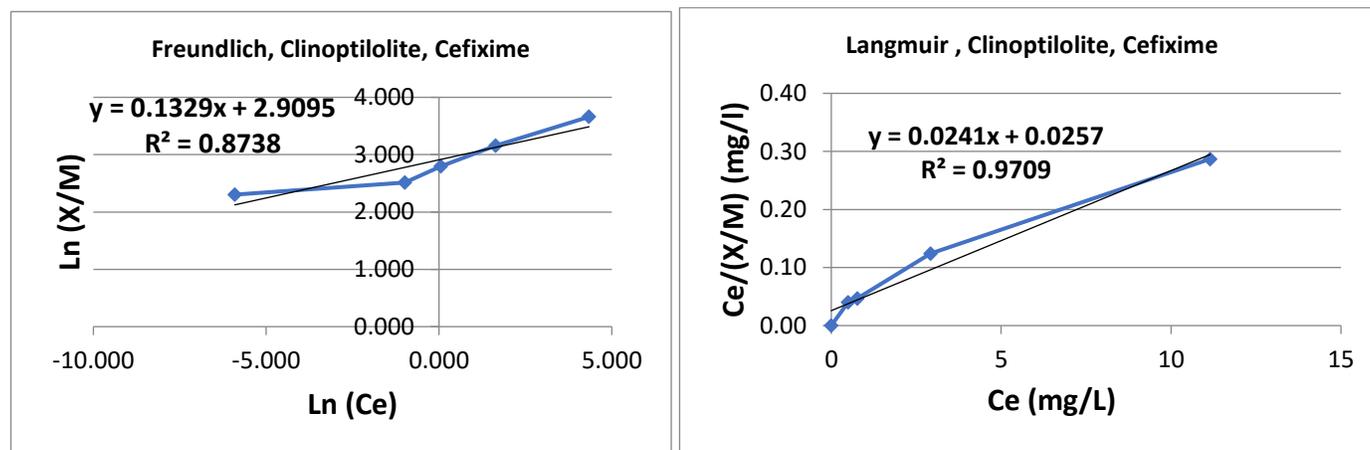

Fig. 3. The Freundlich and Langmuir isotherms of Cefixime onto Clinoptilolite

proportion of cefixime during the batch process (Figure 3).

The nonlinear representations of the Freundlich and Langmuir models were employed to appropriately fit the experimental data pertaining to the equilibrium adsorption of CFX onto MWCNTs and clinoptilolite. The Freundlich isotherm represents an empirical framework that elucidates the phenomenon of adsorption occurring as multilayer formations on heterogeneous surfaces. Conversely, the Langmuir isotherm quantitatively characterizes the development of a monolayer of adsorbate on the external surface of the adsorbent

material. The results pertaining to the adsorption isotherm of MWCNTs-CFX are illustrated in Figure 2. Analyzing Figure 2 reveals that the correlation coefficient (R^2) for the Freundlich isotherm of the MWCNTs-CFX adsorption ($R^2 = 0.9038$) surpasses that of the Langmuir isotherm ($R^2 = 0.8996$); similarly, in the case of the MWCNTs-Amoxicillin adsorption isotherm, the Freundlich isotherm ($R^2 = 0.9918$) also exceeds the Langmuir isotherm ($R^2 = 0.9773$). Furthermore, in the clinoptilolite-CFX adsorption isotherm analysis, the Freundlich isotherm ($R^2 = 0.8738$) is found to be inferior to the Langmuir isotherm ($R^2 = 0.9709$) (Figure 3).

Table 1. Optimization conditions for the cefixime and amoxicillin adsorption on MWCNTs and Clinoptilolite in batch process

Entry	pH	Time (min)	Drug (mg/L)	Adsorbent (mg/L)	Adsorption percentage (%)
1	7.5	15	Amoxicillin (30)	MWCNTs (3.5)	95%
2	8.7	15	Cefixime (30)	MWCNTs (3.6)	97.6%
3	8.5	20	Cefixime (30)	Clinoptilolite (2.5)	96.8%

Typically, the mechanism of adsorption in the liquid phase presents a greater degree of complexity when compared to adsorption occurring in the gas phase. In the liquid phase, numerous factors influence the adsorption process, including temperature, the structural similarity of the adsorbate to the solvent, the pH of the solution, and the concentration of the adsorbent, among others. Within the context of amoxicillin and cefixime adsorption, the pH of the solution emerges as the most critical determinant in the adsorption process, as it has the potential to alter the charge of the amoxicillin molecule. As demonstrated in

Table 1, during the batch process, an increase in adsorption time correlates with a rise in the percentage of amoxicillin adsorbed onto multi-walled carbon nanotubes (MWCNTs); however, an increase in the quantity of amoxicillin, while maintaining a constant amount of adsorbent, results in a decline in the percentage of adsorption. Furthermore, a simultaneous increase in the quantities of both amoxicillin and MWCNTs leads to an enhancement in the percentage of adsorption. Additionally, an elevation in the pH further contributes to an increase in the percentage of adsorption. The elevated

percentage of amoxicillin adsorption was observed at a pH of 7.5, with the concentration of amoxicillin being 30 mg/L, the concentration of multi-walled carbon nanotubes (MWCNTs) at 3.5 mg/L, and the duration of adsorption equating to 15 minutes (refer to Table 1, entry 1). It is pertinent to note, as illustrated in the findings presented in Table 1, that the adsorption of amoxicillin did not occur on clinoptilolite when employed as the adsorbent material. As evidenced in Table 1, the optimal conditions for the maximization of cefixime adsorption were established at a pH of 8.7, with cefixime concentration maintained at 30 mg/L, the concentration of MWCNTs at 3.5 mg/L, and an adsorption duration of 15 minutes (refer to Table 1, entry 2). The pronounced adsorption of cefixime utilizing clinoptilolite occurred at a pH of 8.5, with the cefixime concentration at 30 mg/L, the concentration of

clinoptilolite at 2.5 mg/L, and the adsorption time recorded at 20 minutes (refer to Table 1, entry 3).

2.1.1. Effect of pH

The solution pH of cefixime and amoxicillin in bath system is a significant parameter which able to affect the adsorption of CFX on the MWCNTs due to the pH can change adsorption pathways. So, the elimination of cefixime and amoxicillin *via* bath tests carried out in range of 2–9 with the initial CFX concentration fixed at 30.0 mg L^{-1} and 3.6 and 3.5 mg of MWCNTs respectively. As can be seen in Figure 4, of cefixime and amoxicillin adsorption efficiency increases from 76.2% to 97.6 and 95% respectively as the solution pH increase from 2.0 to 9.0 and a maximum adsorption for cefixime and amoxicillin was obtained at pH 8.7 and 7.5 respectively.
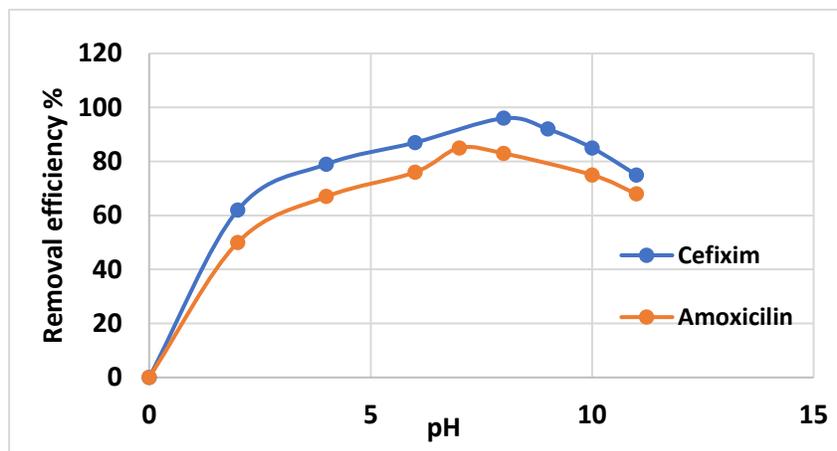

Fig. 4. Effect of pH on the adsorption of CFX and amoxicillin by MWCNTs (C_0 = 30 mg L^{-1}, adsorbent dose = 3.6 and 3.5 mg respectively).

2.1.2. Effect the amount of MWCNTs

The amount of MWCNTs nanocomposite is one of the most significant factors that determines the capacity of the MWCNTs nanocomposite for an initial concentration of the cefixime and amoxicillin. Different doses of MWCNTs nanocomposite (varying from 2 to 5 mg) were utilized with initial concentration of 30 mg L^{-1} CFX and amoxicillin obtained optimum amount of MWCNTs while keeping other empirical parameters fixed (Figure 5). The elimination of cefixime and amoxicillin using MWCNTs increased from 76.5% to 98.2 and 97% with an increase in MWCNTs from 2 to 5 mg.

2.2. Kinetic of cefixime and amoxicillin adsorption on the MWCNTs

The impact of contact duration on the removal efficacy of CFX by MWCNTs in a bath system was examined over a

temporal range of 0 to 50 minutes at a pH of 8.7 and a MWCNTs dosage of 3.6 mg, across varying concentrations of CFX (10, 20, 30, and 40 mg L^{-1}). The findings demonstrated that the rate of CFX removal was markedly rapid during the initial phase, achieving equilibrium within a brief period (15 minutes). This phenomenon can be attributed to two primary factors: (1) the accessibility of adsorption sites on the surface of MWCNTs and (2) the sheet-like configuration of MWCNTs, which facilitates the adsorption of CFX onto the MWCNTs. In the present investigation, the pseudo-first-order (PFO) and pseudo-second-order (PSO) models were employed to analyze the adsorption dynamics of CFX molecules onto the MWCNTs. The linear representations of the PFO and PSO models are delineated as Equations 1 and 2, respectively:

$$log\ (q_e - q_t) = log\ (q_e) - \frac{k_1 t}{2.303} \qquad (1)$$

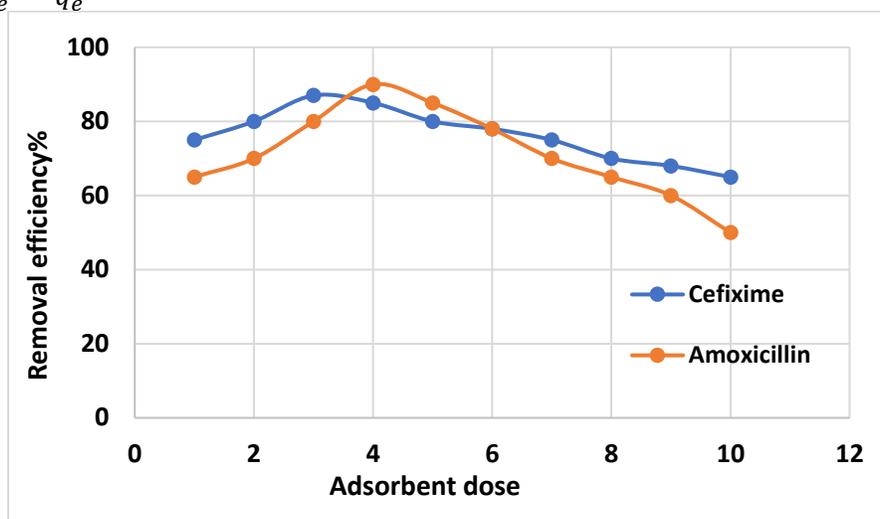$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

Fig. 5. Effect of adsorbent dose on the adsorption of CFX and amoxicillin ($C_0 = 30$ mg L^{-1}, pH = 8.7 and 7.5 respectively).

The parameters qe and qt (mgg^{-1}) signify the adsorption capacity of Multi-Walled Carbon Nanotubes (MWCNTs) for CFX at equilibrium and at any given time t (min), respectively, while k1 (min^{-1}) and k_2 (mgg^{-1} min^{-1}) represent the fixed rates of the Pseudo-First-Order (PFO) and Pseudo-Second-Order (PSO) models,

correspondingly. Figure 6 illustrates the diverse linearized plots pertaining to PFO and PSO for CFX adsorption onto the MWCNTs, with the parameters for each respective model delineated in Table 2. It can be inferred that the PSO model is well-suited to elucidate the kinetic empirical data.

Table 2. The kinetic parameters for the adsorption of cefixime on MWCNTs

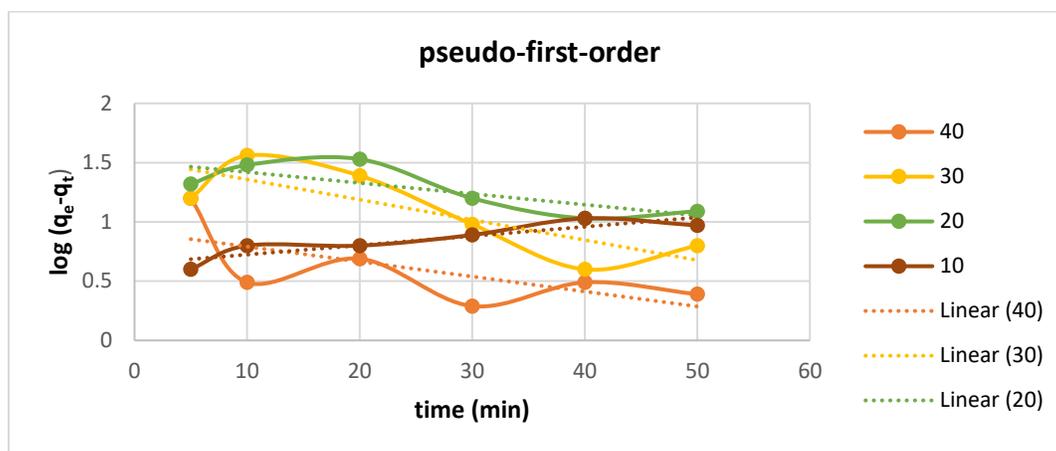| C_o, mg/L	q_{exp}, mg/g	Pseudo-first order			Pseudo-second order		
		K_1, min^{-1}	q_e, mg/g	R^2	K_2, g/mg.min	q_e, mg/g	R^2
10	68.92	0.0542	34.67	0.9558	3.02×10^{-3}	72.86	0.9956
20	76.98	0.0652	42.86	0.8759	2.98×10^{-3}	81.87	0.9913
30	74.89	0.0738	28.75	0.9187	2.68×10^{-3}	78.89	0.9962
40	92.84	0.0492	26.62	0.9497	3.14×10^{-3}	94.69	0.9976
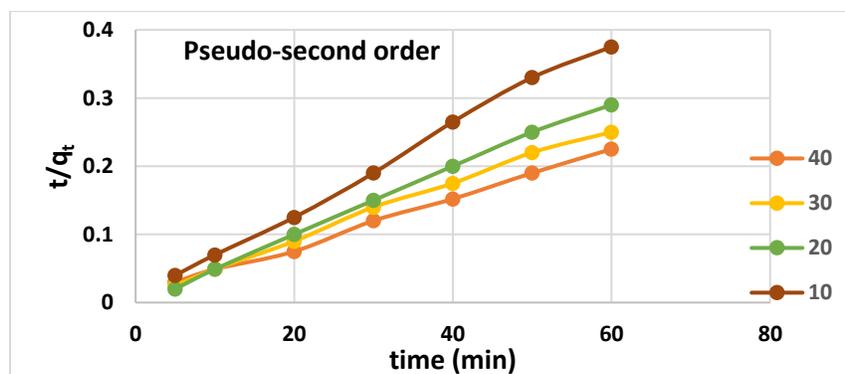
Fig. 6. Adsorption kinetics for the adsorption of CFX onto MWCNTs at primary concentrations of 10.0, 20.0, 30.0, and 40.0 mg L^{-1} (pH = 8.7, adsorbent dose = 3.6 mg).

3. Experimental

3.1. Materials and methods

General

All materials utilized in this investigation were produced from Fluka and Merck, without undergoing any additional purification processes. The antibiotics employed in this study, namely cefixime and amoxicillin, were sourced from an antibiotic production facility situated in Sari, Mazandaran, Iran. This antibiotic production facility is located in the city of Sari, Iran. All solutions were formulated using distilled water as the solvent.

3.2. Adsorption of cefixime and amoxicillin

CFX and amoxicillin adsorption tests with 2-5 mg of MWCNTs and clinoptilolite were accomplished in 25 mL stoppered conical flask containing 10 mL of various concentrations of CFX and amoxicillin solution (10 to 40 mg L^{-1}). The pH of the CFX solution altered to 2.0–9.0 (HCl and NaOH).

4. Conclusion

In this research, the adsorption process of amoxiciline and cefexime as two antibiotics was investigated by batch process in different pH, different amounts of amoxiciline and cefexime and different amounts of MWCNTs and clinoptilolite. The best conditions for high adsorption of cefixime was happened at pH=8.7, 30 mg/L of cefixime and 3.6 mg/L of MWCNTs after 15 min. Also, the high adsorption of cefixim by clinoptilolite was happened at pH=8.5, 30 mg/L of cefixime and 2.5 mg/L of clinoptilolite after 20 min. The high adsorption percentage of amoxicillin was happened at pH=7.5 mg/L of

amoxicilline and 3.5 mg/L MWCNTs after 15 min. It should be mentioned the adsorption of amoxicillin wasn't performed by the clinoptilolite as adsorbent. The advantages of this procedure are cheap adsorbent, high efficiency and simple procedure.

Acknowledgements

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