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Tailoring Metal-Organic Frameworks for Polyurethane Foams to Improve Tetracycline Removal from Aqueous Solutions

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Abstract

For the effective removal of tetracycline (TC) from aqueous solutions, a novel Grafted Polyurethane Foam (GPUF) functionalized with iron or copper metal-organic frameworks (FeMOF-PUF and CuMOF-PUF, respectively) was created. By adjusting experimental parameters such as adsorbent dosage, initial pH, contact time, initial TC concentration, and temperature, the adsorption performance of both GPUF materials was examined. Based on the Langmuir isotherm model, the FeMOF-PUF showed a higher maximum adsorption capacity of 500.0 mg g-1 than the CuMOF-PUF which is 375.0 mg g^{-1}. This finding suggests that the incorporation of MOF into the PUF matrix not only preserves but also improves the base material's adsorption capacity. The spontaneous and endothermic nature of the adsorption process, as demonstrated by thermodynamic measurements, points to a chemically driven interaction between TC and FeMOF-PUF. The synergistic combination of porosity, Lewis acidity of the iron sites within the MOF structure, and electrostatic interactions with TC molecules is responsible for FeMOF-PUF's excellent adsorption capability. The result shows that GPUFs, especially FeMOF-PUF, have a promising future as effective and useful adsorbents for the removal of pharmaceutical pollutants in water treatment applications.

Keywords: Tetracycline, Adsorption, Metal-Organic Frameworks (MOFs), Polyurethane Foam (PUF), Grafted Polyurethane Foam (GPUF), Wastewater treatment, Antibiotic removal, Environmental remediation.

1. Introduction

The increasing presence of pharmaceutical contaminants, such as antibiotics, in water sources presents a significant environmental and public health challenge[1, 2]. Tetracycline (TC), a widely used antibiotic, poses particular concern due to its persistence and potential for promoting antibiotic resistance[3]. Therefore, developing effective methods for removing TC from wastewater is crucial[1, 4, 5]. Adsorption techniques utilizing porous materials have emerged as promising solutions due to their cost-effectiveness, ease of operation, and high efficiency.

Adsorption is an inexpensive method that offers great potential for water purification with less technical complications[6]. Some adsorbents widely used to remove tetracycline from wastewater include carbon nanotubes, graphene oxide, activated carbon, zeolites, metal oxides, covalent-organic frameworks (COFs)[6-11]. Overall, MOFs have been recognized as some of the most effective adsorbents[12]. These materials constitute a novel type of porous materials, composed of metallic clusters and organic linkers[13]. MOFs also have a large specific surface area with high porosity, ease of structural functionalization, and stability against chemicals and heat[14, 15]. More importantly, pore diameters can be precisely designed to interact with pollutant molecules through various mechanisms such as coordination bonds, π–π interactions, hydrogen bonding, and electrostatic interactions[16]. For MOFs to increase the adsorption capacity of organic pollutants, pore characteristics that match the size of pollutant molecules must be designed, together with optimal adsorption sites[17].

Metal-organic Frameworks (MOFs), crystalline porous materials made from metal ions and organic ligands, have attracted considerable attention for their outstanding adsorption properties[13]. MOFs exhibit high surface areas, tunable pore sizes, and diverse functionalities, making them ideal candidates for targeted pollutant removal[1]. However, the practical application of MOFs in wastewater treatment can be limited by their powder form, which can be difficult to recover and reuse[18].

The tetracyclic naphthacene carboxamide ring system makes up the basic structure of tetracycline (Fig. 1). Several chemical functional groups and substituents, including -OH, -CO-, $-CONH_2$, $-CH_3$, and $-N(CH_3)_2$, encircle the ring structure of tetracycline[7, 19]. A simulated size of 14.8 × 9.00 × 7.47 Å is displayed by the TC molecules, and they cannot enter pores smaller than 15 Å. Mesoporous metal-organic framework MIL-101(Fe)-NH_2 was modified with a polyamine cage with free internal diameters between 29 and 34 Å. After the removal of the guest molecules, they found it showed a larger adsorption capacity.

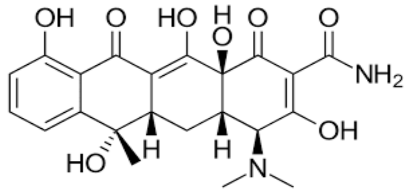

Fig.1 Tetracycline hydrochloride (TC) chemical structure.

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In this study, MOFs/PU foam was constructed by growing MOF nanoparticles on a modified polyurethane foam substrate as an adsorbent for the removal of tetracycline from wastewater.

The novelty lies in the creation of a new adsorbent material by grafting metal-organic frameworks (MOFs) onto polyurethane foam (PUF). This approach combines the benefits of both materials, MOFs are known for their high surface area, tunable pore sizes, and diverse functionalities, making them excellent candidates for targeted pollutant removal, and PUF provides a robust and easily manageable platform for the MOFs, overcoming challenges associated with the powder form of MOFs, such as recovery and reuse.

2. Experimental

2.1. Materials and reagents

Polyurethane (PU) foam was prepared from materials kindly provided by TAKI VITA Company (Abbasiya, Cairo, Egypt) which included polypropylene glycol, toluene diisocyanate, polysiloxane surfactant, and amine. Iron nitrate.9H_2O (SDFCL company, India), Copper (II) nitrate trihydrate (Cu $(NO_3)_2{\cdot}3H_2O$, 99%) and N,N-dimethyl formamide (DMF, 99.9%) were purchased from Sigma–Aldrich Co. Benzene-1,3,5- tricarboxylic acid (H3BTC, 98%) was obtained from Merck, (Darmstadt, Germany). Other chemicals used: $AgNO_3$, Ethanol (95%), HCl , and NaOH were purchased from Sigma Aldrich Co (Germany). Double distilled water was used for the preparation of stock solutions, as reaction media, and during other preparative work. Tetracycline hydrochloride ($C_{22}H_{24}N_2O_8$) (Sumycin, Achromycin V) was obtained from Sigma (India).

2.2 Instrumentation

Unless otherwise indicated, all potentiometric measurements were performed at (25±1◦C) using a Jenway pH/Ion meter Model (3310). For all pH measurements, a double junction Ag/AgCl reference electrode with three mol L−1 potassium chloride in the outer and inner tubes was utilized, along with a combination glass pH electrode Model Jenco (6173). BIBBY Stuart Scientific conducted the melting point measurements (SMP3). A JASCO double-beam spectrophotometer Model (V-630) was used for all spectrophotometric measurements.

2.2.1 Spectrophotometric Analysis

A stock solution of tetracycline hydrochloride (480.9 g/mol) was prepared by dissolving 0.05 g of tetracycline hydrochloride in 100 mL of distilled water, a 500 mg/L tetracycline stock solution was produced. The stock solution was diluted to provide the various tetracycline solution concentrations utilized in the adsorption tests. The pH 4.5 using phosphate buffer solution. Tetracycline concentrations at 375 nm were measured using an ultraviolet-visible spectrophotometer which corresponds to the maximum absorbance of tetracycline hydrochloride in the phosphate buffer solution [35]. Tetracycline's calibration curve was evaluated between 1.0 and 160.0 mg/L.

2.3 Synthesis of adsorbent

2.3.1 Synthesis of metal-organic framework (MOF)

2.3.1.1 Synthesis of Fe MOF

The following procedure for the synthesis of MIL-101(Fe)-NH_2 was prepared by solvothermal method as described in previous work [34] from mixing amino terephthalic acid NH_2-BDC (0.3623 g, 1.65 mmol) and $FeCl_3.6H_2O$ (1.0812 g, 4.00 mmol) and suspended in DMF (24 mL) and then heated at 110 °C for 24 h. The brown microcrystalline product obtained was filtered and washed 3 times with DMF and 3 times with dichloromethane before being dried at room temperature under a vacuum. Yield: 66%. 0.72 g[12]. All characterization in S2 file.

2.3.1.2 Synthesis of Cu-BTC MOF

A solution of $Cu(NO_3)_2{\cdot}6H_2O$ (weight, 3.6 mmol) was dissolved in 60 mL of a solvent mixture of ethanol, water, and benzene tricarboxylate (BTC) (8.1 mmol) in 60 mL of ethanol were both stirred for 10 min in a 250 mL beaker, separately. A 50/50 mixture of Cu $(NO_3)_2$ and BTC (benzene-1,3,5-tricarboxylic acid) solution was stirred for 10 min, and then placed in a Teflon autoclave. The sealed autoclave was heated to 120 °C for 18 h in a convective oven and then left to cool to room temperature[20]. All characterization in S2 file.

2.3.2 Synthesis of grafted polyurethane foam (GPUF)

The reagent-grafted foam was prepared by mixing 2.5 g of the polyols (polyether) with 0.02 g of the reagent (Cu-MOF or Fe-MOF) with continuous stirring till complete homogeneity of the mixture was achieved. 0.034 g (one drop) of tertiary amine (dimethylene ethanolamine), 0.04 g of stannous octoate, 0.2 g of silicon (polyether polysiloxane), and 0.035 g of distilled water were added, and the mixture was stirred continuously for 5 min. 1.55 g of toluene diisocyanate (TDI) was gradually poured onto the mixture and stirred at 500 rpm for 15 s. The GPUF produced was left to rise and cure at room temperature, then was cut into small cubes (about 1 cm x 1 cm). The cubes were washed with 0.1 M HCl followed by double distilled water to remove all chloride ions (which are detected by using $AgNO_3$ solution). After that, the foam was washed with acetone and allowed to dry at room temperature or in a drying oven at 80 ºC. The Cu-MOF and Fe-MOF grafted foam colors obtained were pale blue and dark brown, respectively[21].

2.4 Adsorption experiments

The produced foam's adsorption capacities were investigated through batch testing[14]. Using Freundlich and Langmuir isotherm models, the adsorption capacity and removal efficiency of MOF, the primary thermodynamic parameters, kinetic investigations, and the isothermal studies were carried out and were computed using the following formulas and equations:

Adsorption capacity
$$\mathbf{q_t} = \frac{(\mathbf{C_o} - \mathbf{C_t})\mathbf{V}}{\mathbf{m}} \quad (1)$$

Removal efficiency(%)
$$= \left[\frac{(\mathbf{C_o} - \mathbf{C_t})}{\mathbf{C_o}}\right] \mathbf{x\ 100} \quad (2)$$

Primary thermodynamic
$$\Delta G = -RT\ \mathbf{lnk_e} \quad (3)$$

Van 't Hoff equation
$$\mathbf{lnk_e} = \frac{\triangle S}{\mathbf{R}} - \frac{\triangle \mathbf{H}}{\mathbf{RT}} \quad (4)$$

	$k_e = \frac{C_0 - C_e}{C_e}$	(5)
Pseudo-1st order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	(6)
Pseudo-2nd order	$\frac{t}{q_t} = \left(\frac{1}{K_2\, q_e}\right) + \left(\frac{1}{q_e}\right) t$	(7)
Freundlich	$\log q_e = \log k_f + \frac{1}{n} \log C_e$	(8)
Langmuir isotherm	$\frac{1}{q_e} = \left(\frac{1}{q_m}\right) + \left(\frac{1}{q_m} + K_L\right) \frac{1}{C_e}$	(9)
The Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_{max\,K_L}} + \frac{C_e}{q_{max}}$	(10)
Thermodynamic parameters	$\triangle G° = \triangle H° - T\triangle S°$	(11)

All equations parameters are found in the S1 file.

3. Results and discussion

3.2 Adsorption parameters optimization

Tetracycline hydrochloride adsorption was fine-tuned by adjusting five factors: adsorbent dosage, MOF additives, initial pH value, contact time, initial analyte concentration, and temperature. This allowed for the best possible adsorption process to remove the target analyte and achieve satisfactory efficiency[22, 23].

3.2.1 The Effect of adsorbent weight

Figure 2 illustrates how the adsorbent dose of FeMOF-PUF and CuMOF-PUF influences the removal of tetracycline from the solution. The findings demonstrate that the removal percentage rises as the adsorbent dose increases from 0.02 to 0.06 g. However, further increments in adsorbent weight beyond 0.05 g do not significantly enhance adsorption efficiency, indicating that an equilibrium between the adsorbent and adsorbate has been reached[24].

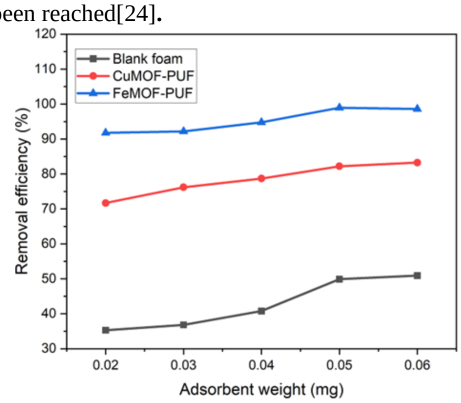

Fig. 2. The effect of adsorbent weight upon tetracycline removal using FeMOF-PUF and CuMOF-PUF (pH=5 and 6, vol=50 mL, time= 55 and 60 min, C_o=20mg/L).

3.2.2 The Effect of MOF's Additives Ratio

The removal efficiency should theoretically be improved by adding more additives at the same starting tetracycline concentration. This is because an increased MOF provides the adsorbate with more active sites. Fe-MOF and CuMOF were shown to be the best additives on PUF when different concentrations of MOF (0.01%, 0.02%, and 0.03%) were used. After 0.02 g, a drop in adsorption efficiency was seen in all adsorbent weights, suggesting that equilibrium had been reached as a result of saturation of the adsorbent active sites (Figure 3).

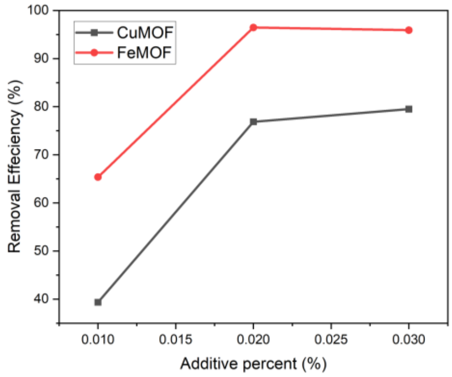

Fig. 3. The effect of additives MOF on PUF upon tetracycline removal using FeMOF-PUF and CuMOF-PUF (pH=5 and 6, vol=50 mL, time= 55 and 60 min, C_o=20mg/L).

3.2.3 Effect of pH

Tetracycline (TC) adsorption onto Cu-MOF or Fe-MOF grafted polyurethane foam is mostly impacted by the surface charge of the adsorbent, which is established by the solution's pH[25]. Tetracycline can exist in three different forms depending on pH: cationic species (pH < 3.3), zwitterionic species (3.3 < pH < 7.69), and anionic species (pH > 7.69). TC molecules are polyprotic molecules with three ionization constants (pKa 3.3, 7.69, and 9.4). With pH 6 for Cu-MOF grafted foam and pH 5 for Fe-MOF grafted foam, the maximum sorption capacity for tetracycline was found. The lower adsorption at more acidic pH values is probably caused by the extra H^+ ions vying with the drug's cationic groups for adsorption sites. Lower adsorption at a more basic pH is probably caused by extra OH^- ions vying with the drug's anion groups for the adsorption site (Figure 4).

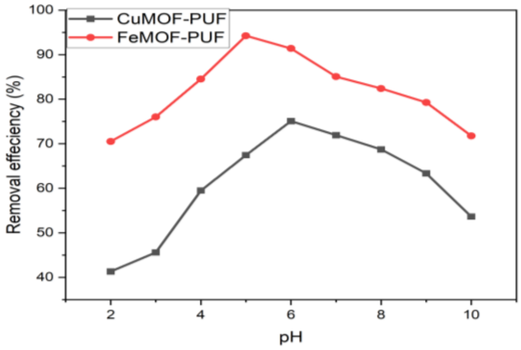

Fig. 4. The effect of initial pH on tetracycline removal using Cu-MOF and Fe-MOF at (adsorbent weight =0.02 g, vol =50 mL, time= 55 and 60 min, C_o=20 mg/L).

3.2.4 Effect of contact time

FeMOF- and CuMOF-based tetracycline elimination was studied at various contact periods. Figure 5 presents the findings. The results clearly show that extending the duration from 5 to 70 minutes causes a significant improvement in tetracycline adsorption efficiency onto the produced adsorbents. The adsorption efficiency, however, stayed constant when the contact times were extended over 55 minutes for FeMOF-PUF and 60 minutes for CuMOF-PUF, suggesting that equilibrium was attained as a result of saturation of the adsorbent active sites[26].

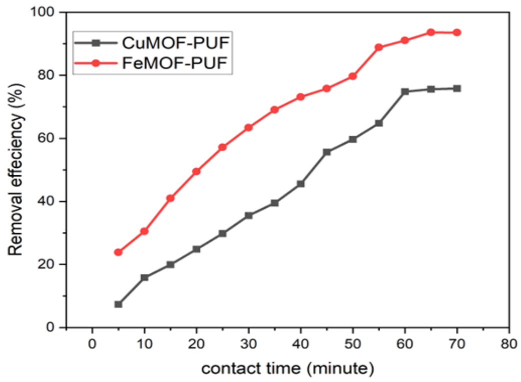

Fig. 5 Effect of contact time upon Tetracycline removal using FeMOF-PUF and CuMOF-PUF (pH= 5 and 6, vol=50 mL, initial concentration=20 mg/L, adsorbent weight=0.02 g).

3.2.5 Effect of temperature

The study examined the adsorption of tetracycline (TC) onto Cu-MOF or Fe-MOF grafted foam at varying temperatures (15º, 25º, 30º, 35º, 40º, and 45ºC). The findings (Figure 6) showed that the adsorption was not significantly affected by temperature increases[27].

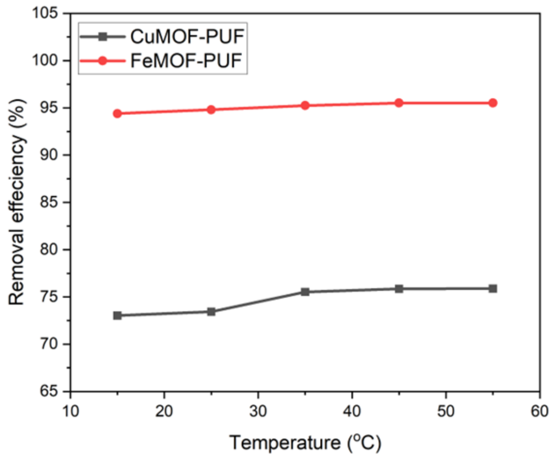

Fig. 6. The effect of varying the solution temperature upon the removal of tetracycline using FeMOF-PUF and CuMOF-PUF (pH= 5 and 6, volume= 50 mL, adsorbent weight =0.02g, time=55 and 60 min, C_o =20 mg/L).

3.3 Isothermal experiments.

3.3.1 Langmuir isotherm.

The Langmuir adsorption isotherm is an empirical model that assumes monolayer adsorption, a uniform surface, and a finite number of adsorption sites[28]. Therefore, once a site is occupied, no additional adsorption can take place at that site[29]. The Langmuir equation is expressed as equation (10).

3.3.2 Freundlich isotherm

The foundation of the Freundlich isotherm is heterogeneous and multilayer adsorption sites[30]. Equation (8) yields the Freundlich equation. According to Table 1's fitting results, the Langmuir model's R^2 value was greater than the Freundlich model's[31]. This implies that the homogeneous Fe-MOF surface and monolayer adsorption are best explained by the Langmuir model as in figure 7.

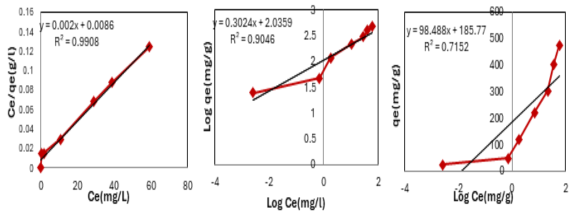

Fig. 7. sorption isotherm of tetracycline by FeMOF-PUFfitted by(a) Langmuir model (b)Freundlich model (c)Tempkin model.

Table 1. Adsorption isotherm fitting parameters for tetracycline adsorption onto Fe$_{MOF}$-PUF

Isotherms	Parameters	R^2
Langmuir	**Qm=500** **Kl=0.0086**	**0.99**
Freundlich	**n=3.31** **Kf=108.61**	**0.90**
tempkin	**B1=98.49** **Kt=6.59**	**0.72**

3.4 Analysis of Kinetics

The pseudo-1st order and pseudo-2nd order kinetic models were utilized to investigate the adsorption kinetics of TC in accordance with equations 6 and 7, respectively, in order to investigate the adsorption behavior of TC on FeMOF-PUF and CuMOF-PUF. 6 and 7, in that order[32].

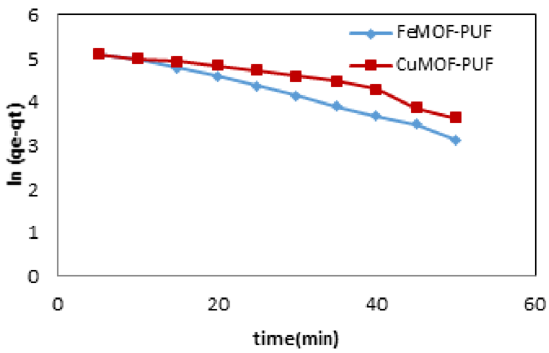

Fig .8 a. pseudo 1st order kinetic model for the tetracycline adsorption onto Fe$_{MOF}$-PUF and Cu $_{MOF}$-PUF.

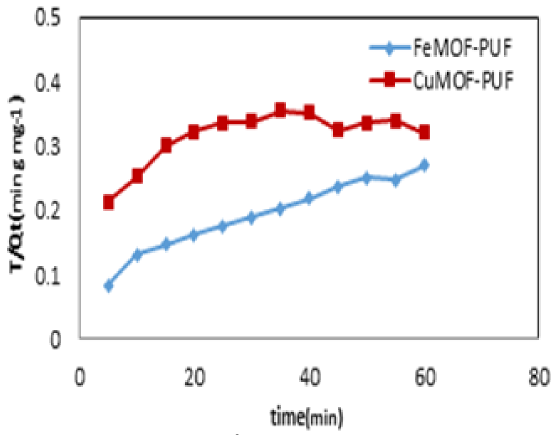

Fig. 8 b. pseudo 2nd order kinetic model for the tetracycline adsorption onto Fe_{MOF}-PUF and Cu $_{MOF}$-PUF.

The findings suggest that the pseudo-1st-order and pseudo-2nd-order models can adequately explain the elimination of tetracycline hydrochloride. For tetracycline hydrochloride, the adsorption of FeMOF-PUF and CuMOF-PUF is better described by the first kinetic model.

3.5 Thermodynamic studies

Equations 4 and 11 were used to compute the thermodynamic parameters for the adsorption of tetracycline onto FeMOF-PUF and CuMOF-PUF, including the standard Gibbs free energy (ΔG°), the standard enthalpy (ΔH°), and the standard entropy (ΔS°)[33]. The thermodynamic characteristics of tetracycline adsorption on FeMOF-PUF at various temperatures are displayed in the following table. G°'s negative values suggested that the adsorption processes were advantageous and spontaneous. The G° value progressively dropped as the temperature rose, indicating that the adsorption process benefited from the higher temperature. FeMOF-PUF and CuMOF-PUF both had a positive S° value that demonstrated their affinity for tetracycline, but an endothermic adsorption was suggested by a positive H° value.

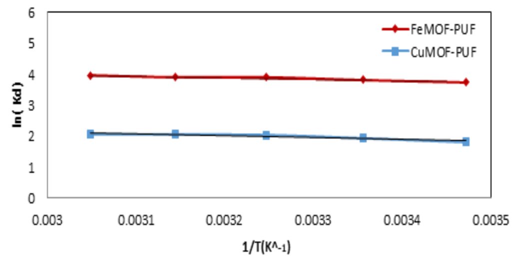

Fig. 9. Van 't Hoff plot for an endothermic reaction of TC adsorption onto FeMOF-PUF and Cu_{MOF}-PUF.

4. Application

4.1 Determination of tetracycline in Actual water

Natural water samples, including tap water and river water, were used to evaluate the practical application of FeMOF-PUF for the adsorption of Tetracycline. Tetracycline with three concentrations of (100ppm, 150 ppm, and 200 ppm) was spiked into actual water samples (river water and tap water). The removal efficiency results are shown in the table.

Table 2. The parameters of kinetic models for the tetracycline adsorption onto Fe_{MOF}-PUF and Cu $_{MOF}$-PUF.

	Pseudo-first order	Pseudo-second order
(Fe_{MOF}-PUF)	K=0.044 R^2=0.99	K=0.000096 R^2=0.96
(Cu_{MOF}-PUF)	K=0.031 R^2=0.92	K=0.0000097 R^2=0.46

Table 3. Thermodynamics parameters for TC adsorption onto Fe_{MOF}-PUF.

Temp	**ΔG°(Fe) (KJ.mol-1)**	**ΔH°(Fe) (KJ.mol-1)**	**ΔS°(Fe) (J K-1 mol-1)**	**ΔG°(Cu) (KJ.mol-1)**	**ΔH°(Cu) (KJ.mol-1)**	**ΔS°(Cu) (J K-1 mol-1)**
15	-13.41	4.43	46.59	-9.5	5.1	33.01
25	-13.88	4.43	46.59	-9.83	5.1	33.01
35	-14.35	4.43	46.59	-10.16	5.1	33.01
45	-14.81	4.43	46.59	-10.49	5.1	33.01
55	-15.28	4.43	46.59	-10.82	5.1	33.01

Table 4. The results of removing tetracycline from tap water and river water with Fe_{MOF}-PUF

Sample	**Add Tetracycline**	**Found Tetracycline**	**Removal Efficiency(٪)**
tap water	100 ppm	82.18	82.18
	150 ppm	124.50	83
	200 ppm	168.32	84.16
river water	100 ppm	79.48	79.48
	150 ppm	121.11	80.74
	200 ppm	167.56	83.78

4.2 Determination of tetracycline in human urine samples

A human urine sample was taken by a healthy volunteer who took a dose of tetracycline. The sample was analyzed by using a UV-Vis spectrophotometer (at 375 nm) to know if there was any drug residue in the sample or not. A percentage of the drug was found in the sample, whose concentration was 34.99 ppm.

4.2.1 The treatment of tetracycline in human urine samples by two different techniques (batch and column adsorption)

4.2.1.1 Batch Adsorption Experiment

The treatment was done by mixing 50 ml of the sample (Ci=34.99 ppm) with 0.02 gm of FeMOF-PUF and adjusted to pH 4.5. The flask was shaken using a mechanical shaker at 35 °C for 55 minutes. Aliquots of the sample were withdrawn and analyzed by using a UV-Vis spectrophotometer. The concentration of the sample after treatment was 9.91 ppm.

4.2.1.2 Adsorption experiment using a fixed-bed column

A glass column with an internal diameter of 1.5 cm and a height of 30 cm was used for the column adsorption tests. To improve flow distribution and stop adsorbent loss, a 0.5 mm layer of glass wool was added to the bottom of each adsorbent bed. The column was filled with a known weight of adsorbent (FeMOF-PUF) layered on top of a layer of glass wool at the bottom, reaching heights of 0.3 cm, 0.6 cm, and 3.0 cm. A urine sample was pumped through the column with an initial concentration of 34.99 parts per million. Using a UV-Vis spectrophotometer, the urine sample's residual concentration in the outlet was measured after being removed from the column's exit.

4.2.2 Effect of bed height

The effect of bed height (mass of adsorbent) on adsorption was investigated by varying the height of the column (0.3, 0.6, and 3.0 cm) while maintaining a constant urine sample concentration (34.99 ppm).

Table 5. Tetracycline adsorption by FeMOF-PUF and the effect of a fixed adsorption bed

Bed height	Inlet Concentration	Outlet Concentration	%Removal
0.3 cm	**34.994 ppm**	**25.82**	**26.21**
0.6 cm	**34.994 ppm**	**20.58 ppm**	**41.18**
3.0 cm	**34.994 ppm**	**9.27 ppm**	**73.51**

The tetracycline removal percentage increases from 26.21% to 73.51% As the bed height increases from 0.3 cm to 3.0 cm, the surface area of the adsorbent also increases, offering more binding sites for adsorption to take place.

4.2.3 Effect of different solvents on the recovery of tetracycline

A urine sample containing tetracycline was passed through the column packed with 0.4 gm of reagent foam. The column was then washed, and the tetracycline was recovered from the foam in the column with different eluting agents. It was washed first with distilled water. The concentration of tetracycline was measured in distilled water, which was 11.53 ppm, and then it was washed with ethanol. The concentration of tetracycline was measured in ethanol, which was 5.49 ppm.

5. Conclusion:

To address this limitation, we have developed a novel adsorbent material by grafting MOFs onto polyurethane foam (PUF), a widely available and versatile material. This approach combines the high adsorption capacity of MOFs with the structural integrity and ease of handling of PUF. In this study, we investigated the adsorption performance of two types of Grafted Polyurethane Foams (GPUFs), namely Fe_{MOF}-PUF and Cu_{MOF}-PUF, for the removal of TC from aqueous solutions. We systematically evaluated the influence of key experimental parameters on the adsorption process, including MOF type, adsorbent dosage, pH, contact time, initial TC concentration, and temperature. Furthermore, we employed adsorption isotherm and thermodynamic studies to elucidate the underlying adsorption mechanisms and assess the feasibility of this approach for TC removal. Our findings demonstrate that GPUFs, especially Fe_{MOF}-PUF, exhibit excellent adsorption capacity for TC, highlighting their potential as effective and practical adsorbents for wastewater treatment.

6. Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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