Fabrication of Easy Separable and Reusable Adsorbent Composite based on MIL-125/MIL-53 Binary MOF/CNT/Alginate Microbeads for Removal of Tetracycline from Water Bodies

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Fabrication of easy separable and reusable adsorbent composite based on MIL-125/MIL-53 binary MOF/CNT/Alginate microbeads for adsorptive removal of tetracycline from water bodies

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Abstract

During the turbulent period of COVID-19, the medical staff is exerting great efforts to preserve humanity. However, the tons of pharmaceutical residues especially antibiotics that is being disposing daily into water bodies may be the seed to an even more ferocious pandemic. Thence, it is inevitable to find out effective strategies for removing these noxious pharmaceutical residues from water. We aimed in this investigation to fabricate easy separable composite microbeads for efficient adsorption of tetracycline (TC) drug. Herein, MIL-125/MIL-53 binary metal organic framework (MOF) was synthesized and incorporated with carbon nanotube (CNT) into alginate (Alg) microbeads to form MIL-125/MIL-53/CNT@Alg composite microbeads. Various tools including FTIR, XRD, SEM, BET, Zeta potential and XPS were applied to characterize the composite microbeads. The results revealed that the adsorption of TC was augmented with rising TC proportion up to 15 wt% in the

microbeads matrix. In addition, the adsorption process followed the pseudo-second-order and well-fitted to Freundlich and Langmuir models with a maximum adsorption capacity of 294.12 mg/g at 25 °C, while the adsorption process was endothermic, randomness and spontaneous. Besides, reusability test signified that MIL-125/MIL-53/CNT@Alg composite microbeads retained admirable adsorption properties for six consecutive cycles, emphasizing its potentiality for removing of pharmaceutical residues.

Keywords: Binary MOF; Alginate; Carbon nanotube; Tetracycline; Adsorption; Reusability.

1. Introduction

Presently, the scarcity of drinking water is the major problem that is sweeping the world, menacing humanity with annihilation¹. During the cruel circumstances of COVID-19, one source of water pollution has reached its peak which is pharmaceutical contaminants. In this regard, antibiotics such as tetracyclines (TCs) have been recommended in new research that they may be able to treat COVID-19 infection through their anti-inflammatory and anti-apoptotic activities²⁻⁴. However, humans could not completely metabolize TCs and around 50-80% of the applied dosage is secreted via urine⁵. Thence, numerous developing techniques have been used for TCs removal from wastewater including; adsorption⁶, ultrasonic irradiation⁷, photocatalytic degradation⁸, membrane process⁹, and fenton oxidation¹⁰. Among the mentioned techniques; adsorption has been considered as the most favorable technique for the removal of TCs from wastewater owing to it is simple, economic, low-energy consumption, etc.^{11,12}.

Metal organic frameworks (MOFs) is a new brilliant class of crystalline materials that has increasingly drawn a vast consideration owing to its versatile applications^{13,14}. Notably, owing to the unique characteristics of MOFs such as water stability, ultrahigh porosity, easy functionalization, thermal stability and high surface area, MOFs have successfully been utilized for the adsorptive removal of heavy metals¹⁵, pharmaceutical contaminants¹⁶ and synthetic dyes¹⁷. One of iron-based MOFs that has been exhibiting notable adsorptive behavior is MIL-53 owing to its structure flexibility, stability in water and chemical stability¹⁸. Furthermore, MIL-125 is one more bright member in MIL-family that possesses promising photo-catalytic and adsorptive behavior due to its photo-reactivity, thermal and chemical stability, etc.¹⁹. Although, the individual features of MOFs, there is a huge obstacle to apply them in practical applications which is the difficulty of their recycling as well as their difficult separation from the adsorption mediums. Fabrication of the shaping MOFs like membrane, fiber and beads is considered an effective solution to get rid of MOFs drawback^{20,21}. Sodium alginate (Alg); is a water-soluble anionic polysaccharide that is smoothly extracted from brown seaweed²². Alginate has acquired huge fame owing to its unique merits such as biodegradability, nontoxicity, strong gelation, biocompatibility, high chemical stability, chelating ability and possession of abundant function groups onto its surface (i.e. hydroxyl and carboxyl)²³⁻²⁶. Therefore, Alg has been considered a premium-supporting host of chemical and biological compounds in several potential applications including pharmaceutical, biomedical and especially in wastewater treatment owing to its ability to capture the cationic ions from the target contaminants whether heavy metals or dyes via ion-exchange mechanism^{22,27,28}.

The remarkable features of carbon nanotubes (CNTs) including high mechanical strength, high surface area, low cost and its ability to form strong bonds with other

molecules or atoms, make them promising candidates for the adsorptive removal of diverse pollutants from wastewater ²⁹. Moreover, multi-walled CNTs are higher accessible and lower cost than single-walled CNTs which render multi-walled CNTs more favorable for the potential applications than single-walled CNTs ³⁰.

Herein, we aimed to fabricate a novel binary MOF/ CNT composite embedded into Alg microbeads to facilitate the separation of MIL-125/MIL-53 binary MOF after the adsorption process as well as ameliorate its efficiency and reusability. The fabricated MIL-125/MIL-53/CNT@Alg composite microbeads were characterized by bountiful tools as well as their adsorption aptitude towards TC was assessed utilizing a batch adsorption technique. The kinetics, isotherms and thermodynamics were adequately studied. Furthermore, to prove the economic viability of the fabricated MIL-125/MIL-53/CNT@Alg composite microbeads, recyclability test was investigated.

2. Experimental part

2.1. Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and carbon nanotubes (multi-walled type) were purchased from Alpha Chemika (India). Titanium isopropoxide (TBOT), sodium alginate (medium viscosity) and N,N dimethyl formamide (DMF) were obtained from Shanghai Chemical Reagent (China). Tetracycline and 1,4-benzene dicarboxylic acid (BDC) were bought from Loba Chemie Ltd (India). Ethanol, ammonium solution (NH_4OH) and dimethyl sulfoxide (DMSO) were provided by Ninghai Jiahe (China).

2.2. Synthesis of MIL-125/MIL-53 binary MOF

MIL-125/MIL-53 binary MOF was fabricated as follows; exactly, 0.679 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.415 g BDC were dissolved in 50 mL DMF and then the reaction

mixture was kept under continuous stirring at 60 °C for 2 h. In another container, 1.990 g BDC was dissolved in 50 mL DMF and then 2.7 mL TBOT was added drop by drop under vigorous stirring followed by stirring at 60 °C for 2 h. Next, the two solutions were mixed, then transferred to 500 mL autoclave and heated at 140 °C for 20 h. finally, the obtained powder was collected by centrifugation, washed and dried at 100 °C for 24 h.

2.3. Fabrication of MIL-125/MIL-53/CNT@Alg composite microbeads

MIL-125/MIL-53/CNT@Alg composite beads were fabricated as follows; Alg was dissolved into 50 mL (5 % wt/v) dist. H₂O under robust mechanical stirring until a clear jelly solution was formed. In another beaker, 5 g MIL-125/MIL-53 binary MOF and CNT (5, 10, 15 and 20 wt%) were soaked into 50 mL dist.H₂O and sonicated for 2 h. Then after, the homogenous solution of MIL-125/MIL-53 binary MOF/CNT was added to Alg solution dropwise and stirred for 1 h. MIL-125/MIL-53 binary MOF/CNT/Alg solution was added by syringe into a pre-prepared gelling agent of CaCl₂ (2% wt/v) and kept the obtained microbeads under slow stirring for 1 h. Finally, MIL-125/MIL-53/CNT@Alg composite microbeads were collected, washed several times with distilled water and dried at room temperature.

Figure 1 represents a schematic representation for the fabrication of MIL-125/MIL-53/CNT@Alg composite beads

Figure 1. Schematic representation for the fabrication of MIL-125/MIL-53/CNT@Alg composite microbeads and their adsorption process for TC removal.

2.4. Characterization

MIL-125/MIL-53/CNT@Alg composite microbeads were thoroughly characterized by; Fourier Transform Infrared spectra (FTIR- Tensor II, Bruker) to investigate the chemical composition of the synthesized microbeads. Furthermore, X-ray diffractometer (XRD- MAC Science M03XHF) was used to distinguish the crystal phase. The morphology was defined by a Scanning Electron Microscope (SEM- Hitachi-S4800), while the thermal stability of the developed composite microbeads

was identified by Thermogravimetric Analysis (TGA- Shimadzu-50). Besides, X-ray photoelectron spectroscopy (XPS- Thermo scientific-ESCALAB-250Xi VG) was employed to clarify the elemental compositions of the adsorbent. The specific surface area of composite microbeads was measured by Bruner-Emmett-Teller method (BET- Beckman coulter SA3100), while their surface charges were determined by Zeta potential (ZP- Malvern-UK).

2.5. Batch experiment

The key parameters that affect the efficiency of the TC adsorption onto MIL-125/MIL-53/CNT@Alg composite microbeads were studied precisely using batch mode. During the whole adsorption experiments TC solution was wrapped with aluminum foil to prevent photodegradation of TC. For specifying the optimum pH, 20 mg of dry adsorbent microbeads were soaked into 25 mL TC solution at pH range from 2 to 10 and stirred for 60 min under agitation rate 150 rpm. While, for investigating the effect of adsorbent dose, various doses of MIL-125/MIL-53/CNT@Alg composite microbeads at range from 10 to 80 mg were added to TC solution at the identified optimum pH. Furthermore, the TC adsorption isotherm was studied at an initial concentration range from 50 to 300 mg/L. Besides, the thermodynamic study was executed at a temperature range from 25 to 55 °C. At a set time, the un-adsorbed TC concentration was evaluated by withdrawing a sample and measured using spectrophotometry at 354 nm. The removal (%) and adsorption capacity (q) were computed by the following equations;

$$R \% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_t) \times V}{w} \quad (2)$$

Where, C_0 and C_t symbolize the TC initial concentration and its concentration at certain time, respectively. While, V and w symbolize the TC solution volume and the weight of MIL-125/MIL-53/CNT@Alg composite microbeads, respectively.

2.6. Reusability study

Undoubtedly, regeneration behavior is one of the main criteria for choosing an adsorbent. Consequently, the reusability study was implemented for five successive cycles as follows; after each adsorption process, MIL-125/MIL-53/CNT@Alg composite microbeads were collected and soaked in (50 mL, 0.01 M) NaOH under constant stirring. After 1 h, MIL-125/MIL-53/CNT@Alg composite microbeads were collected and examined in the next cycle.

3. Results and Discussion

3.1. Characterization of MIL-125/MIL-53/CNT@Alg composite beads

3.1.1. XRD

Figure 2 depicts XRD patterns of MIL-125/MIL-53 binary MOF, CNT and MIL-125/MIL-53/CNT@Alg composite microbeads. **Figure 2A** implies the successful fabrication of MIL-125/MIL-53 binary MOF at which the prime peaks of both MIL-125 and MIL-53 obviously appeared^{18,31}. Moreover, XRD pattern of CNT (**Figure 2B**) illustrates the distinguishing peaks of CNT at $2\theta = 25.81^\circ$ and 43.28° which correspond to 100 and 101 planes, respectively³². Besides, XRD pattern of MIL-125/MIL-53/CNT@Alg (**Figure 2C**) infers the successful combination of MIL-125/MIL-53, CNT and Alg since the distinctive peaks of the components emerged with decreasing in the crystallinity of the peaks which might be due to the amorphous phase of Alg.

Figure 2. XRD patterns of (A) MIL-125/MIL-53 binary MOF, (B) CNT and (C) MIL-125/MIL-53/CNT@Alg composite microbeads

3.1.2. FTIR

In order to thoroughly investigate the functional groups of the fabricated MIL-125/MIL-53/CNT@Alg composite microbeads and the pristine components, FTIR analysis was executed and the results are presented in **Figure 3**. FTIR spectrum of MIL-125/MIL-53 binary MOF (**Figure 3A**) depicts the main distinctive peaks of both MIL-125 and MIL-53. The bands at around 650 and 735 cm^{-1} could be attributed to Fe-O and Ti-O bending vibrations^{33,34}. Whereas, the bands at 1101 and 1291 cm^{-1} are assigned to C-H and C-O, respectively³⁵. Besides, the two bands at 1385 and 1581 cm^{-1} are ascribed to the vibration of the carboxyl group of BDC that coordinates to the metal centers (i.e. Ti and Fe)³¹. **Figure 3B** depicts the distinguishing bands of CNT at 1650, 2330 and 2675 cm^{-1} which are attributed to C=C, the formed H-bond and C-H^{36,37}. In the Alg spectrum (**Figure 3C**), the band at 799 cm^{-1} is related to C-H vibration of pyranose, while the band at around 2916 cm^{-1} is ascribed to C-H stretching vibration. Besides, the band at 1019 cm^{-1} is ascribed to C-O stretching and

the band around 3250 cm^{-1} belongs to OH stretching vibration ^{38,39}. In addition, the belonging peaks to asymmetric and symmetric COO^- group emerged at 1401 and 1592 cm^{-1} , respectively. Besides, the observed band at 2330 cm^{-1} is assigned to CO_2 group ⁴⁰. **Figure 3D** clarifies the main characteristic bands of the pristine components, suggesting the successful combination between them.

Figure 3. FTIR spectra of (A) MIL-125/MIL-53 binary MOF, (B) CNT, (C) alginate and (D) MIL-125/MIL-53/CNT@Alg composite microbeads

3.1.3. SEM

Figure 4A points out aggregated quasi-spherical particles of MIL-125/MIL-53/CNT@Alg. Whereas, **Figure 4B** depicts the typical cylindrical shape of CNT in nano size. Furthermore, SEM image of pristine Alg microbeads (**Figure 4C**) reveals that the beads have an elongated shape. In addition, the closer image of the surface of Alg microbeads (**Figure 4D**) clarifies a rugged surface with large crevices, reflecting the low mechanical strength that causes the collapse of Alg layers during dehydration.

On the other hand, **(Figure 4E)** shows a perfectly spherical shape of the fabricated MIL-125/MIL-53/CNT@Alg composite microbeads. Furthermore, the surface of the microbeads **(Figure 4F)** has no fissures, assorting an ameliorated mechanical strength of MIL-125/MIL-53/CNT@Alg composite microbeads compared to pristine Alg microbeads.

Figure 4. SEM images of (A) MIL-125/MIL-53 binary MOF, (B) CNT (C, D) alginate microbeads and (E, F) MIL-125/MIL-53/CNT@Alg composite microbeads.

3.1.4. XPS

XPS was utilized for an in-depth inspection of the elemental composition of MIL-125/MIL-53/CNT@Alg composite microbeads and assuring from the successful

combination of the fabricated matrix. It is apparent from the XPS survey (**Figure 5A**) that MIL-125/MIL-53/CNT@Alg consists of four main elements; C1s, O1s, Fe2p and Ti2p. The C1s-spectrum (**Figure 5B**) points out peaks at 284.54, 285.54 and 289.14 eV which are ascribed to the carbon-containing groups in MIL-125/MIL-53/CNT@Alg C-C, C-O and O=C-O/O=C, respectively ^{41,42}. Moreover, the O1s-spectrum (**Figure 5C**) obviously clarifies the belonging peak to M-O (i.e. M; Ti or Fe) at BE of 532.14 eV, proving the formation of both MIL-125 and MIL-53. Besides, the appearance of peaks at 530.14 and 533.54 eV are related to C-O and O=C-O, respectively ^{43,44}. In addition, Fe2p-spectrum (**Figure 5D**) infers the existence of Fe²⁺ and Fe³⁺ at which the related peaks to Fe²⁺ revealed at 710.66 and 756.33 eV. While pertinent peaks to Fe³⁺ at 712.88 and 729.33 eV ⁴⁵. Besides, the Ti2p-spectrum (**Figure 5E**) shows the relevant peaks of Ti⁴⁺ (titanium dioxide) at BE of 458.74 and 464.67 eV, as well as the distinctive peaks to Ti³⁺ (titanium suboxide) at BE of 450.68 eV ⁴⁶.

Figure 5. XPS spectra (A) wide scan, (B) C1s, (C) O1s, (D) Fe2p, and (E) Ti2p of MIL-125/MIL-53/CNT@Alg composite microbeads.

3.1.5. BET

N₂ adsorption/desorption isotherm of MIL-125/MIL-53/CNT@Alg is presented in **Figure 6** along with pore size distribution (inset). The MIL-125/MIL-53/CNT@Alg

composite showed type IV isotherm with H_4 hysteresis loop demonstrating a mesoporous structure of MIL-125/MIL-53/CNT@Alg microbeads composite. The S_{BET} surface area of MIL-125/MIL-53/CNT@Alg microbeads was found to be 273.77 m^2/g with pore volume of 0.0131 cm^3/g .

Figure 6. N_2 adsorption/desorption isotherm and pore size distribution (inset) of MIL-125/MIL-53/CNT@Alg composite microbeads

3.2. Effect of the adsorption condition.

3.2.1 Effect of CNT proportion

Figure 7A demonstrates the effect of CNT proportion on the adsorption capacity and the removal efficiency of TC onto MIL-125/MIL-53/CNT@Alg composite microbeads. It is apparent that the presence of CNT in the fabricated microbeads has vast leverage since it boosts the adsorptive performance of MIL-125/MIL-53 binary MOF@Alg composite microbeads towards TC. Furthermore, it was found that the

increase in CNT proportion from 5 to 15 wt% increases the removal (%) from 44.20 to 65.10 % and the adsorption capacity from 29.76 to 42.02 mg/g. While the excessive CNT proportion over 15 wt% causes a slight decrease in the removal (%) from 65.10 to 61.29 % and the adsorption capacity from 42.02 to 39.76 mg/g which may be due to the pore blocking effect, resulting from the excessive CNT proportion in the microbeads matrix ³⁴.

3.2.2. Effect of pH

The pH influence on the adsorption behavior of MIL-125/MIL-53/CNT@Alg composite microbeads towards TC was scrutinized at a pH range from 2 to 10. In fact, TC molecule exists in multi forms, depending on the solution pH at which TC is cationic (TCH_3^+) at $\text{pH} < 3.3$, zwitterionic (TCH_2^0) at $3.3 < \text{pH} < 7.7$ and anionic (TCH^- or TC^{2-}) at $\text{pH} > 7.7$ ¹². **Figure 7B** elucidates an evolution in the adsorption capacity and the removal (%) from 37.69 mg/g and 56.25 % to 42.68 mg/g and 64.70 %, respectively, with the rising in pH from 2 to 6. Nevertheless, at this pH range, the positive charges on the TC molecule diminish and the negative charges on the surface of the composite microbeads increase from -12.5 to -23.3 mV based on the ZP result (**Figure 7C**), inferring that the adsorption of TC onto MIL-125/MIL-53/CNT@Alg composite microbeads is not dominated by electrostatic interaction. Also, this result is confirmed by the slight diminution in the adsorption capacity and the removal (%) beyond pH 6 from 42.68 mg/g and 64.70 % to 39.23 mg/g and 58.63 %, respectively. However, the electrostatic repulsion between TC and MIL-125/MIL-53/CNT@Alg composite microbeads at which TC molecules dwell at this pH region as anionic and the microbeads surface significantly charged with negative charge reach -30.1 mV at pH 10. Accordingly, it was deduced that the adsorption of TC onto MIL-125/MIL-53/CNT@Alg composite microbeads is not controlled by electrostatic interaction and

there is another predominant interaction such as H-bond, hydrophobic interaction, and π - π interaction. This result is consistent with the previous studies by Zhang, Xiong, Gao, and Alatalo^{5,47-49}

Figure 7. (A) Effect of CNT proportion and (B) Effect of pH, Effect of dosage on the removal efficacy and adsorption capacity of MIL-125/MIL-53/CNT@Alg composite microbeads and (C) zeta potential versus pH for MIL-125/MIL-53/CNT@Alg composite microbeads.

3.2.3. Effect of adsorbent dose

Figure 8A points out the impact of the increase in the dose of MIL-125/MIL-53/CNT@Alg composite microbeads on the removal (%) and adsorption capacity of TC. As expected, the increment in the adsorbent dose from 0.01 to 0.08 g results in an increasing in the removal (%) from 43.08 to 86.33 % and a dropping in the adsorption capacity from 58.02 to 13.62 mg/g. This behavior may be interpreted by the increment in the adsorbent dose leads to an increase in the provided active sites that renders the

removal (%) goes up. Contrariwise, the adsorption capacity dwindles due to the particles aggregation²⁰.

3.2.4. Effect of initial TC concentration

Figure 8B demonstrates an increase in the adsorption capacity from 61.52 to 258.10 mg/g with the increase in the TC initial concentration from 50 to 300 mg/L which most likely due to the increase in the driving force of TC molecules towards MIL-125/MIL-53/CNT@Alg composite microbeads. On the contrary, the increase in the TC initial concentration decreases the removal (%) from 98.19 to 65.08% (**Figure 8C**) which may be due to the insufficient active sites on the surface of the microbeads for adsorbing a high concentration of TC.

Figure 8. (A) Effect of adsorbent dose, (B, C) effect of initial concentration of the removal efficiency and adsorption capacity of TC onto MIL-125/MIL-53/CNT@Alg composite microbeads.

3.3. Isotherm study

For interpreting the nature of interaction between TC and MIL-125/MIL-53/CNT@Alg composite micrbeads, the experimental data were comprehensively analyzed by; Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models (**Figure 9**). The linear form of These models are expressed as follows ^{50,51};

$$\text{Langmuir equation: } \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

$$\text{Freundlich equation: } \log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

$$\text{Temkin equation: } q_e = B \ln A + B \ln C_e \quad (5)$$

$$\text{D-R equation: } \ln q_e = \ln q_s - K_{ad} \varepsilon^2 \quad (6)$$

Where, q_e and q_m the equilibrium adsorption capacity and the monolayer adsorption capacity, respectively. C_e is the residual concentraion of TC at equilibrium and K_L is Langmuir constant. K_F and n are Freundlich constants. $B = \frac{RT}{b}$, b is Temkin constant related to heat of adsorption and A is the equilibrium binding constant. T is the absolute temperature and R is the gas constant (8.314 J/mol.k). $\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$ is the Polanyi potential. K_{ad} is a constant related to mean free energy of adsorption per mole of adsorbate and q_s is the saturation adsorption capacity.

Figure 9. Isotherms plots for the TC adsorption onto MIL-125/MIL-53/CNT@Alg composite microbeads; (A) Langmuir, (B) Freundlich, (C) Temkin and (D) D-R.

According to the R^2 values (**Table 1**), the adsorption of TC onto MIL-125/MIL-53/CNT@Alg composite microbeads fits Freundlich (0.995) and Langmuir (0.993) models, suggesting a monolayer and multilayer adsorption of TC. Furthermore, it was estimated from Langmuir that the maximum adsorption capacity is 294.12 mg/g. Interestingly, n value proves the favorability of the adsorption of TC onto MIL-125/MIL-53/CNT@Alg composite microbeads where $n > 1$, as well as the R_L values that fall in the range between 0-1, is one more proof to confirm the favorability of the studied adsorption process. Besides, the calculated E value that less than 8, confirming that the adsorption of TC onto MIL-125/MIL-binary MOF/CNT@Alg composite microbeads is physisorption.

Table 1. The parameters derived from isotherm models for the adsorption of TC onto MIL-125/MIL-53binary MOF/CNT@Alg composite microbeads

Isotherm model	Parameter	Value
<u>Langmuir</u>	q_m (mg/g)	294.12
	b (L/mg)	0.063
	R^2	0.993
	n	2.265
<u>Freundlich</u>	k_F (L/mg)	42.806
	R^2	0.995
<u>Temkin</u>	A (L/g)	1.015
	B (J/mol)	53.583
	b (KJ/mol)	46.238
	R^2	0.981
<u>D-R</u>	q_s	178.11
	K_{ad} (mol ² /K ² J ²)	1×10^{-6}
	R^2	0.863

3.4. Kinetic study

To deduce the adsorption mechanism of TC onto binary MIL-125/MIL-53 MOF/CNT@Alg composite microbeads, the experimental data were thoroughly modeled by pseudo-first-order, pseudo-second-order and Elovich model (**Figure 10A-C**). Equations 7-10 symbolize the linear forms of these kinetic models ⁵⁰.

$$\text{pseudo-first-order; } \ln(q_e - q_t) = \ln q_e - k_1 (t) \quad (7)$$

$$\text{pseudo-second- order; } t/q_t = 1/k_2 q_e^2 + 1/q_e (t) \quad (8)$$

$$\text{Elovich model; } q_t = \frac{1}{\beta} \ln (\alpha\beta) + \frac{1}{\beta} \ln (t) \quad (9)$$

Where, q_e represents the amount of TC that adsorbs onto MIL-125/MIL-53/CNT@Alg composite microbeads at equilibrium, while q_t expresses the amount of TC adsorption at time t . k_1 is the rate constant of pseudo-first-order and k_2 is the rate constant pseudo-second-order. α and β are Elovich coefficients that represent the initial adsorption rate and the desorption coefficient, respectively, also relate to the extent of surface coverage and activation energy for chemisorption.

To find out the suitable kinetic model that fits the experimental data there are two main criteria; R^2 of the suitable kinetic model should be higher than R^2 of the other applied models as well as the presence of an analogy between q_{exp} and q_{cal} from the suitable model. Accordingly, pseudo-second-order is the most suitable model to represent the adsorption of TC onto MIL-125/MIL-53/CNT@Alg composite microbeads (**Table 2**). It is apparent from the computed Elovich coefficients that α values are greater than β values, indicating that the rate of adsorption is higher than desorption²⁰.

Figure 10. (A) Pseudo-first-order, (B) Pseudo-second-order and (C) Elovich kinetic models for adsorption of TC onto MIL-125/MIL-53/CNT@Alg composite microbeads. (D) Regeneration and reusability of MIL-125/MIL-53/CNT@Alg composite microbeads.

Table 2. Adsorption kinetic model parameters of the adsorption of TC onto MIL-125/MIL-binary MOF/CNT@Alg composite microbeads

Kinetic models and parameters	Concentration (mg/L)				
	50	100	150	200	300
$q_{e, \text{exp}}(\text{mg/g})$	61.52	115.95	162.31	207.65	268.10
<u>Pseudo-first- order</u>					
$q_{e, \text{cal}}(\text{mg/g})$	45.07	48.01	120.83	168.85	199.60
$k_1(\text{min}^{-1})$	0.018	0.017	0.016	0.018	0.015
R^2	0.995	0.981	0.989	0.961	0.958
<u>Pseudo-second-order</u>					
$q_{e, \text{cal}}(\text{mg/g})$	64.94	123.46	172.41	222.22	285.71
$k_2(\text{g.mg}^{-1}.\text{min}^{-1})$	0.007	0.004	0.003	0.002	0.001
R^2	0.996	0.992	0.993	0.988	0.986
<u>Elovich</u>					
$\alpha(\text{mg/g min})$	20.239	32.980	43.730	65.319	80.940
$\beta(\text{g/mg})$	0.101	0.059	0.040	0.031	0.025
R^2	0.941	0.935	0.931	0.894	0.892

3.5. Thermodynamic study

As a matter of fact, the change in the process temperature directly affects the nature and the mechanism of adsorption. For deducing the effect of change the temperature from 298-328 K on the adsorption of TC onto MIL-125/MIL-

MIL-125/CNT@Alg composite microbeads, equations (11-13) were utilized for calculating the thermodynamics parameter; change in free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°). The negative values of ΔG° (**Table 3**) prove the spontaneity of this adsorption process.

$$\ln K_e = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

$$K_e = \frac{C_{Ae}}{C_e} \quad (12)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

Where, K_e is the thermodynamic equilibrium constant. C_{Ae} is the TC concentration onto the surface of MIL-125/MIL-53/CNT@Alg composite microbeads, while C_e is the concentration of TC in solution at equilibrium. T is the adsorption temperature and R is gas constant.

Figure S1 represents Van't Hoff Plot that elucidates ΔS° and ΔH° from the intercept and slope, respectively. The positive value of ΔS° and ΔH° indicates that the adsorption of TC onto the surface of MIL-125/MIL-53/CNT@Alg composite microbeads randomness and endothermic, respectively.

Table 3. Thermodynamic parameters of the adsorption of TC onto MIL-125/MIL-53/CNT@Alg composite microbeads

ΔG° (kJ/mol)				ΔH° (kJ/mol)	ΔS° (J/mol K)
298 K	308 K	318 K	328 K	21.11	76.46
-22.77	-23.53	-24.29	-25.06		

3.6. Regeneration study

To assert the viability of our study, the recyclability of the fabricated MIL-125/MIL-53/CNT@Alg composite microbeads was examined for six consecutive adsorption/desorption cycles. **Figure 10D** depicts an inconsiderable decrease in the removal (%) and the adsorption capacity from 65.10 % and 42.02 mg/g to 53.50 % and 35.22 mg/g, respectively, confirming the good recyclability of MIL-125/MIL-53/CNT@Alg composite microbeads that renders us recommend our novel composite microbeads as a promising candidate for the removal of TC from an aqueous solution.

3.7. Comparison study

To sum, MIL-125/MIL-53/CNT@Alg composite microbeads possess a superb adsorption capacity toward TC compared with other MOFs-, carbon materials- or alginate beads-based adsorbents (**Table 4**). This finding suggests that the fabricated composite beads may be utilized in actual wastewater treatment taking into consideration the advantage of their easy separation and remarkable renewability.

Table 4. Comparison between the adsorption capacity of MIL-125/MIL-53binary MOF/CNT@Alg composite microbeads and other adsorbent towards the adsorption of TC.

Adsorbent	q_e (mg/g)	Reference
CuCo/MIL-101	54.00	52
BM-BC composite	84.54	53
UiO-66-(COOH) ₂ /GO composite	164.91	54
MSABC composite	98.33	55
NiCoFe-MOF-74 composite	102.94	56
Alg-Cu beads	53.26	57

UiO-66-(OH) ₂ / GO composite	37.96	58
MWCNT/MIL-53(Fe) composite	180.68	49
Co-SCGBC composite	370.37	59
ZIF-8	277.80	60
UiO-66	16.70	61
MIL-125/MIL-53binary	294.12	This study
MOF/CNT@Alg beads		

Conclusion

All in all, this study presented the fabrication of MIL-125/MIL-53/CNT@Alg composite microbeads for removing of tetracycline drug residue from aqueous solutions. The formulated adsorbent composite was proved its chemical structure, thermal stability and surface morphology, while batch adsorption experiments were conducted to evaluate its aptitude for adsorption of TC under several optimization conditions. The results clarified that incorporation of CNC into the composite matrix played a significant role in the adsorption process, since the removal (%) of TC was increased with increasing CNC quantity up to 15w%. A sequence of adsorption isotherm models and kinetic studies led us to conclude that the adsorption of TC onto MIL-125/MIL-53/CNT@Alg composite microbeads process was fitted to Freundlich and Langmuir isotherm model with a maximum adsorption capacity of 294.12 mg/g at 25 °C, and followed the pseudo-second-order kinetic model, spontaneous. The results of thermodynamic studies clarified that the adsorption process could be described as spontaneous, endothermic and randomness process. Reusability studies confirmed that the developed adsorbent exhibited a superior recycling capability even after six repeated cycles with good performance for adsorption of TC. Thus, the fabricated adsorbent composite has some operational benefits such as easy separation, decent

adsorption performance and better reusability, suggesting its applicability for removing TC residue from aquatic mediums.

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Author contributions

A.M.O. and A.S.E. proposed the research concept; E.M.A. conducted the experiments; E.M.A. and A.S.E. prepared figures; A.S.E., A.M.O. and E.M.A. analyzed, interpreted the data and wrote the manuscript; A.M.O., A.S.E., G.M.E. and M.M.A. revised the manuscript.

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