



OPEN Zr-based MOF gel prepared by ultrasonication for effective removal of antibiotic drug from aqueous environments

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Herein a Zr-based metal organic framework hydrogel (MOF-Zr; UiO-66) is synthesized. The prepared MOF is characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared (FTIR), Brunauer-Emmett-Teller (BET) surface area measurements and thermogravimetric analysis (TGA). The UiO-66 MOF is used effectively for the removal of an antibiotic; Ciprofloxacin, which is considered harmful when accumulated in water sources. The variation of operational factors that alter the drug removal are studied such as initial drug concentration, hydrogel (sorbent) used and the addition of some anions and cations. The study shows that the uptake efficiency of the MOF to the drug increases upon the addition of humic acid or sodium chloride to the solution matrix. A maximum uptake capacity of Ciprofloxacin onto the MOF reaches 333 mg g⁻¹. Different isotherms (Langmuir, Freundlich, and Temkin) are applied to the adsorption process and their corresponding parameters are reported. The kinetic model follows a pseudo-second order mechanism. Conclusively, UiO-66 is a promising super adsorbent material for pharmaceutical pollutants from waters.

Keywords Hydrogel MOF, Ciprofloxacin antibiotic, Water purification, Isotherms, Kinetic models

Fresh water is very limited in nature mainly in remote and desertification regions. Dependence on treated wastewater as nonconventional water source is one of solution for water shortage. Most studies focused on the removal of different types of pollutants from wastewater to generate clean water. One of the most important classes of pollutants is the pharmaceutical compounds (e.g. antibiotics) due to their risky effect on both public health¹ and the environment^{2,3}. They affect the quality of water greatly and they could be toxic to aquatic organisms⁴. Exposure to these compounds above certain limits can cause different health problems such as brain damage, liver impairment, and carcinogenic diseases⁵.

Several treatment methods have been proposed to remediate this challenge such as adsorption, reverse osmosis, nanofiltration and ion exchange^{6–8}. However, they are challenging as complete pollutants removal is not easy by the conventional techniques as they may discharge in the environment or persist in the treated water as traces.

Among these antibiotic pollutants, ciprofloxacin (CIP) which is an important fluoroquinolone, is commonly used in the treatment of infectious diseases. In microorganisms, it can inhibit DNA replication as it interacts with topoisomerases II (DNA gyrase) and IV⁹. In human body, it cannot be fully metabolized while it is very stable chemically and this led to becoming the most frequently detected fluoroquinolone in European wastewater treatment plant effluents (WWTP) because of its release to the environment and excretion into wastewater^{10,11} also it can be toxic at extended time exposure¹² having cytotoxic effects on human immune cells and it showed hemolysis < 2%, no thrombosis risk¹³. During the last fifty years, the bacterial resistance to these compounds also increased because of the increased exposure^{14,15}.

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Novel class of porous materials have been introduced in the last two decades namely metal organic frameworks (MOFs) which were first synthesized by Yaghi et al.¹⁶. These materials showed promising results in several applications such as light capture and energy conversion¹⁷, drug delivery¹⁸, catalysis^{19–21}, gas purification²² and in wastewater treatment^{23–26}.

MOFs consists of metal centers and organic linkers forming infinite crystalline networks²⁰ and their structure is spongy like with the metal coordinately linked to the ligands²⁷. This hybrid structure is characterized by thermal stability, high surface area and great flexibility in pore size, shape and functionality²⁸. These features increase their ability for contaminants removal.

In this work, Zr-based MOF hydrogel is synthesized by reacting terephthalic acid and zirconium oxychloride. The novelty of our study comes from preparation of MOF in hydrogel form, this hydrogel can be easily removed from water after adsorption while solid MOFs needs filtration and centrifugation. It is prepared with no additives, and at room temperature Sono chemically. MOF hydrogels based on Zr do not have the full characteristics of a solid material. Three-dimensional networks made of UiO-66 nanoparticles that are linked and hold a lot of water inside their structures.

The conventional preparation methods for MOF hydrogels generally require high temperature, long time solvothermal heating, or secondary auxiliary matrices (e.g., organic polymers, alginate, or graphene oxide) to produce the gel form, which often occludes the active pores. The structure and morphology of the resulting material were ascertained. The MOF was used for removal ciprofloxacin drug from aqueous media. The kinetics and isotherm model of the removal process were scrutinized, derived and compared with different models.

The formula of the prepared hydrogel is $Zr_6O_4(OH)_4(BDC)_6 \cdot X H_2O$ where X represents the variable amount of trapped moisture and BDC refers to benzene dicarboxylic acid.

Experimental

Preparation of ciprofloxacin (CIP) solution

A stock solution of 1000 ppm CIP was prepared by dissolving 1 g of CIP in 1000 mL deionized water. The required concentration was prepared for further investigation by dilution; the pH of the solution was adjusted using HCl (Merck) 1 M and/or NaOH sodium hydroxide (Merck) 1 M. JASCO (V-730) UV-Vis spectrophotometer was used for CIP determinations at wavelength of 274 to 278 nm. A WTW digital pH meter model 525 (Germany) was used for the pH adjustments. A shaker was also used for mixing the samples.

Preparation of MOFs hydrogel

Terephthalic acid (Lobe Chemie, India) is used as the organic linker (BDC) (Benzene-1,4-dicarboxylic acid) (0.8 mmol dissolved in DMF) (Lobe Chemie, India) and is mixed with zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) (Merck, USA) (0.8 mmol) dissolved in a 1:1 mixture of DMF and deionized water) using probe ultra-sonication for 30 min (30 s sonication followed by 10 s rest) via room temperature with no external heating. The hydrogel produced is washed several times with deionized water and ethanol then filtered.

Characterization of the hydrogel MOF

A scanning electron microscope was used to study the produced MOF's surface morphology and porosity structure (SEM; JEOL model JSM-IT100). Energy-dispersive X-ray spectroscopy (EDX), which was used to identify the elements in the produced MOF, was connected to the SEM. Using an X-ray diffractometer (XRD-6000 Shimadzu) set at 40 kV with current adjusted at 30 mA and $CuK\alpha 1$ radiation $\lambda = 1.54056 \text{ \AA}$, the angle range was $10\text{--}80^\circ$. The X-ray diffraction (XRD) technique was utilized to examine the crystallinity/amorphous nature of the synthesized MOF. The FTIR analytical measurements of the generated MOF were provided on a JASCO spectrometer to detect the functional groups information in MOF; the scanning was in the range of $4000\text{--}400 \text{ cm}^{-1}$. The specific surface area was measured using the Brunauer–Emmett–Teller (BET) method with correlation coefficient r of 0.9919 and C constant of 1.7134, while the pore size distribution was derived using the Barrett–Joyner–Halenda (BJH) model using the adsorption branch of the nitrogen adsorption–desorption isotherm. The measurements were analyzed using Quantachrome TouchWin™ v1.2 software, supporting NOVAtouch™ gas sorption analyzers. The Thermogravimetric analysis (TGA) was performed on a Shimadzu thermal analyzer in a nitrogen atmosphere (20 mL/min flow), over a temperature range of $30\text{--}800 \text{ }^\circ\text{C}$ with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

Adsorption procedure

The adsorption experiments were carried out using 50 mL glass beakers containing ascertained doses of the hydrogel in different concentrations of CIP solution at different pH values. The pH of the solutions was adjusted by adding either HCl or NaOH 1 M solutions. After stirring at constant temperature of 298 K for different time-intervals, the solid/liquid phases were separated by filtration using membrane filter of $0.45 \text{ }\mu\text{m}$ pores size. Then the concentration of CIP filtrate was measured spectrophotometrically. The adsorption rate (Ads %) was calculated based on the following equation:

$$\text{Adsorption rate} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

C_0 and C_e are the initial and the equilibrium concentrations of CIP in solution phase, respectively. Kinetic experiments were performed on 20 mg/L of CIP with gel dose of 4 g/L at a temperature of 298 K. Samples were collected on regular time intervals for the determination of the CIP concentration. The rate constants were calculated using the conventional rate expression. Adsorption isotherm studies were carried out with

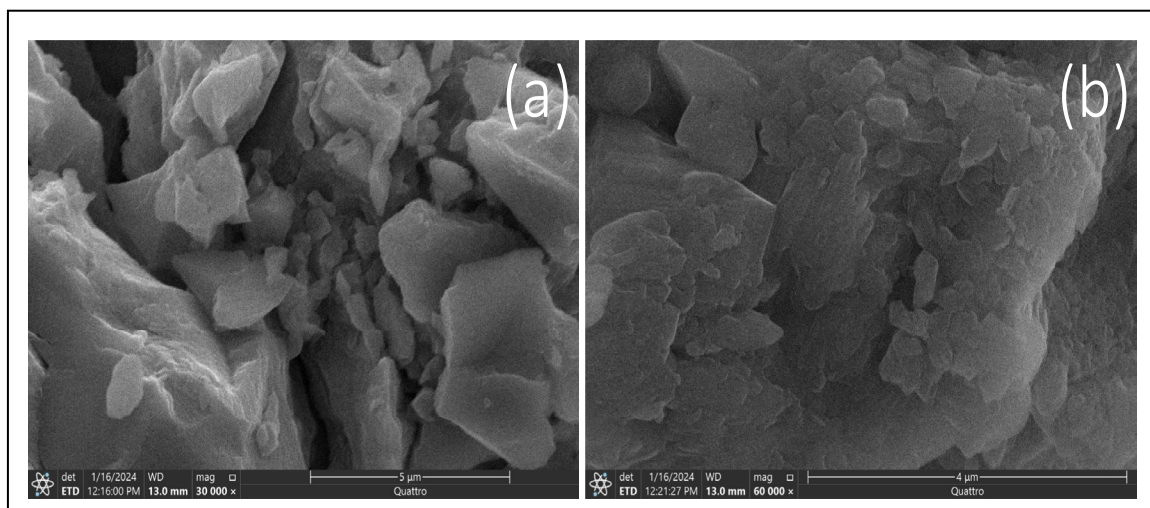


Fig. 1. The SEM images for the prepared UiO-66 from various spots at magnification scales 4 μm and 5 μm .

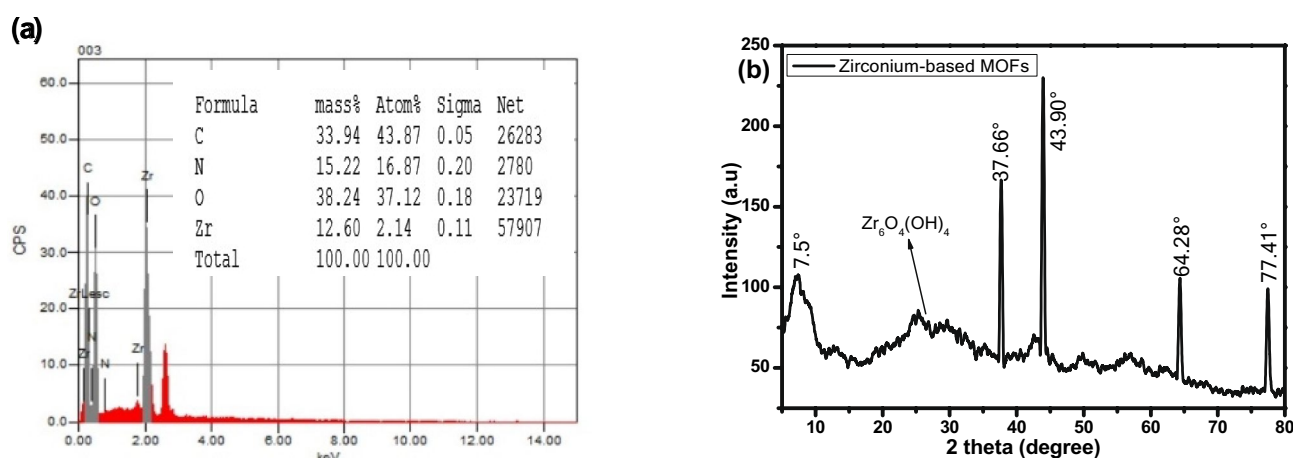


Fig. 2. The EDX analysis (a) and the XRD pattern (b) for the prepared UiO-66.

initial concentrations of CIP varying from 10 to 100 mg/L, the amount of sorbent was kept constant, and the experimental temperatures were controlled at 298 K.

Results and discussion

Characterization of hydrogel

Scanning electron microscope

SEM imaging was performed to get insights into the morphological properties of the synthesized UiO-66. The SEM images (Fig. 1a, b), showed the formation of highly crystalline MOFs, the particles displayed a well-defined polyhedral structure with variable shapes²⁹. The homogeneity in particles distribution suggests controlled nucleation and growth during the synthesis process. Additionally, surface roughness, and porosity are characterized for the observed MOFs particles, due to the high surface area of MOFs³⁰. Some agglomerated particles were observed due to insufficient solvent removal³¹.

Energy-dispersive X-ray spectroscopy (EDX)

The EDX pattern (Fig. 2a) of the synthesized UiO-66 revealed the presence of several elements of Zr (12.60%), N (15.22%), O (38.24%), and C (33.94%), these results supporting the successful formation of the UiO-66. The prominent of N, O, and C signals with zirconium signal indicate the successful incorporation of Zr atom into organic compound to form the metal-organic framework (UiO-66). Furthermore, the presence of signals for nitrogen atoms suggests the coordination of nitrogen-containing ligands, that may be derived from the solvent used. The oxygen and carbon signals may derive from the carboxylate linkers and organic framework backbone of UiO-66³².

XRD analysis

The X-ray diffraction (XRD) pattern of the synthesized zirconium-based metal–organic framework (MOF) is shown in Fig. 2b. The pattern demonstrates the appearance of peaks at 2θ values of 7.5° , 37.66° , 43.90° , 64.28° , and 77.41° (2θ) correspond to the face-centered cubic (fcc) topology of a crystalline structure of the UiO-66 framework³³.

The intense low-angle peak at 7.5° is assigned to the (111) plane and serves as a fingerprint for the UiO-66 structure³⁴. The significant low-intense broad peak at $2\theta = 20\text{--}30^\circ$ corresponds to the $(\text{Zr}_6\text{O}_4(\text{OH})_4)$ ³⁵ that formed by the coordination of zirconium clusters with terephthalic acid (1,4-benzenedicarboxylic acid) linkers.

The additional higher-angle peaks, such as those observed at 37.66° , 43.90° , 64.28° , and 77.41° , are associated with higher-order planes and further support the presence of a well-ordered crystalline framework. The sharpness and intensity of the peaks reflect a well-ordered³⁶.

FTIR analysis

The FTIR spectrum of the synthesized UiO-66 exhibits characteristic vibrational bands indicative of successful zero-based framework formation, as shown in Fig. 3a. The broad and intense peak around $\sim 3400\text{ cm}^{-1}$

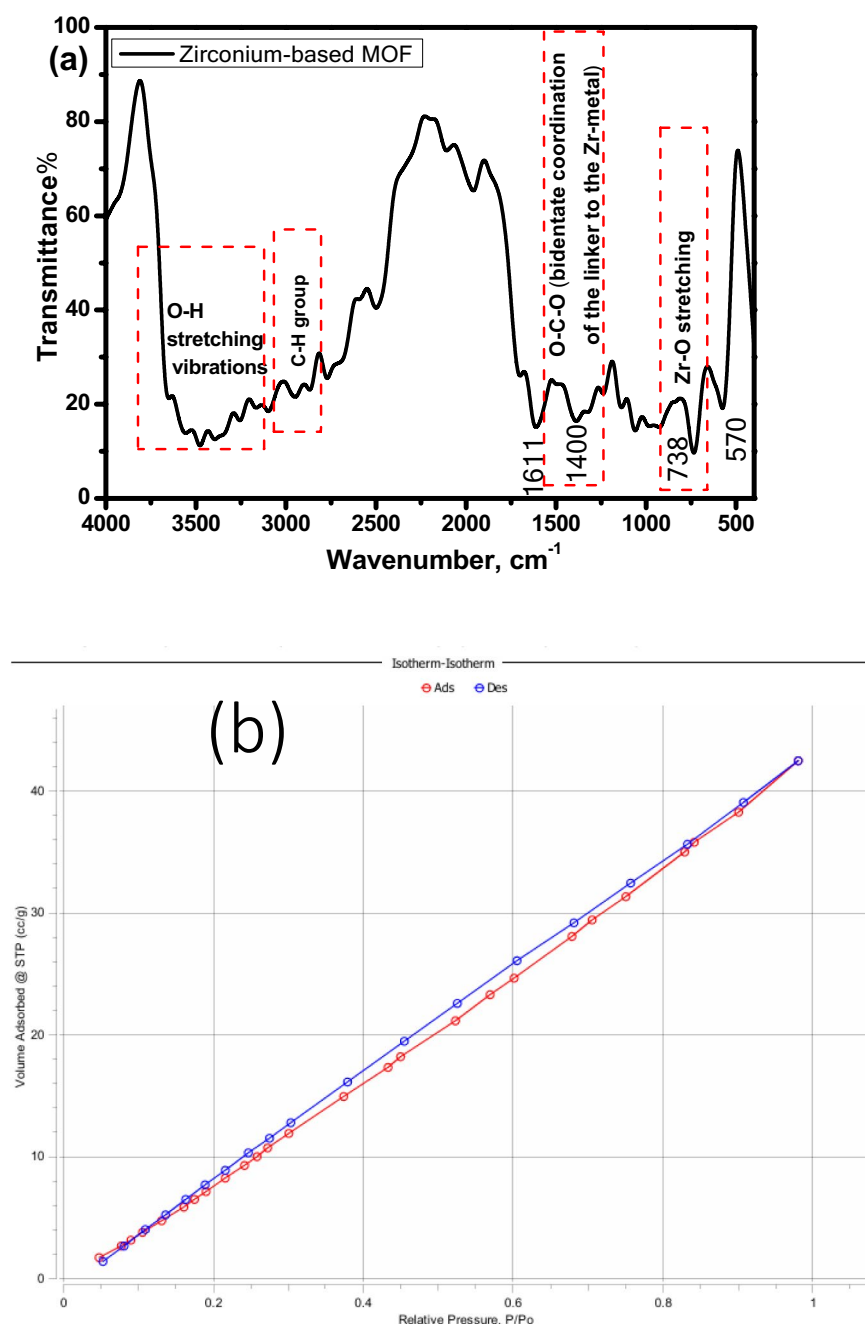


Fig. 3. The FTIR analysis (a); the N_2 adsorption-desorption isotherms (b).

corresponds to the O–H stretching vibrations, suggesting the presence of $\text{Zr}_6\text{O}_4(\text{OH})_4$ group (the building unit of the MOF)³⁷ or the appearances of this peak may be due to the adsorbed moisture. The noticed absorption band near $\sim 1611\text{ cm}^{-1}$ is attributed to the C=O stretching of the coordinated carboxylate groups from terephthalic acid, confirming successful coordination with zirconium clusters.

The aromatic and aliphatic stretching (C–H) modes of residual DMF are seen as weak bands in the spectra of MOF in the region from 2850 to 3100 cm^{-1} . Further, the peaks at the range of 1400 – 1700 cm^{-1} , may correspond to stretching vibrations of C=C and C=O bonds^{36–38}, which are found in the symmetric and asymmetric stretching vibrations of the carboxylate groups, indicating bidentate coordination of the linker to the Zr-metal centers. This is matched with Azhar, M. R et al.³⁷, who attributed the distinct peak at 1408 cm^{-1} to the symmetric stretching of O–C–O of deprotonated BDC in the UiO-66 structure. The multiple peaks in the fingerprint region (below $\sim 1000\text{ cm}^{-1}$) are associated with Zr–O stretching modes, characteristic of the formation of $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters within the UiO-66 framework³⁹. These FTIR spectral features collectively confirm the successful synthesis of UiO-66 with the expected coordination to form $[\text{Zr}_6\text{O}_4(\text{OH})_4][\text{C}_6\text{H}_4(\text{COO})_2]_6$.

BET surface area and porosity analysis

The nitrogen adsorption–desorption isotherm analysis of the synthesized UiO-66 revealed a multipoint BET surface area of $86.39\text{ m}^2/\text{g}$, indicative of moderate surface development relative to highly crystalline UiO-66 frameworks $1827\text{ m}^2/\text{g}$ and $1258\text{ m}^2/\text{g}$ ^{40,41}. This may be attributed to the fact that BET experiment was measured with dry powder of MOF that led to lose the large specific surface area in the wet beads. However the significant adsorption results were achieved due to the displaying on gel form not the powder form. The total pore volume was calculated at $P/P_0 = 0.995$. The single-point BET area ($36.27\text{ m}^2/\text{g}$) and BJH surface areas for adsorption ($39.98\text{ m}^2/\text{g}$) and desorption ($39.31\text{ m}^2/\text{g}$) support this observation and reflect a porous structure with significant microporous and mesoporous characteristics and suggesting a type IV isotherm³⁸. This is supported by the hysteresis loop observed between adsorption–desorption curves (Fig. 3. b) which shows the microporous nature in combination with some meso-structures. This result is consistent with the one obtained by Boix, G et al.⁴². They mentioned that this behavior is typical of MOF beads made by spray-drying and can be attributed to the existence of the mesoporosity derived from the nanocrystal assembly that forms the beads.

The Langmuir surface area was reported as zero, which may indicate limitations in the Langmuir model applicability to this material or experimental inconsistencies.

The pore volume analysis showed consistent cumulative micropore volumes across BJH and DFT methods, ranging between 0.059 and 0.063 cc/g that is smaller than what detected before for UiO-66⁴³, suggesting the presence of a microporous network typical of UiO-type MOFs. The average pore radii were found to be in the range of 1.68 – 2.84 nm indicating microporous to small mesoporous domain, indicating partial retention of porosity during synthesis or freeze drying.

The DFT analysis further confirmed a mode pore radius of 2.84 nm , supporting a partially hierarchical pore structure. The V-t method analysis yielded an external surface area of $51.51\text{ m}^2/\text{g}$, which is relatively high and suggests potential structural imperfections or external surface roughness due to defects or interparticle voids.

TGA analysis

The thermal stability and decomposition pattern of the synthesized UiO-66 were studied via thermogravimetric analysis (TGA). The TGA pattern (Supplement Fig. 2) shows a weight loss of 9.54% below 200°C , due to the vaporization of water molecules.

The second decomposition observed of weight losses about 50.42% between 200°C and 450°C , which may be attributed to the partial decomposition of the organic linker (terephthalic acid). The complete degradation of the organic moieties of the terephthalic acid occurred over the temperature range 450 – 600°C with weight loss (22.93%), leaving the thermally stable zirconium oxide (ZrO_2). At 600°C , the mass remained nearly constant, indicating the formation of a stable oxide (ZrO_2) residue. The obtained TGA results are comparable to those discussed before⁴⁴.

Adsorption of CIP from water

Effect of initial CIP concentration

The effect of varying the concentration of CIP on the adsorption efficiency is illustrated in (Fig. 4). The results show that the percentage of removal decreases with increasing initial concentration of CIP.

In the first monitored interval of 15 min , the hydrogel showed fast capture ability in low concentrations with a removal efficiency of about 85% and 89% for 10 mg/L and 20 mg/L CIP solutions, respectively. Whereas, at the starting concentration of 80 mg/L and 100 mg/L the removal efficiencies were significantly lower at 15 min of around 33% and 40% . All investigated concentrations showed an obvious kinetic turning point at $t = 30\text{ min}$ with increasing contact time, following which the adsorption curves reached a steady plateau phase till equilibrium achieved at $t = 90\text{ min}$ where the values for the final removal efficiencies varied among three different performance bands depending on the initial concentration: low concentrations 10 – 20 mg/L showed maximum removals of about 93% – 94% ; moderate concentrations 40 – 60 mg/L symmetrically appeared at around 81% and high concentrations 80 – 100 mg/L leveled off at an equilibrium removal efficiency of 63% .

This behavior is owed to increasing of initial concentration of CIP that result in lowering the probability of collision between the drug and the active sites of the surface of gel. It can be explained in terms of the limited number of available active sites on the surface of adsorbent causing decrease in the percentage of removal. At low concentrations all the sites on the adsorbent surface are available that allow increase the percent adsorption. As the concentration of CIP increases the collisions between its molecules increases that results in hindering their adsorption to the MOF surface and minimizes their removal.

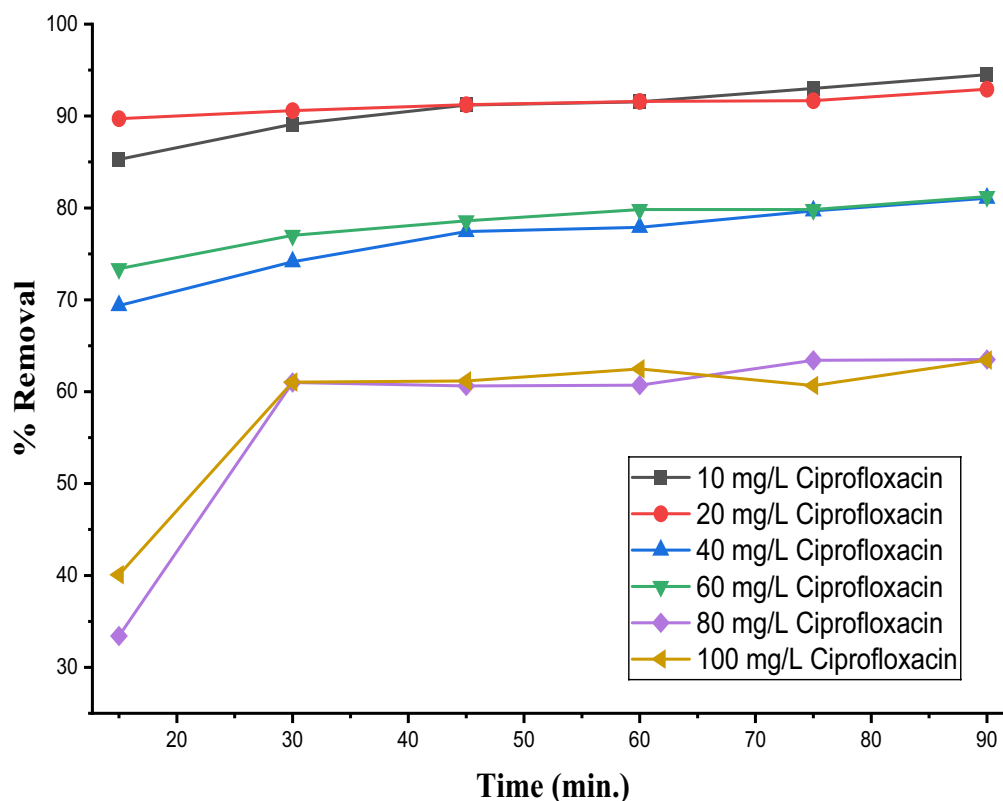


Fig. 4. Effect of initial CIP concentration on its removal with time.

Kinetic studies of initial CIP concentration

The kinetics of the reaction was studied to provide useful information regarding the adsorption mechanism and interaction of CIP species with the adsorbing surface which mainly depends on several factors. Those include the properties of the surface, the structural characteristics of the CIP and the conditions under which the adsorption is being carried out^{45,46}. The kinetics of adsorption of CIP on the gel is initially evaluated by measuring the adsorption capacity with time as depicted in (Fig. 5). It was stated earlier that the shape and classification of isotherms define to a great extent the adsorption mechanism that allows the description of type of adsorption interactions⁴⁷. Further theoretical treatment of the mechanism of solute adsorption based on the classical kinetic model by Langmuir was also published⁴⁸. In their studies, Giles and coworkers introduced four main classes of isotherms and their corresponding subgroups^{47,48}: S or L based on Langmuir type adsorption; H type based on high affinity; and C class based on constant partition. The shape of the curve displayed in (Fig. 5) shows similar behavior to that displayed in the isotherm model H-type presented previously in Giles and coworker's investigation. In this model, the solute has such high affinity to completely adsorb in dilute solutions with the initial shape of the curve is vertical. The rise in the plateau was assigned to the development of fresh surface of the adsorbent. The exposure of some sites of the surface that allows further adsorption of the solute may arise from the substrate swelling and the creation of some channels, this situation results in the formation of fresh surface sites.

Each kinetic model is a mathematical representation of the rate at which physical or chemical process takes place. Here in this study, four different adsorption kinetic models were applied to evaluate the extent of utilization of the adsorption capacity versus contact time between the adsorbate and the adsorbent. These models are namely pseudo-first-order, pseudo-second-order, Weber-Morris diffusion model and Boyd plot.

Pseudo-first-order model In the beginning, Lagergren was the one who presented the equation for pseudo-first order kinetics PFO⁴⁹. The differential form is defined by the equation:

$$dq_t/dt = k_1 (q_e - q_t) \quad (2)$$

Measuring the difference between the average concentration of the species in the adsorbed phase and the final concentration of the phase adsorbed in equilibrium with the fluid phase reveals that the differential Eq. (2) shows inversely correlation between the adsorption capacity and the "distance to equilibrium."

The pseudo-first-order equation is given as the following Eq.⁵⁰:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

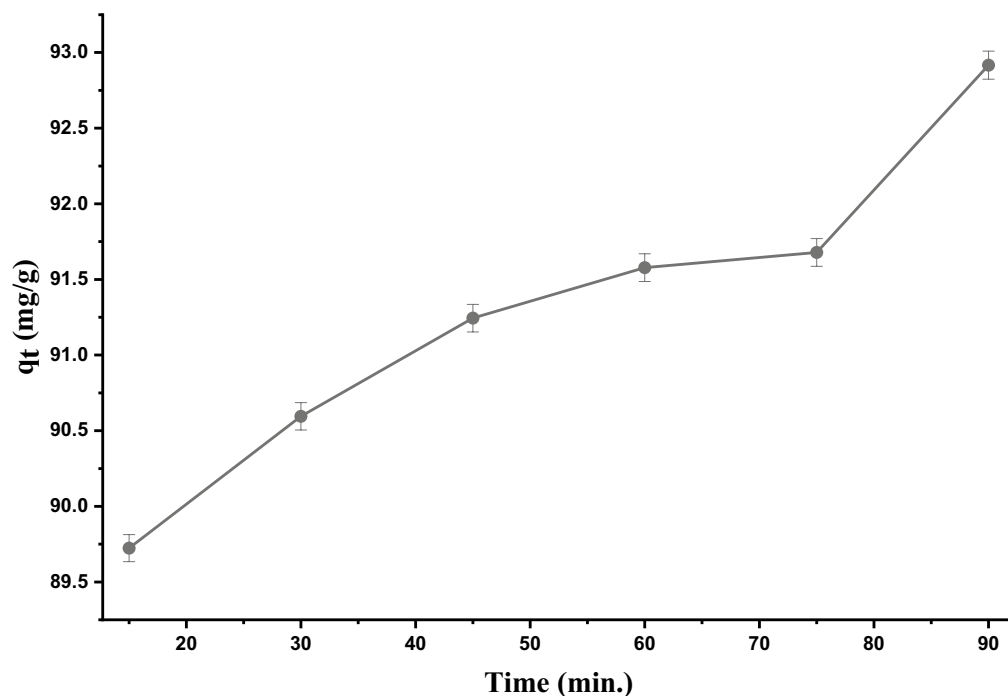


Fig. 5. Time-dependent adsorption capacity of CIP on the MOF hydrogel.

Where q_e and q_t are the amount of CIP adsorbed on the sorbent (mg/g) at equilibrium and at time t , respectively; and k_1 is the rate constant of the first-order adsorption (min^{-1}) that shows how fast the adsorption equilibrium is reached. The values of k_1 for CIP adsorption on gel were determined from the plot of $\ln(q_e - q_t)$ against time for different CIP concentrations ranging from 10 to 100 mg/L (Fig. 6). The results of the kinetic parameters and initial calculated adsorption rate values with each concentration are listed in Table 1. As shown in (Fig. 6) there is an acceptable linear relationship at concentrations up to 60 mg/L. For higher concentrations of 80 and 100 mg/L the linearity of the relationship is disturbed. Also q_e increases consistently with increasing concentration. This is expected as.

higher initial concentration provides a stronger driving force for mass transfer to the adsorbent. However, the rate of increase slows down between 80 and 100 mg/L suggesting approaching saturation. The fluctuation in k values indicates no consistent trend which may reflect mixed mechanisms.

The linearity of the pseudo first order kinetics usually indicates a physical adsorption process (physisorption) with forces like Van der Waals attractions but no chemical bonds are involved with also any activation energy required. Adsorption rate slows down over time as fewer sites are available and it approaches a steady state (equilibrium) gradually with time where no more adsorption occurs. On the other hand comparing the values for the squared correlation coefficient, R^2 the best fit is for 10–60 mg/L ($R^2 \geq 0.95$). For 80 mg/L, the fit worsens significantly ($R^2 = 0.72$). For 100 mg/L, the fit is very poor ($R^2 = 0.48$), indicating the model no longer describes the data. This led us to conclude that at higher concentrations, the pseudo-first-order model becomes less reliable. The process may shift toward chemisorption or involve.

multiple steps like pore-diffusion. Also there is a huge difference between the values of the experimental and calculated q values that confirm the poor agreement with this model.

Pseudo-second-order model Initially, the pseudo-second-order model (PSO), which is represented by Eq. (3), was utilized to model the adsorption of lead onto peat⁵¹. Next, the PSO model became the standard for describing the adsorption processes, and it was widely used.

$$dq_t/dt = k_2(q_e - q_t) \quad (4)$$

For the purpose of calculating the parameters of the model, the linear form of the equation is utilized. This form of the equation was typically utilized in the form that was proposed by Ho and McKay⁵² as follows:

$$t/q_t = t/q_e + 1/k_2q_e^2 \quad (5)$$

Where, k_2 is the second-order adsorption rate constant (g/mg/min). Linear graphs of t/q_t versus t were tested to obtain the rate parameters. The results of the kinetic parameters and initial calculated adsorption rate values for the adsorption process of different concentrations of CIP were calculated from plotting the relation with each concentration as shown in (Fig. 7) and are listed in Table 2.

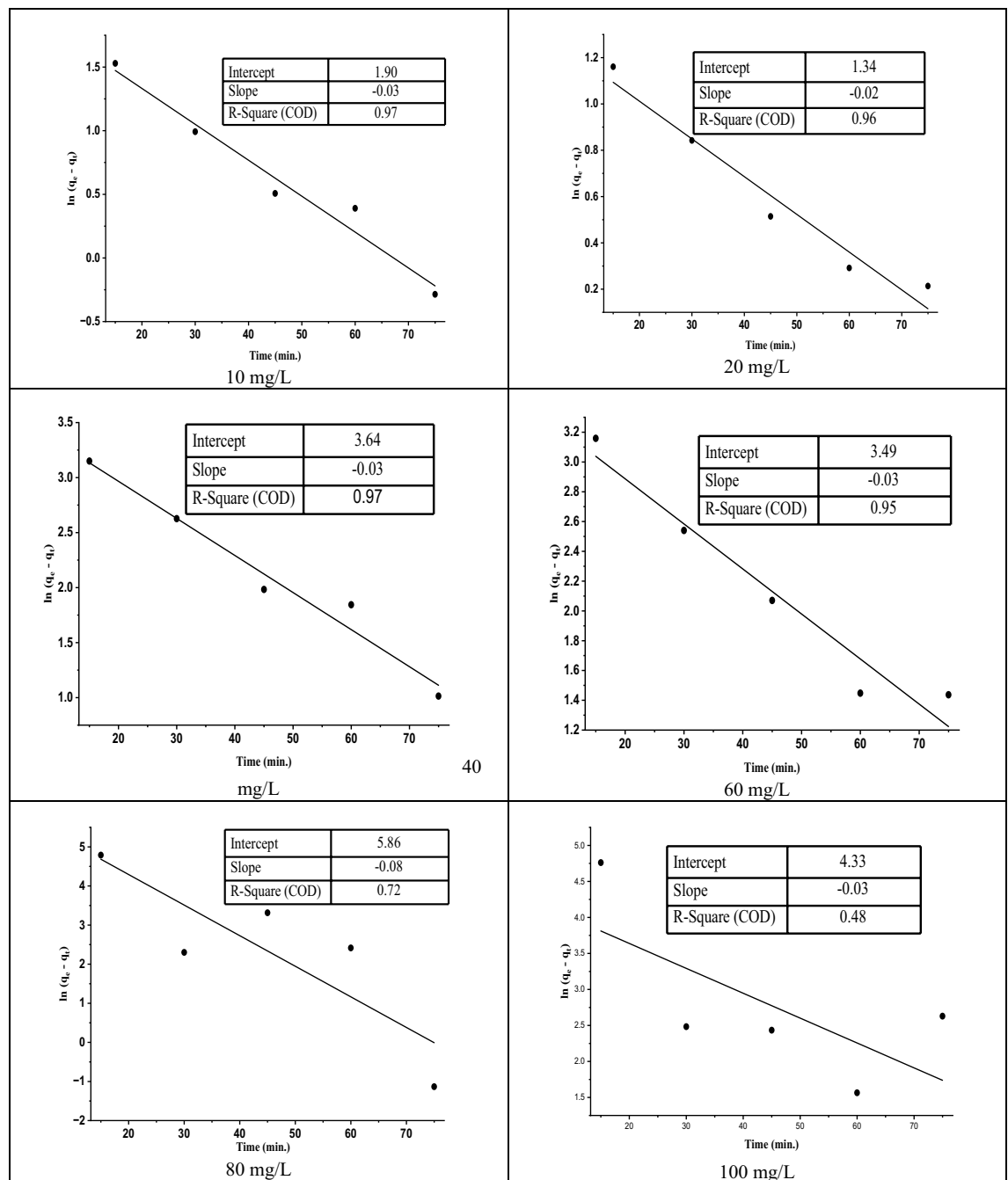


Fig. 6. Pseudo-first-order model of CIP on the hydrogel at different concentrations.

Conc. (mg/L)	q_e (exp.) (mg/g)	q_e (cal.) (mg/g)	k_1 (min^{-1})	R^2
10	47.25	6.68	0.03	0.97
20	92.91	3.82	0.02	0.96
40	162.10	38.09	0.03	0.97
60	243.71	32.79	0.03	0.95
80	254.02	350.72	0.08	0.72
100	317.21	75.94	0.03	0.48

Table 1. The kinetic parameters for the pseudo first order model.

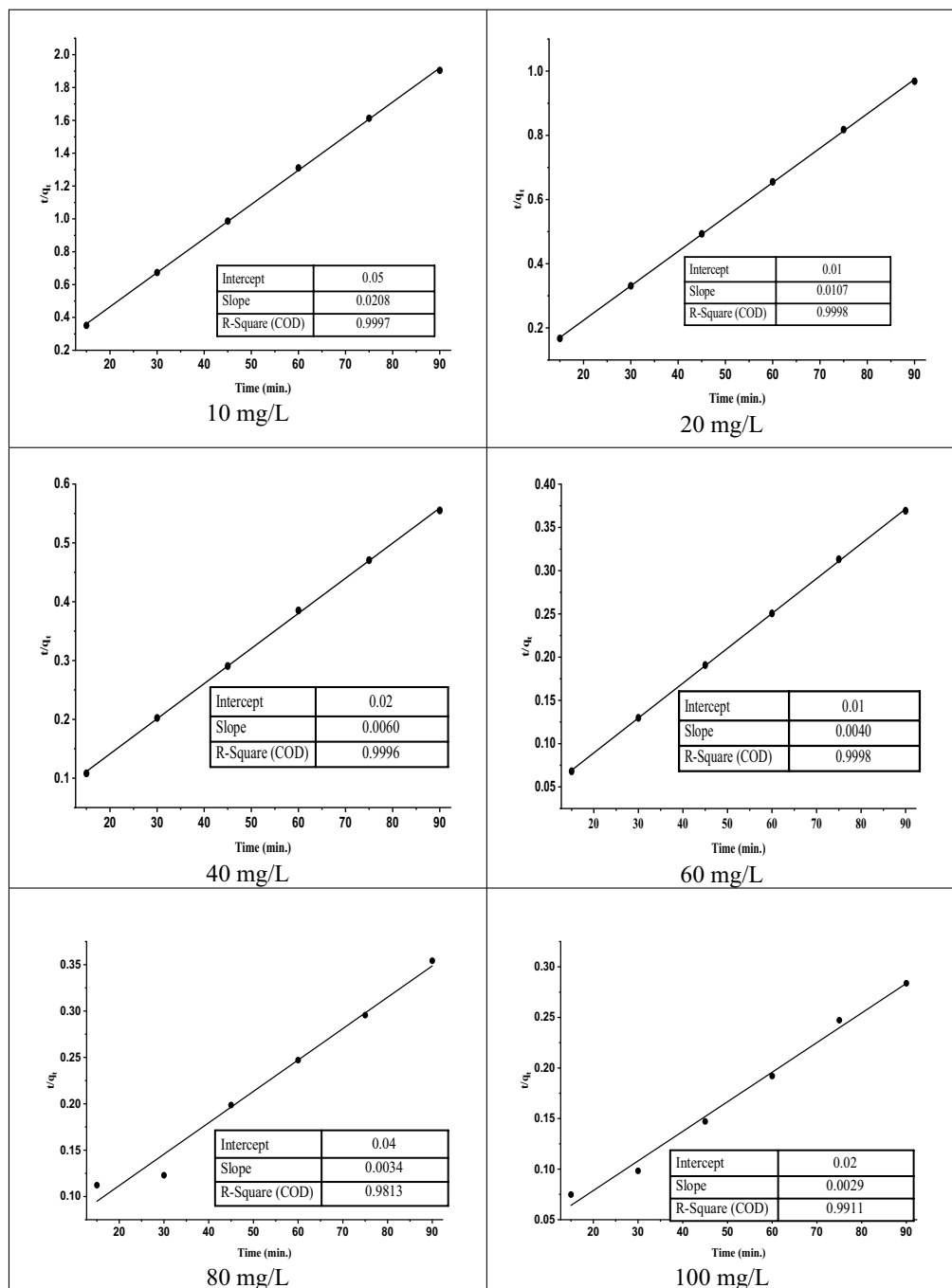


Fig. 7. Pseudo-second-order model of CIP on the hydrogel at different concentrations.

Conc. (mg/L)	q_e (exp.) (mg/g)	q_e (cal.) (mg/g)	k_2 (g. mg ⁻¹ .min ⁻¹)	R^2
10	47.25	48.1	0.009	0.9997
20	92.91	93.6	0.0114	0.9998
40	162.10	166.7	0.0018	0.9996
60	243.71	250	0.0016	0.9998
80	254.02	294.1	0.00029	0.9813
100	317.21	344.8	0.00042	0.9911

Table 2. The kinetic parameters for the pseudo second order model.

As shown above the data show excellent fitting linear relationships in all initial concentrations from 10 to 100 mg/L which proves that our system follows a pseudo second order kinetic model with a likely strong adsorption and interaction mechanism that may involve chemical bonding (chemisorption) as controlling step by electron sharing or electron transfer. The value of the squared correlation coefficient, R^2 , all R^2 values are very high, especially from 10 to 60 mg/L (all >0.999). Even at higher concentrations (80–100 mg/L), R^2 shows high value (0.98+), which are higher compared to the pseudo-first-order model. So Pseudo-second-order model fits the data significantly better overall concentration ranges studied, especially at high concentrations where the first-order model failed.

The calculated q values are very close to experimental values, especially for 10–60 mg/L. At 80 and 100 mg/L, the q value is slightly overestimated, but still within reasonable range. The values of k_2 decrease with increasing concentration while slightly fluctuating, there is a general decrease in k_2 as the concentration increases, especially beyond 40 mg/L because of higher concentrations. This is because more active sites are occupied, and the adsorption slows down per unit time leading to lower k_2 values and this is typical in adsorption systems approaching site saturation.

Weber–Morris kinetic model The Weber–Morris kinetic model and the Boyd diffusion model will be discussed later, are used to characterize the rate-determining step of the adsorption process. In this case, two rate-determining steps are considered: films of liquid and intra-particle diffusion while the mass action is ignored⁵³. (Supplement Fig. 3) shows the Weber–Morris model of the adsorption of CIP on the hydrogel at different CIP concentrations. As shown in (Supplement Fig. 3), the fitting of the Weber–Morris model to the adsorption process yielded acceptable linear relationships at concentrations from 10 mg/L to 60 mg/L. While at relatively higher concentrations of 80 and 100 mg/L the plot of q_t versus $t^{1/2}$ deviates from linearity. It was previously shown that linear relationships of the Weber–Morris model suggest that intra-particle diffusion dominates the kinetics of adsorption⁵⁴. In this case the adsorption kinetics of CIP on the hydrogel is controlled by the intra-particle diffusion at relatively lower concentrations. As the concentration increases the rate-determining step of the adsorption process is not only dominated by intra-particle diffusion. Therefore two scenarios are considered: intra-particle diffusion takes place and boundary diffusion of the CIP layer on the gel is also possible.

The intra-particle mass transfer diffusion suggested by Weber and Morris can be represented by the following Eq.⁵⁵:

$$q_t = k_i t^{1/2} + C_i \quad (6)$$

In this equation, k_i represents the intra-particle diffusion rate ($\text{mg.g}^{-1}.\text{min}^{-1/2}$); C_i (mg/g) signifies the thickness of the boundary layer. Both the k_i and C_i values can be deduced when a linear relationship is realized in the Weber–Morris model plot.

The following intra-particle diffusion rates are obtained as 0.77, 0.50, 3.99 and 3.90 $\text{mg.g}^{-1}.\text{min}^{-1/2}$ at concentrations of 10, 20, 40 and 60 mg/L, respectively. While the C_i values are: 40.04, 87.78, 125.31 and 207.64 mg/g , respectively. In general, it is concluded that as the rate of intra-particle diffusion increases the increase in C_i -values reflects the rise in the boundary layer⁵⁶. More information is obtained by considering other models to analyze the results such as the Boyd model⁵⁷.

The results of the kinetic parameters and initial calculated adsorption rate values with each concentration are listed in (Supplement Table 1).

Boyd plot To confirm the adsorption mechanism of CIP on the hydrogel in the present study, the Boyd plot was used and further investigated. The B_t is expressed by the following Eq. (7) where B_t is a mathematical function of F ($F = q_t/q_e$)⁵⁸, q_e and q_t are the amount of CIP adsorbed on the sorbent (mg/g) at equilibrium and at time t , respectively:

$$B_t = -\ln\left(1 - \frac{q_t}{q_e}\right) - 0.4977 \quad (7)$$

The Boyd plot profile was obtained by plotting the calculated B_t versus time t as depicted in (Fig. 8). The linearity of the plots provides useful indicator to differentiate between external mass transfer and intra-particle diffusion controlled mechanism of adsorption. It was observed that the plots did not pass through the origin, indicating that external mass transfer is involved in the entire adsorption process. Henceforth, the intra-particle diffusion and the external mass transfer have driving involvement in adsorption of CIP over the hydrogel. The results of the kinetic parameters values with each concentration are listed in (Supplement Table 2).

Effect of the amount of hydrogel (hydrogel dose)

In order to determine the optimum amount of hydrogel for the efficient removal of CIP, the adsorption experiments were performed by adding 100–500 mg of hydrogel to a series of 100 ml beakers containing each 20 mg/L CIP solution. It was obvious that by increasing the dosage of the hydrogel to 200 mg, the removal percentage is increased that was followed by no significant increase (Supplement Fig. 4). Therefore, 200 mg hydrogel dose was chosen to be the optimum amount of hydrogel to be used for CIP adsorption. In (Fig. 9) it was also shown that at 100 mg gel dose there was an increase in the removal % at 90 min then almost no further adsorption takes place while at 200, 300 and 400 mg gel dose there was a rapid increase in removal till 45 min then no significant increase afterwards. At hydrogel dose of 500 mg, it could be conclude that the equilibrium was attained after 15 min and this could be attributed to the fact that high amount of hydrogel dose infers a large

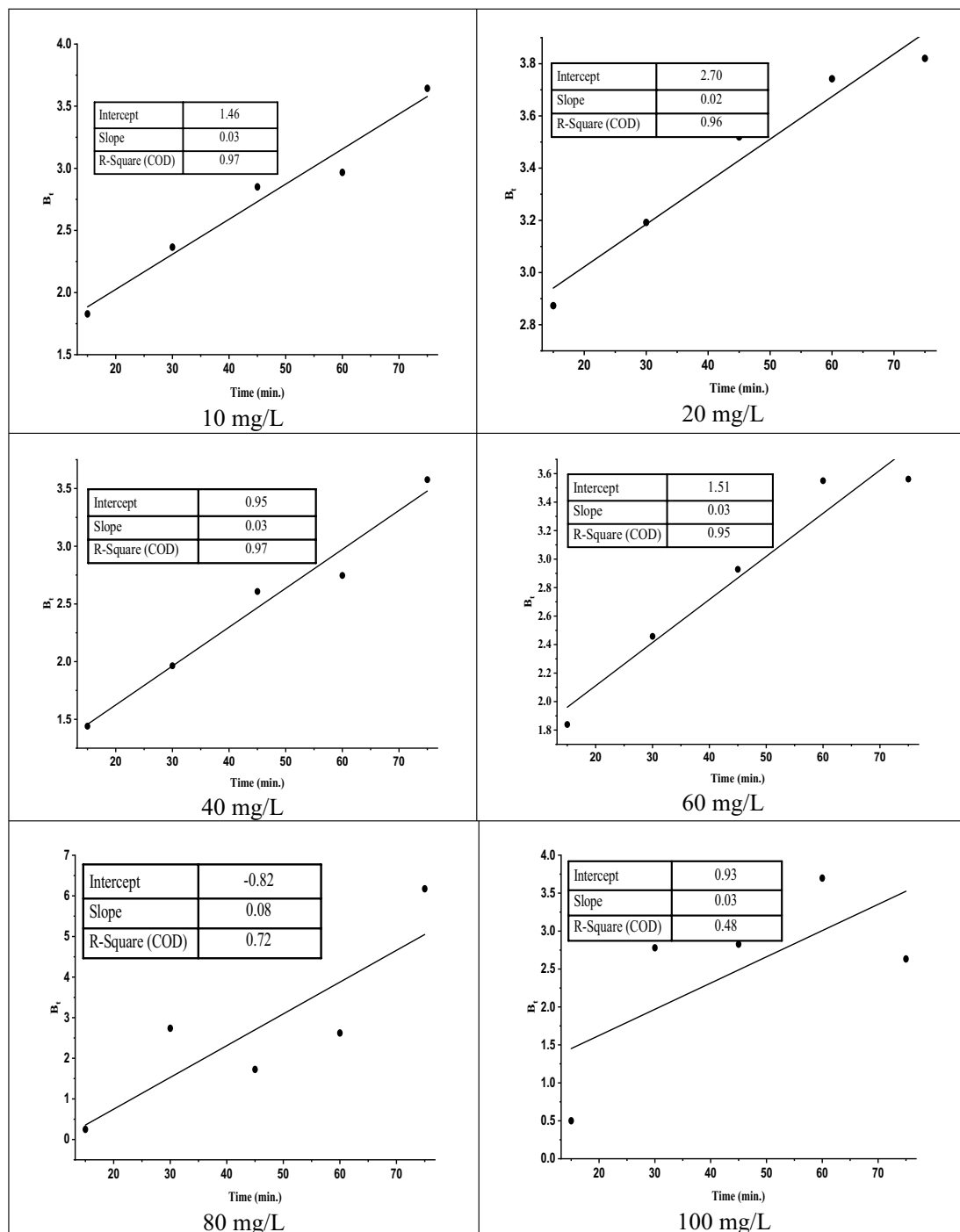


Fig. 8. Boyd Plot model of CIP on the hydrogel at different concentrations.

surface area available for adsorption at the beginning of the interaction and then no more sites are available or saturation of these sites is clear due to the aggregation caused by CIP adsorption.

Applying the previous four models of kinetics on the effect of gel dose on the adsorption process reveals also that the pseudo second order model is the one that best fits the process as shown in the following (Fig. 10).

Effect of pH

In this part, a 50 mL aliquot of 20 mg/L of CIP was applied to test the adsorption performance of the hydrogel at different pH values. The result is shown in (Supplement Fig. 5). It is shown that the adsorption reaches relatively higher values at pH 5.4 and 9 than that at pH 7. CIP has two pKa values 5.9 and 8.9 where it is present as a zwitterion between those pH values and consequently it is expected that no electrostatic attraction takes place with the adsorbent surface. While at pH values rather than 7, there is an extra electrostatic attractions of CIP

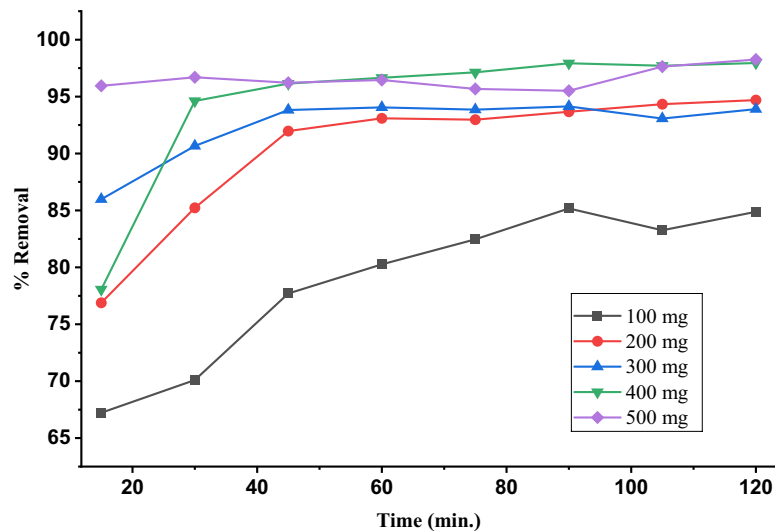


Fig. 9. Effect of hydrogel dose (100–500 mg) on removal of CIP with time.

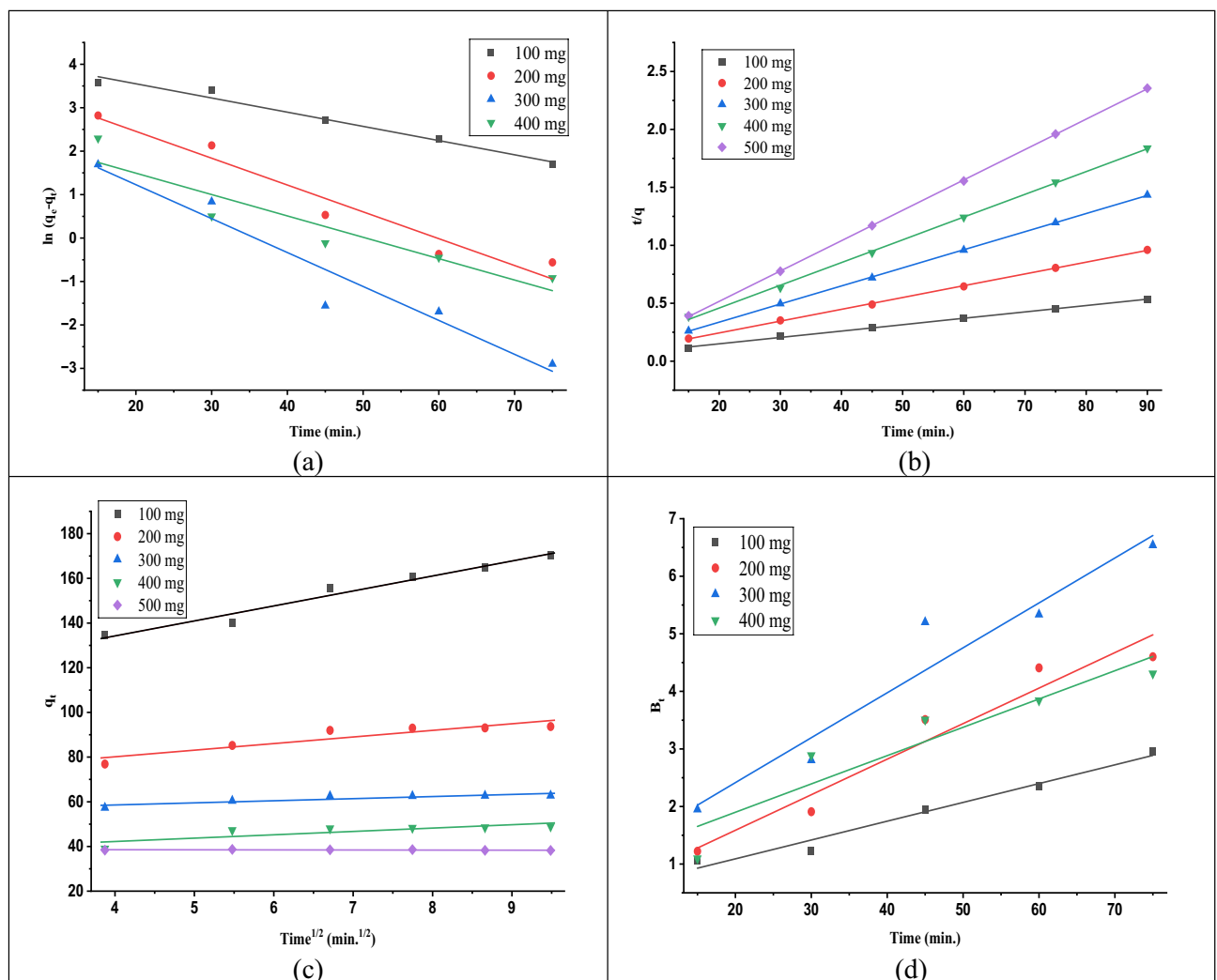


Fig. 10. Kinetics models for the effect of hydrogel dose 100 mg – 500 mg: (a) Pseudo first order; (b) Pseudo second order; (c) Weber Morris model and (d) Boyd plot.

Isotherm models	Equation	Parameters Value
Langmuir	$\frac{c_e}{q_e} = \frac{1}{k_L q_{\max}} + \frac{c_e}{q_{\max}}$	K_L L/mg 0.03 $q_{\max}$ 333.33 R^2 0.97
Freundlich	$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e$	K_f mg/g 70.10 $1/n$ 0.43 R^2 0.959
Temkin	$q_e = B_T \ln k_T + B_T \ln c_e$	K_T L/g 3.43 B_T J/mol 60.15 R^2 0.94

Table 3. Adsorption isotherm parameters for the adsorption of CIP on hydrogel.

Adsorbents	Maximum adsorption capacity (mg/g)
Al-MOF/rGO alginate beads ⁶³	40.76
MIL-101(Fe)/HAP/Fe ₃ O ₄ composite ⁶⁴	112.35
MIL-100-based imprinted MOF polymer ⁶⁵	273.65
Fe/Ni-MOF bimetallic ⁶⁶	232.1
Porphyrinic Zr-MOF ⁶⁷	207.16
Co-doped UiO-66 ⁶⁸	45.17
Zr-MOF@AC composite was synthesized using banana peel-derived activated carbon ⁶⁹	280.08

Table 4. Adsorption capacities for some adsorbents towards ciprofloxacin.

towards the surface of adsorbent also ciprofloxacin has different zeta potential values depending on the medium where for example at acidic medium till pH = 5 zeta potential is positive, at neutral medium it shifts to a slight negative value while at basic medium pH 9 and above the values for zeta potential increase in negativity⁵⁹.

Applying the previous four models of kinetics on the effect of pH on the adsorption process reveals also that the pseudo second order model is the one that best fits the process as shown in (Supplement Fig. 6).

Adsorption isotherms

Langmuir adsorption isotherm

The adsorption of CIP was observed to increase until equilibrium. The equilibrium adsorption isotherm is usually described by the following Eq.

$$\frac{c_e}{q_e} = \frac{1}{k_L q_{\max}} + \frac{c_e}{q_{\max}} \quad (8)$$

Where $q_{\max}$ is the maximum monolayer adsorption (mg/g) and K_L is the Langmuir constant related to the affinity of binding sites (L/mg). The Langmuir isotherm constant is determined from the plot of C_e/q_e versus C_e . The obtained isothermal constants and correlation coefficients are shown in Table 3. The plot in (Supplement Fig. 7) shows a straight line with $R^2 = 0.97$ which reveals that the adsorption equilibrium obeys the Langmuir equation. The calculated maximum adsorption capacity ($q_{\max}$) was 333.33 mg/g as shown in Table 3 which is considered a very good value compared to literature as shown in Table 4. The shape of the isotherm has been discussed to predict whether the adsorption system is favorable or unfavorable^{60–62}. The essential feature of the Langmuir isotherm can be expressed in terms of R_L , a dimensionless constant known as the separation factor or equilibrium parameter. R_L is calculated by the following Eq.

$$R_L = \frac{1}{1 + K_L C_0} \quad (9)$$

In this study, as shown in (Supplement Fig. 8) the equilibrium parameter R_L is between 0 and 1, so the adsorption process is quite favorable.

Freundlich adsorption isotherm

The widely used empirical Freundlich equation based on adsorption on heterogeneous surfaces is given by the following equation:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e \quad (10)$$

Where, k_F and $1/n$ are Freundlich constants indicating the adsorption capacity (mg/g) and intensity, respectively. The Freundlich isotherm constant was determined from the graphs of $\ln q_e$ versus $\ln C_e$ at 298 K. The obtained isotherms and correlation coefficients are shown in Table 3 and (Supplement Fig. 9). The Langmuir and Freundlich isotherm models showed good matching with experimental data. It can be seen that the adsorption

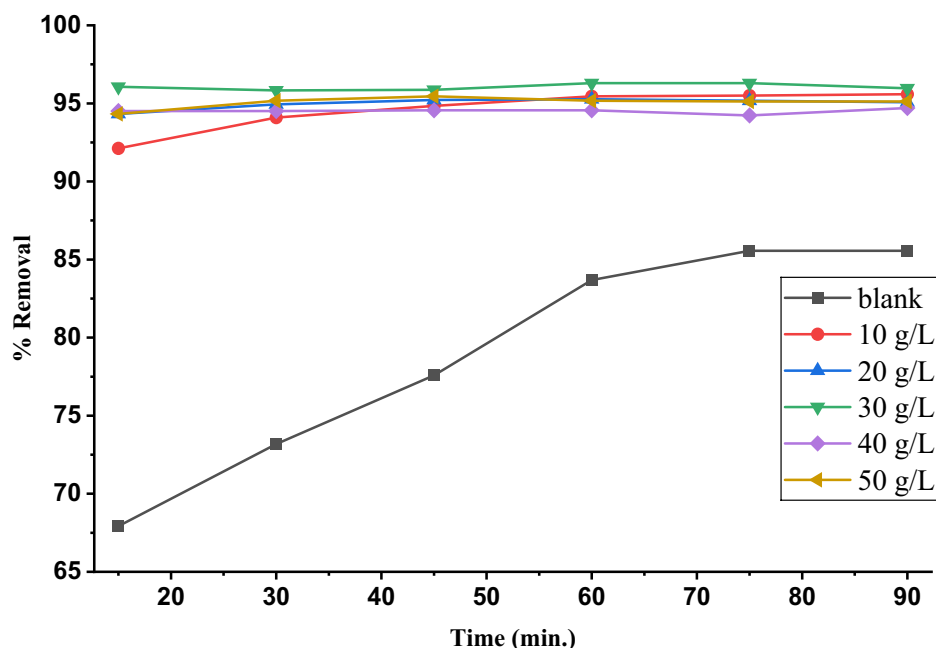


Fig. 11. Effect of salinity on adsorption of CIP.

of CIP on hydrogel has correlation well with the Langmuir equation ($R^2 > 0.97$) in the concentration range given and moderate ($R^2 > 0.95$) with the Freundlich equation. Therefore, the Langmuir isotherm fits better with experimental data which implies that the removal of drug proceed via monolayer adsorption. Also from the BET measurements it was found that the pore volume for UiO-66 is ranging between 0.059 and 0.063 cm^3/g while the average volume for ciprofloxacin molecules is only about 3.3 to $3.6 \times 10^{-22} \text{ cm}^3$ which means that the drug molecule can fit properly inside the MOF pores.

Temkin adsorption isotherm

Temkin's isotherm equation assumes that the heat of adsorption of all molecules in the layer decreases linearly with the coverage of the molecules because the adsorbate-adsorbate repulsions and the adsorption of adsorbate are uniformly distributed. And the reduction in the heat of adsorption is linear rather than logarithmic. The linearized Temkin Eq.⁶¹ is given by the following equation:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (11)$$

where $B_T = RT/b$ is the constant relative to the heat of adsorption (J/mol), T is the absolute temperature (K), R is the ideal gas constant 8.314 (J/mol), b is the constant related to the heat of adsorption (J/mol) and K_T is Temkin's isotherm constant (L/g). The isotherm constants B_T and K_T are calculated from the slope and intercept of the plot q_e as a function of $\ln C_e$ as shown in (Supplement Fig. 10) and (Table 3).

Effect of matrix on adsorption efficiency

Effect of humic acid

The effect of adding different concentrations of humic acid on the adsorption efficiency is illustrated in (Supplement Fig. 11). The concentrations used were 1, 5 and 10 mg/L humic acid in 50 mL of CIP solution. The data shows that the addition of humic acid enhances the adsorption efficiency of CIP especially at lower concentrations (1 mg/L) suggesting that small amounts of humic acid facilitate the interaction and binding of CIP to the adsorbent. At higher humic acid concentrations (5 mg/L and 10 mg/L), the decrease in removal efficiency indicates that while humic acid can enhance adsorption, increasing amounts may lead to saturation or competitive interactions that hinder the adsorption process.

Applying the previous four models of kinetics on the effect of humic acid on the adsorption process reveals also that the pseudo second order model is the one that best fits the process as shown in the following (Supplement Fig. 12).

Effect of salinity

The effect of adding different concentrations of NaCl on the adsorption efficiency is illustrated in (Fig. 11). The concentrations used were 10, 20, 30, 40 and 50 g/L NaCl. The data shows that the addition of NaCl enhances the removal of CIP as the equilibrium is reached after 15 min of reaction. While increasing the concentration of NaCl has no significant effect on the extent of removal indicating that even low concentrations of NaCl can enhance the adsorption process. This enhancement may be attributed to the increased ionic strength offered by NaCl that facilitates better interaction between CIP and the adsorbent due to the competition of NaCl ions with

antibiotic on water molecules in the favor of NaCl ions forcing the antibiotic molecules towards the pores of MOFs. These results highlight the importance of using NaCl as an effective additive in adsorption processes for CIP removal, offering a cost-effective and efficient solution for water treatment applications.

The four models of kinetics were applied on the effect of salinity on the adsorption process reveals also that the pseudo second order model is the one that best fits the process as shown in the following (Supplement Fig. 13).

Effect of added anions

The effect of adding 1 mmol of different anions on the adsorption efficiency is illustrated in (Supplement Fig. 14). The figure shows that, the addition of anions enhances the removal efficiency of CIP, with Cl^- and NO_3^- which shows the most significant improvements. On the contrary, the addition of SO_4^{2-} anion appears to have less pronounced effect on CIP removal.

These variations in removal percentage may be attributed to the different chemical properties and interactions of the anions with CIP. For instance, Cl^- and NO_3^- anions are monovalent anions that enhance better interaction and adsorption with CIP molecules. On the other hand, the divalent SO_4^{2-} anions might result in different interaction mechanism, leading to a less removal efficiency.

The previous four models of kinetics were applied on the effect of different interfering anions on the adsorption process reveals also that the pseudo second order model is the one that best fits the process as shown in the following (Supplement Fig. 15).

Effect of added cations

The effect of adding 1 mmol of different cations on the adsorption efficiency is illustrated in (Supplement Fig. 16) shows that the addition of cations significantly improves the removal efficiency of CIP with Na^+ and Ca^{2+} showing the most pronounced effects.

The previous four models of kinetics were applied on the effect of different interfering cations on the adsorption process reveals also that the pseudo second order model is the one that best fits the process as shown in the following (Supplement Fig. 17).

Limitation of the study

During the bench-scale batch trials, a major operational limitation was the very viscoelastic tackiness and sticky surface properties of the native UiO-66 hydrogel matrix. The sonochemical assembly of the network without subsequent stiff polymer scaffolds yields a wet gel with a very cohesive and viscous surface, which makes accurate physical manipulation and gravimetric weighing during the dosing phase challenging.

Quantitative green chemistry metric

In our study, the prepared UiO-66 was obtained in the form of a hydrogel, not as a pure dry powder framework. Since a hydrogel network contains a large and variable amount solvent within its matrix this makes the calculation of a standard empirical Process Mass Intensity (PMI) or E-factor based on the mass of isolated dry product is mathematically impossible and would not truly represent the structural nature of our material. However, we still can calculate the Atom Economy (AE) for the chemical formation of the ideal UiO-66 structural unit from our precursors from the equation below⁷⁰ and it was found to be very efficient 56.8%.

$$\text{Atom Economy(\%)} = \left(\frac{\text{Molecular Weight of your MOF}}{\text{Total Molecular Weight of ALL Reactants}} \right) \times 100 \quad (12)$$

Concerning energy consumption MOF was synthesized via ultrasonication using an ultrasonic probe at room temperature with no external heating.

The sonochemical synthesis of pure UiO-66 hydrogel takes 30 min at room temperature and costs only 0.030 \$ per batch. Using high-purity Sigma-Aldrich reagents, the entire batch of tests costs only \$12.262, resulting in a remarkably low cost of 0.339 \$ per gram (about 34 cents) for the ready-to-use hydrogel. Solvents employed in the synthesis and washing stages account for over 91% of this cost, therefore industrial solvent recycling loops can further lower hydrogel production costs. The material is viable for scale-up to real-world water treatment because to its low energy requirements, unit cost, and direct hydrogel network utilization.

Conclusions

The Zr- MOF was prepared using ultrasonic probe and was used to perform the adsorption experiments for ciprofloxacin from aqueous solutions. Results showed that the maximum adsorption capacity was 333.33 mg/g. Furthermore, the presence of humic acid increases the adsorption from about 67 to 93% at the first 15 min even for the addition of low concentration from the acid, also addition of NaCl as interfering matrix enhances the adsorption process especially at the first 15 min from about 67% to 93% while the different concentrations of NaCl has no significance. Kinetic and isotherm studies showed that the adsorption process follows pseudo second order kinetics and Langmuir adsorption isotherm which indicates that the removal process proceed via monolayer adsorption with a likely strong adsorption and interaction mechanism which may involve chemisorption as controlling step. Also as CIP is present as zwitterion at pH 5.9 and 8.9 so it is favorable to perform the adsorption experiment near those values where there is extra electrostatic attraction of CIP towards adsorbent surface. The presence of some interfering anions as Cl^- and NO_3^{2-} was found to increase the removal percentage of CIP rather than the divalent anions. For the interfering cations also the presence of both the monovalent and divalent cations increases the removal percentage. UiO-66 hydrogel is an excellent super adsorbent for application of water/wastewater decontamination from pharmaceutical pollutants.

Data availability

All the data are included in the manuscript and in the supplement.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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