Construction of Multifunctional NH₂-UiO-66 Metal Organic Framework: Sensing And Photocatalytic Degradation of Ketorolac Tromethamine And Tetracycline In Aqueous Medium

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Abstract

Existence of pharmaceutical residues in water has endangered environmental pollution worldwide, which makes it ineludible to develop prospective bifunctional materials which not only possess excellent fluorescence behaviour to monitor pharmaceuticals but also exhibits simultaneous photocatalytic removal efficiency. Strengthened by functionalized metal organic framework (MOF) materials, we present here an amine functionalized zirconium based MOF $\text{NH}_2\text{-UiO-66}$ which has been successfully synthesized using solvothermal approach. The as prepared MOF was subjected to numerous structural, morphological and compositional characterizations. Interestingly, featured by the excellent fluorescent intensity of MOF modulated by LMCT effect, $\text{NH}_2\text{-UiO-66}$ was screened to detect pharmaceutical compounds with KTC and TC in aqueous solution. The prepared functionalized MOF showcased excellent sensing platform with magnificent response range (0–3 μM), lower limit of detection (160 nM; KTC and 140 nM; TC), excellent selectivity and influential anti-interference capability. More importantly, the practical utility of the proposed sensor was further explored for the determination of pharmaceutical drugs in real water samples with suitable recoveries. Simultaneously, the synthesized MOF also exhibited high photocatalytic efficiency towards the removal of KTC and TC under solar light irradiation. The degradation efficiency for KTC and TC was found to be 68.3 % and 71.8 % within 60 and 280 min of solar light, respectively. Moreover, excellent recyclability was demonstrated by the current synthesized system over five cycles. Overall, this study presents a feasible route for the utilization of functionalized MOFs as potential dual functional materials towards the simultaneous detection and degradation of specific pharmaceuticals from aqueous medium.

Introduction

Potential hazards derived from the continuous and improper ejection of new contaminants into water has governed serious issues related to natural environment and human health globally. Typically, the release of contaminants encompasses wastes from agrochemicals, veterinary, hospitals, human excreta, food additives industries and pharmaceuticals. The pharmaceuticals are oftenly more dangerous and non biodegradable compounds and mainly constitutes anticonvulsants, β -blockers, hormones and lipid regulators, nonsteroidal anti-inflammatory drugs (NSAIDs), contrast agents and antibiotics (Awfa et al. 2018). The escalation in demand for these drugs has evolved in the production of several pharmaceuticals, resulting in direct discharge of these biological and chemical compounds into almost all aquatic matrices, involving groundwater, surface water and even drinking water (Khan et al. 2020). Amongst the various existing pharmaceuticals, NSAIDs and antibiotics owing to their excessive utilization for clinical purposes/medicines have been frequently identified in water samples (Rasheed et al. 2020; Uresti et al. 2016).

Ketorolac tromethamine (KTC) is widely employed as NSAID while tetracycline (TC) is most prevalently used antibiotic. With high analgesic activity, KTC is being used for reducing acute pains (Wagh et al. 2019). Biologically, half life of KTC is short which therefore requires dose repetition to sustain therapeutic level. This long period exposure of KTC dose may results in several complexities such as severe renal

failure, peptic ulceration and gastrointestinal toxicity (Reinhart 2000; Suhail et al. 2021). Likewise, TC, which is well known for its major use in veterinary and aquaculture medicines, is also associated with diseases such as liver damage, hepatic dysfunction because of its overconsumption (Xu et al. 2018). Release of both KTC and TC into the environment occurs directly via wastewater and indirectly through metabolised by-products of various other chemicals and has been determined at concentrations upto $\mu\text{g/mL}$ in effluent wastewater (Mabrouk et al. 2021; Chu et al. 2016). Considering the frequent usage and associated threats of these pharmaceutical drugs, development of an efficacious approach for incessant monitoring and treatment of residues in water necessitates urgent administration.

Until now, numerous common methods including Raman spectroscopy, high performance liquid chromatography (LCMS), mass spectrometry (MS), capillary electrophoresis, ion mobility spectrometry and LC with UV detection (LC-UV) have been progressed in literature for the quantitative detection of pharmaceuticals (Maduraiveeran et al. 2018; Blasco et al. 2009; Novakova et al. 2006; Gonzalez et al. 2015; Pena et al. 2009; Camara et al. 2013). Nevertheless, these analytical techniques are still not well effectively developed by virtue of their higher cost, careful handling, professional operator and incommensurate pretreatment (Wang et al. 2015; Chatzimitakos et al. 2020). Noticeably, fluorescence (FL) sensing ascribing to higher sensitivity, lower cost, easier handling and energy savings is being considered as the prominent approach for quantitative determination of pharmaceutical compounds. On the other side along with detection, removal of these carcinogenic compounds is also important for which different strategies have been delineated such as membrane filtration, adsorption, chemical precipitation, biodegradation, chemical reduction/oxidation, photocatalytic degradation and ion exchange (Li et al. 2010; Daghrir et al. 2013; Xiong et al. 2017). To address the environmental problems efficiently, photocatalytic degradation amongst all the methods has evolved as the propitious one and gained tremendous interest of researchers. Persuading above findings, framing an influential approach to integrate detection and photocatalysis together into one scaffold will be devastatingly favourable for the simultaneous recognition and degradation of pharmaceutical drugs.

One of the most arousing categories of nanomaterials; MOFs, have been triggering colossal attraction by scientists in recent times. Exhibiting various networks, MOFs are esteemed for their exceptional properties viz. permanent porosity, peculiar electronic and optical properties, excellent designability, large surface area and smoothly tailored structures (Zhao et al. 2020; He et al. 2018) which bestows them to be utilized in prospective fields like sensing, separation, gas sorption, drug delivery, adsorption, catalysis etc. (Parmar et al. 2020; Gupta et al. 2020; Kavak et al. 2019; Abazari et al. 2018; Abazari et al. 2018; Newar et al. 2020). Benefited from such distinctive features, MOFs are further capable to be decorated at different parts via introducing different functionalities into MOF structure comprising metal nodes/clusters, organic linkers and empty void inside the framework (Razavi et al. 2019). Realizing this, abundant functionalized MOFs have been engineered because of countless availability of the organic functional groups in the world of chemistry. The linker functionalization of MOFs provides easier access to host guest interactions between competitive molecules and MOFs imparting us with excellent desired characteristics for enhanced detection and removal of wide range of contaminants.

Remarkably, functionalization of MOFs with amine (-NH_2) groups due to their reactivity and basicity can effectively be used for improving the efficiency of MOFs. In accordance therefore, amine functionalized Zr based UiO-66 is one of the tempting MOF amongst several reported MOFs. Constructed from 2-aminoterephthalate organic linkers and cationic Zr_6O_{32} clusters, NH_2 -UiO-66 is widely investigated material for various applications owing to its excellent adjustability, higher aqueous stability and optical activity (Ahmadijokani et al. 2020; Long et al. 2012; Cavka et al. 2008). Concerning sensing applications, the availability of free electrons on amine functionality have tendency to act as strong recognition sites and form coordinate bonds with analytes, which enhances selectivity of MOF towards target analytes (Zhang et al. 2018). Recently, Zhu and co-workers reported the detection of fluoride ions utilizing highly fluorescent NH_2 -UiO-66 (Zhu et al. 2019). In another study, quantitative determination of Cu(II) was investigated by Wu *et al.* employing NH_2 -UiO-66 as FL sensor (Wu et al. 2016). Captivated by this material, some more studies regarding detection of aspirin (Xu et al. 2016), DNA (Zhang et al. 2014), formaldehyde (Vellingiri et al. 2017), NO (Desai et al. 2015), phosphate (Yang et al. 2015) and nitrite (Hao et al. 2020) have also been sketched in literature. Besides detection, immobilization of amine group in MOFs also renders its crucial role in photocatalytic reactions by endowing more extent in conjugation which thereby extends the light absorption capability of MOFs (Sun et al. 2018; Chen et al. 2016). Silva and group studied hydrogen generation using NH_2 -UiO-66 and UiO-66 (Silva et al. 2010) while Long et al. 2008 employed NH_2 -UiO-66 as photocatalyst for aerobic organic transformations. Sun et al. 2018 successfully prepared Zr modified MOF by the use of extended conjugated amine linker and explored it as a photocatalyst for CO_2 reduction. However, studies concerning the detection and degradation of pharmaceutical compounds is scarcely been reported. Hence stimulated by these findings, further advancement in the utilization of amine functionalized MOFs for monitoring pharmaceutical compounds will be highly conducive. To construct a precise bifunctional system including two major applications i.e. sensing and photocatalysis on one platform largely remains a significant challenge according to studies. So far as we know, there is no record on the viability of NH_2 -UiO-66 as a dual functional material for the simultaneous detection and removal of both KTC and TC in aqueous phase. Therefore, the current research presents a suitable and easy going approach for the treatment of pharmaceutical drugs.

Herein, we proffers a strategy for exploring simultaneous recognition and photocatalytic removal of KTC and TC in aqueous phase by employing amine functionalized UiO-66, synthesized by facile solvothermal method. The fabricated material has been characterized by various spectroscopic and analytical techniques. Various process parameters each for detection and photocatalysis were optimized throughout experimental procedures. Furthermore, scavenger studies were also investigated to estimate the probable photocatalytic mechanism. Additionally, practical applications have also been demonstrated by detecting KTC and TC in real water samples.

Experimental Section

Materials used

All reagents purchased for this work are commercially available and were of analytical grade and used as received. Cobalt nitrate hexahydrate ($\geq 98\%$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium carbonate ($\geq 99.5\%$, Na_2CO_3), 2-amino terephthalic acid (99%, $\text{NH}_2\text{-BDC}$), tetracycline ($\geq 88\%$, TC; $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8$), ciprofloxacin ($\geq 98\%$, CPX; $\text{C}_{17}\text{H}_{18}\text{FN}_3\text{O}_3$), ibuprofen ($\geq 98\%$, IBP; $\text{C}_{13}\text{H}_{18}\text{O}_2$) and paracetamol (98–102%, PCM; $\text{C}_8\text{H}_9\text{NO}_2$) were procured from Sigma Aldrich. Zinc sulphate monohydrate (99–102%, ZnSO_4), hydrochloric acid (36.5–38%, HCl), copper chloride dihydrate ($\geq 99\%$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), lead nitrate ($\geq 98.5\%$, $\text{Pb}(\text{NO}_3)_2$), mercury sulphate ($\geq 99\%$, HgSO_4), sodium fluoride ($\geq 99\%$, NaF), iron chloride hexahydrate ($\geq 99\%$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide ($\geq 97\%$, NaOH), *p*-benzoquinone ($\geq 98\%$, BQ; $\text{C}_6\text{H}_4\text{O}_2$), potassium iodide ($\geq 99\%$, KI) and formic acid ($> 99\%$, HCOOH) were bought from Merck, India. Sodium nitrate (98%, NaNO_3), silver nitrate (99.8%, AgNO_3), dimethylformamide (99%, DMF) and sodium sulphite (98%, Na_2SO_3) were obtained from Fischer Scientific, India. Calcium chloride (90%, CaCl_2) and zirconyl chloride octahydrate (99.9%, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) were purchased from S. D. fine chem. Ltd. and Sisco Research Laboratories Pvt. Ltd. (SRL), India. Sodium chloride ($\geq 99\%$, NaCl), aluminium nitrate nonahydrate (95%, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium bromide ($\geq 99\%$, NaBr), chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 98%) and amoxicillin ($\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_5\text{S}$, AMX) were obtained from Himedia, India. Levofloxacin (LVX), ofloxacin (OFX) and ketorolac tromethamine (KTC) were gifted by Saurav Chemicals Limited, Derabassi, India. Aspirin was procured from Central Drug House Pvt. Limited (CDH), New Delhi, India. Double distilled water was used during the whole experimentation.

Characterizations

Several spectroscopic and analytical characterization techniques were employed to examine the nature of fabricated MOF. PANalytical X'Pert PRO diffractometer using Cu K α radiation was utilized for examining the X-ray diffraction (XRD) pattern and crystal properties of the prepared material at 2θ of 5° – 80° . The existence of distinct functional groups was scrutinized by Fourier transform infrared (FTIR) spectroscopy which was carried over Nicolet iS50 FTIR spectrophotometer (Thermo Scientific). Hitachi-8010 microscope and JEM 2100 Plus were used for investigating the FESEM (field emission scanning electron microscopy) and HRTEM (high resolution transmission electron microscopy) images of the synthesized material, respectively. Shimadzu UV – vis spectrophotometer (UV-2600) was utilized for the measurement of the optical properties, taking BaSO_4 as a reference material. Thermal analysis of MOF was investigated by TGA (thermogravimetric analysis), TA SDT650 system, TA instruments; USA under N_2 atmosphere with heating rate of $10^\circ\text{C}/\text{min}$. Photoluminescence spectrum was conducted at an excitation wavelength of 330 nm to explore the fluorescence behavior of the prepared material. X-ray photoelectron spectroscopy (XPS) was recorded on PHI 5000 Versa Probe III model (Physical Electronics). MicrotracBEL analyzer was employed for calculation of specific surface areas and sample was degassed at 120°C for 24 h before measurements. Mettler Toledo pH meter (FEP20) was used to adjust the pH of the solutions.

Synthesis of $\text{NH}_2\text{-UiO-66}$

For the synthesis of zirconium based MOF i.e. $\text{NH}_2\text{-UiO-66}$, simple solvothermal method was carried out as reported in literature (Cavka et al. 2008; Cao et al. 2018). In short, 2 mmol (0.645 g) of zirconyl chloride octahydrate was dispersed in 30 mL DMF followed by the addition of 2 mL glacial acetic acid and kept under stirring for 20 min. Separately, another solution of $\text{NH}_2\text{-BDC}$ (4 mmol; 0.724 g) was prepared in 20 mL DMF. The two solutions were then mixed and stirred vigorously for 60 min. The resultant mixture was then switched to stainless steel teflon lined autoclave and kept in an oven for 24 h at a constant temperature of 120 °C. After the completion of reaction, the procured yellow precipitates were completely washed with a mixture of ethanol and DMF to remove any other impurities in the mixture. Finally, the product was obtained by drying it overnight at 80 °C in an oven.

FL detection of KTC and TC using $\text{NH}_2\text{-UiO-66}$

At first, the capability of $\text{NH}_2\text{-UiO-66}$ for the determination of drugs was explored by immersing 0.01 mg/mL of MOF into double distilled water accompanied by ultrasonication for 15 min. Concurrently, stock solutions of various available drugs (AMX, ASP, LVX, IBP, PCM, OFX, CPX, TC and KTC) and some cationic and anionic species each of 10^{-3} M concentration were prepared in distilled water. Afterwards, a mixture was prepared by the addition of 1 mL aqueous solution of drugs into 1 mL MOF stock solution in a cuvette followed by FL measurements at 330 nm excitation wavelength. Moreover, sensitivity of the fabricated sensor was also examined by adding different concentrations of quenched analyte into stock solution of MOF (1 mL). All the FL assessments were examined at room temperature with some fixed parameters i.e. excitation and emission wavelength as 330 and 430 nm, respectively, response time – 0.5 s, PMT voltage as 330 V and spectral bandwidth as 5 nm.

Evaluation of photocatalytic activity for KTC and TC

The photoactivity of $\text{NH}_2\text{-UiO-66}$ was estimated by the degradation of KTC and TC under natural solar irradiation with average intensity of 55–70 Klux. Initially, certain amount of photocatalyst was suspended in 100 mL of drug solution which was stirred under dark conditions for 30 min to attain adsorption-desorption equilibrium. Afterwards, the suspended solution was irradiated to solar light followed by the extraction of 2 mL of sample from suspension (0.45 μm syringe filters) after the distinct time intervals. Then, UV-Vis spectrum of the collected samples was recorded and the degradation efficiency was calculated as mentioned:

$$\text{Percentage degradation} = [1 - (C/C_0)] \times 100$$

where C and C_0 signifies the concentrations of KTC and TC after and before exposure to sunlight.

Results And Discussions

Characterization of prepared $\text{NH}_2\text{-UiO-66}$

The structural properties of the fabricated MOF were examined using powder XRD technique. Figure 1(a) represents the XRD pattern of $\text{NH}_2\text{-UiO-66}$ with typical Bragg peaks positioned at $2\theta = 7.34^\circ, 8.6^\circ, 12.06^\circ, 17.16^\circ, 19.01^\circ$ and 25.8° . The attained peaks showed good agreement with the simulated pattern as described in literature (Cavka et al. 2008; Chen et al. 2015). The broadness in diffraction peaks depicted less crystallinity of the prepared material. No other peaks corresponding to impurities except for the MOF were detected. Further, FTIR spectrum was probed to determine the functional groups existing in $\text{NH}_2\text{-UiO-66}$ structures (Fig. 1(b)). The characteristic peaks obtained in the FTIR spectrum ranges from $500\text{--}4000\text{ cm}^{-1}$. The absorption bands at lower frequencies i.e. $579, 654$ and 763 cm^{-1} were due to the $\text{Zr}\text{--}(\text{OC})$ symmetric stretching, $\text{O}\text{--}\text{H}$ bending and $\text{Zr}\text{--}\text{O}$ bond vibrations, respectively (Ramezanzadeh et al. 2021; Jin et al. 2017; Han et al. 2015). Moreover, the intense peaks due to stretching modes of $\text{C}\text{--}\text{N}$ bond and carboxylate groups were obtained at 1238 and 1380 cm^{-1} , respectively (Kaur et al. 2020; Molavi et al. 2018). The other peaks allocated at 1571 and 1686 cm^{-1} reflected the presence of $\text{C}=\text{C}$ and $\text{C}=\text{O}$ (carbonyl) functional groups, respectively in the synthesized MOF (Aghajanzadeh et al. 2018). Lastly, the weak peaks occurring at 3370 and 3472 cm^{-1} were accredited to the presence of amino i.e. NH_2 group (Zhang et al. 2016; Neeli et al. 2018).

To ascertain the electronic states of constituent elements existing in the fabricated MOF, XPS measurements were carried out as displayed in Fig. 2. Concretely, all peaks associated to elements Zr, C, O and N were traced in the full scan spectrum of the prepared MOF (Fig. 2(a)). The deconvoluted curves shown in Fig. 2(b) depicted Zr 3d region centered at 182.6 eV and 184.9 eV assigned to $\text{Zr } 3d_{5/2}$ and $\text{Zr } 3d_{3/2}$, respectively, reflecting the presence of Zr(IV) state (Du et al. 2020). In Fig. 2(c), the denconvoluted C 1s spectrum exhibits sharp peaks positioned at $284.4, 285.8$ and 288.3 eV , ascribed to the $\text{C}=\text{C}$ functional group, $\text{C}\text{--}\text{NH}_2$ species and the carbonyl ($\text{C}=\text{O}$) group of terephthalate linkers, respectively (Su et al. 2017; Subudhi et al. 2020). Figure 2(d) delineates the O 1s high resolution XPS spectrum at binding energy of 531.7 eV which corresponded to the O atoms in the coordinated carboxylate (--COOH) groups of amino terephthalate linkers (Hu et al. 2019; Chen et al. 2020). N 1s XPS spectrum displayed peak around 399.2 eV which could be attained due to the existence of N component in the amino (--NH_2) group (Fig. 2(e)) (Hu et al. 2019; Chen et al. 2020).

In order to scrutinize the textural properties i.e. porosity and surface area of the prepared material, BET measurements were conducted. Figure 3(a) demonstrates N_2 adsorption desorption type IV isotherm curve exhibiting sharp rise in lower pressure region which represents the existence of microporous framework (Du et al. 2020; Shen et al. 2013). Also, the hysteresis loop appearing at relatively higher pressures witnessed the accumulation of pores (Shen et al. 2013; Shen et al. 2013). The BET surface area and total pore volume of $\text{NH}_2\text{-UiO-66}$ were calculated to be $199\text{ m}^2/\text{g}$ and 0.1845 cc/g , respectively. Mean pore diameter was determined by BJH desorption curve as showed in Fig. 3(b) and was measured to be 3.715 nm . The obtained surface area bestows as a good characteristic for providing more active sites and adsorbing more contaminants, which thereby contributes to improved photocatalytic efficiency (Hu et al. 2019).

Apart from this, another significant parameter for investigating the photocatalytic proficiency of the prepared MOF is its optical absorption property. UV-Vis DRS studies were conducted over NH₂-UiO-66 in an order to determine the band gap energy as shown in Fig. 3(c) which unveiled the strong absorption of NH₂-UiO-66 in the range 200–460 nm (Meng et al. 2019). The absorption of NH₂-UiO-66 is keenly ascribed to LMCT i.e. ligand to metal charge transfer mediated by Zr-O clusters in the MOF (Yang et al. 2015). In addition, tauc plot, $(ah\nu)^n = A(h\nu - E_g)$ was used for measuring the band gap energy as outlined in inset of Fig. 3(c), where $h\nu$, E_g , α and A corresponds to the photon energy, band gap energy, absorption coefficient and proportionality constant, respectively (Jyotsna et al. 2020). The value of n varies for different semiconductors based on the type of optical transitions and $n = 1$ for NH₂-UiO-66 as it goes through direct transition (Liu et al. 2020; Jaswal et al. 2021). Correspondingly, the band gap of the prepared material was computed to be 2.5 eV. The thermal stability of as-synthesized NH₂-UiO-66 was assessed by TGA as sketched in Fig. 3(d). The TGA curve describes three major weight loss stages. The first weight loss i.e. 12.21 % was observed around 15 °C–160 °C temperature range which could be attained due to the desorption of moisture from the MOF. Another weight loss stage which occurred in the range 170 °C–600 °C was due to the evaporation of DMF solvent and dehydroxylation of Zr-O clusters which was about 37.99 % (Yang et al. 2018). The third and last weight loss above 600 °C with approximately 21.22 % was attributed to the decomposition of the organic molecules in the framework (Chavan et al. 2014; Liu et al. 2016). Thus, TGA results displayed high thermal stability of the synthesized NH₂-UiO-66.

Further, the morphologies of the prepared MOF were examined utilizing the imperative techniques like FESEM and HRTEM as outlined in Fig. 4. Figure 4(a–c) describes the FESEM images of the fabricated material which reveals that NH₂-UiO-66 exhibits rectangular cuboid shaped crystals along with some agglomeration. For further morphological elucidation of NH₂-UiO-66, HRTEM was carried out as displayed in Fig. 4(d–f). The attained images sketched the similar kind of morphology as FESEM. In addition, average size of about 80–100 nm length and 35–45 nm thickness was attained for NH₂-UiO-66. Therefore, it can be concluded that images achieved through both techniques were consistent to each other. Moreover, elemental mapping and EDX analysis were employed to further confirm the existence of Zr, C, O and N elements which are in step with the above characterizations perfectly as displayed in Fig. 5.

Luminescence properties of as-synthesized NH₂-UiO-66

Luminescence properties of the prepared MOF were investigated at room temperature and the results are presented in Fig. 6. Figure 6(a) describes the effect of different excitation wavelengths on the FL intensity of MOF and maximum FL intensity was observed at 330 nm with prominent emission peak at 430 nm. Hence, for all the successive FL measurements the optimized excitation wavelength was fixed as 330 nm. Another important parameter i.e. impact of ionic strength on MOF's FL intensity was also explored by addition of different concentrations of NaCl as shown in Fig. 6(b). No significant change was noticed on the FL spectrum indicating high stability of the prepared sensor. Furthermore, FL behavior of NH₂-UiO-66 was tested under different pH conditions as delineated in Fig. 6(c). For this purpose, HCl and NaOH each

of 0.1 M concentration were employed for the preparation of different solutions of MOF with pH varying from 2–12. From the graph, it is clear that FL emission intensity increased from pH 2 to pH 6 initially, which afterwards becomes nearly constant between 6–10 and then decreased at higher pH values. In acidic conditions MOF exhibited lowest FL emission intensity owing to the protonation of $-\text{NH}_2$ group to $-\text{NH}_3^+$ which ruins the conjugation in the system and thereby weaker FL emission. The fabricated MOF's fluorescence nature displayed substantial stability in the pH range of 6–10 at room temperature and thus natural pH i.e. 7 was selected as the optimized pH. Accordingly, the excitation wavelength and pH were optimized as 330 nm and 7, respectively. Further, photostability of MOF was also examined where the nature of FL intensity was compared after months and negligible change was remarked which again depicted the high stability of $\text{NH}_2\text{-UiO-66}$ in aqueous solution (Fig. 6(d)).

Selective detection of KTC and TC in aqueous solution using $\text{NH}_2\text{-UiO-66}$ as a FL probe

Considering the above excellent FL properties of the synthesized $\text{NH}_2\text{-UiO-66}$, it was further looked for the FL detection capability of the most commonly employed drugs. To establish this, FL response towards different drugs such as AMX, ASP, LVX, IBP, PCM, OFX, CPX, TC and KTC was figured out as displayed in Fig. 7(a). It was noticed that no significant change occurred in the FL intensity of MOF with the addition of these drugs except for TC and KTC to a great extent which is further evident from Fig. 7(b).

Additionally, to monitor the selectivity of the fabricated sensor, some other cationic and anionic species were also taken into account. From Fig. 7(c), no apparent change was discernable on the FL intensity of MOF with these species which states the selective behaviour of MOF for TC and KTC. Besides, impact of interference on the specificity of MOF with mixed drugs was also determined (Fig. 7(d and e)). From graph, it was concluded that the introduction of these mixed competitive species did not interfere with the quenching effect of KTC and TC and thereby, confirmed the specific response of the fabricated fluorogenic sensor. Therefore, great affirmation of the considerable recognition capability of $\text{NH}_2\text{-UiO-66}$ for KTC and TC detection was witnessed by the current sensing system.

Sensitivity of the prepared sensor

By virtue of the excellent selectivity of the MOF, we were immensely encouraged to further understand the FL quenching degree i.e. sensitivity of the MOF. For this, KTC ($0\text{ }\mu\text{M}$ – $7.91\text{ }\mu\text{M}$) and TC ($0\text{ }\mu\text{M}$ – $7.5\text{ }\mu\text{M}$) were added incrementally to the aqueous solution of $\text{NH}_2\text{-UiO-66}$ as visualised in Fig. 8 (a and c) after which the emission spectra was recorded. It was found that the FL emission intensity gradually fades away upon encountering the increase of KTC and TC concentrations in the testing system. Accordingly, excellent linear correlation was disclosed by the present sensor between F_0/F and KTC/TC concentrations in the range $0\text{ }\mu\text{M}$ – $3\text{ }\mu\text{M}$ (Fig. 8(b and d)). Furthermore, in the aforementioned linear ranges, the detection limit was calculated to be 160 nM and 140 nM for KTC and TC, respectively utilizing the slope and deviation of the obtained calibration curve. Moreover, Stern-Volmer equation was used for rationalizing the quantitative description of quenching effect which is as follows:

$$F_0/F = 1 + K_{SV} [C] \quad (1)$$

where [C] corresponds to the analyte's concentration, K_{SV} represents the Stern-Volmer constant, and F_0 and F depicts the emission intensities of $\text{NH}_2\text{-UiO-66}$ in the absence and presence of analyte (Kaur et al. 2020). The K_{SV} values were determined to be $1.2 \times 10^3 \text{ M}^{-1}$ and $1.6 \times 10^4 \text{ M}^{-1}$ for KTC and TC, respectively.

Proposed sensing mechanism towards KTC and TC with $\text{NH}_2\text{-UiO-66}$

Keeping in view the previous studies, the plausible FL quenching mechanism of MOF towards KTC and TC was further elucidated. In general, several detection mechanisms i.e. skeletal destruction, guest adsorption and light energy competition have been accounted in literature for the FL quenching of MOFs (Goswami et al. 2019; Yao et al. 2019; Zhu et al. 2020). From Fig. 13(c), the obtained PXRD pattern was unaffected after sensing experiments (5 cycles) for the detection of KTC and TC and no change in the crystallinity was observed which ruled out the probability of skeletal damage. Furthermore, Fig. 13(d), exhibiting the FTIR spectra after the recyclability showed the consistency with the original MOF which clearly reveals that guest molecule adsorption was also not the reason for quenching. Afterwards, the UV-vis absorption spectra of all the drugs was recorded and shown in Fig. 9. From the graph, no overlapping in the absorption spectrum of analytes was discernable with the excitation spectrum of MOF in the region 200–450 nm except KTC and TC which presented larger overlapping extent. This suggested that the excitation light of $\text{NH}_2\text{-UiO-66}$ was strongly absorbed by KTC and TC and hence, the FL quenching mechanism was mainly ascribed to the light energy competition, resulting in high selectivity and sensitivity.

Recovery in different water samples

To access the feasibility of $\text{NH}_2\text{-UiO-66}$ for practical applications, standard addition method was employed on real water samples. To accomplish this test, initially different water samples from Sukhna lake (Chandigarh), Satluj river (Ropar) and tap water were collected and filtered. Afterwards, different known concentrations of KTC and TC were spiked into the real water samples. As displayed in Table 1, excellent recoveries are attained by the synthesized fluorogenic sensor and are in good accordance with the original introduction of KTC and TC concentrations. Thus, good reliability and practicality for the quantification of KTC and TC in real samples was exhibited by as-prepared $\text{NH}_2\text{-UiO-66}$

Table 1
Detection of KTC and TC in real water samples

Samples	Added (μM)	Found (μM)		Recovery (%)	
		KTC	TC	KTC	TC
Tap water	0.476	0.472	0.481	99.1	101.05
	1.66	1.597	1.577	96.2	95
	3.75	3.69	3.50	98.4	93.3
	5	4.51	4.64	90.2	92.8
Sukhna (Lake water)	0.476	0.472	0.482	99.1	101.2
	1.66	1.696	1.605	102.1	96.3
	3.75	3.69	3.65	98.4	97.3
	5	5.01	4.98	100.2	99.6
Satluj (River water)	0.476	0.516	0.489	108.4	102.7
	1.66	1.75	1.59	105.4	95.7
	3.75	3.92	3.81	104.5	98.4
	5	4.93	4.87	98.6	97.4

Photocatalytic degradation of TC and KTC over $\text{NH}_2\text{-UiO-66}$ under solar illumination

The light harvesting properties of the prepared MOF were determined for the photocatalytic degradation of drugs, where KTC and TC were opted as the target pollutants. To achieve the desired optimal conditions, different parameters like pH of drug solution, loading of catalyst and initial drug concentration were examined by accomplishing series of experiments.

For the photocatalytic reactions to be carried out, the foremost factor to optimize is pH of the solution as it exhibits significant impact on surface properties of the photocatalyst, interactions among pollutants and charged species and hydrolysis of pollutants (Dehghan et al. 2018). Therefore, the pH effect on the degradation of KTC and TC was examined by varying pH of both the solutions. Figure 10(a) revealed that the pH of KTC solution was varied from 4–10 where 10 mg/L was fixed as the initial concentration and catalyst dose was kept 0.25 g/L. As demonstrated, the degradation efficiencies of KTC after 60 min of solar irradiation were 58.4, 64.2, 33.8 and 15 % at pH 4, 6, 8 and 10, respectively, pointing pH 6 (natural pH) as the optimum pH value for whole photocatalytic experiments. The point of zero charge of $\text{NH}_2\text{-UiO-66}$ has been reported to be 7.6 in literature (Zhuang et al. 2019). Therefore, the surface of the MOF is positively charged at pH values smaller than 7.6 and negatively charged at pH values greater than 7.6. It

has been observed that KTC possess pK_a value of 3.5 which means that KTC drug exhibits cationic behaviour at $pH < 3.5$ and anionic behaviour at $pH > 3.5$ (Chaturvedi et al.2019). Therefore, the efficient photodegradation of KTC onto NH_2 -UiO-66 can occur effectively at $pK_a^{KTC} < pH < pH_{zpc}$, because of the electrostatic interactions. Hence, for KTC the maximum degradation efficiency of 64.2 % was attained at natural pH i.e. 6 within 60 min of solar irradiation.

Now taking into account the degradation of TC, the variation in pH of TC solution was done from 2–8 keeping fixed the catalyst dose i.e. 0.25 g/L and TC concentration at 10 mg/L as outlined in Fig. 10(b). It was observed that with increase in pH from 2 to 4 the degradation efficiency increases from 54.3% to 61.7 % in the time period of 280 min under the irradiation of solar light. Upon further increasing the pH above 4 the photocatalytic degradation decreases i.e. at pH 6 and pH 8 the degradation results were achieved to be 54.2 and 39.8 %, respectively. Since TC possesses three pK_a values therefore it can form three molecular species i.e. cationic at $pH < 3.3$, zwitterionic in the pH range 3.3–7.68 and anionic at $pH > 7.68$ (Guo et al. 2021). The maximum photocatalytic degradation is obtained at pH 4, where the behaviour of TC drug is either anionic or cationic and the surface of the photocatalyst i.e. NH_2 -UiO-66 is cationic at this pH. Therefore, pH effect on the degradation of TC cannot be described by the ionization effect between TC and photocatalyst (Kaur et al. 2018). Hence, the optimal pH value for KTC and TC were obtained as 6 and 4, respectively.

Afterwards, the optimal NH_2 -UiO-66 dosage was examined by executing experimentation at different doses under solar light. Figure 10(c) reveals the dose variation from 0.15 g/L to 0.45 g/L for the photocatalytic degradation of KTC keeping other parameters affixed i.e. $pH = 6$ and drug concentration = 10 mg/L. It can be inferred from the graph that when the catalyst dose was increased from 0.15 g/L to 0.25 g/L the photocatalytic efficacy was significantly increased from 57.8 % to 67.5 %. This could be mainly due the availability of more number of active sites for the degradation of KTC. However, upon further increase in catalyst dose, small dip in the degradation efficiency was observed which can be reasoned on account of the growth of turbidity with increased NH_2 -UiO-66 concentration which thereby inhibits light penetration (Xue et al. 2015). The similar explanation goes with the degradation of TC where the decomposition extent was found to be 45.5, 52.7, 62.7 and 59.7 % with catalyst loading 0.05, 0.15, 0.25 and 0.35 g/L, respectively (Fig. 10(d)). Therefore, the optimized dose for the degradation of KTC and TC were found to be 0.25 g/L each.

Considering next key parameter i.e. impact of initial drug concentration was explored on the degradation of KTC and TC by keeping other operational parameters fixed. Figure 10(e) delineates the variation in concentration of KTC drug concentration from 10 to 30 mg/L at optimized natural pH value (i.e. 6) and photocatalyst dose of 0.25 g/L. The degradation efficiencies values for KTC were achieved to be 68.3 %, 55.4 % and 48 % at 10, 20 and 30 mg/L, respectively. Likewise, for TC, Fig. 10(f) describes that the photodegradation extent decreases with increase in initial concentration of TC in the order: 71.8% > 68.8 % > 60.3 % at optimal conditions of $pH=4$ and catalyst dose—0.25 g/L. The observed reduction in photocatalytic efficacy for both KTC and TC was accredited to the decreased penetrating ability of light

with increasing concentration of drug molecules in the solution. Thus, 10 mg/L was found to be the optimal concentration for both KTC and TC.

Figure 11(a) and Fig. 11(b) demonstrate the degradation of KTC and TC, respectively, assessed by time dependent UV-visible absorption spectrum at optimized operational conditions. From graph, significant reduction in the maximum absorption band can be observed with increase in illumination time. This illustrated that 68.3 % of KTC and 71.8 % of TC was degraded under 60 and 280 min of solar irradiation time, respectively. Correspondingly, another experiment to test drug's stability was also performed under same conditions but with no catalyst added. Figure 11(c and d) displayed the photolysis results which stated that both the targeted pollutants were not degraded under the exposure to sunlight. Another control experiment under dark conditions was conducted both for KTC and TC to determine the amount of drug adsorbed on the surface of NH₂-UiO-66 as shown in Fig. 11 (c and d). It was found that about 43.2 % of KTC and 36 % of TC was adsorbed after 60 and 280 min of solar illumination time, respectively.

Further, in order to determine the role of reactive species involved in the degradation process, radical trapping experiments were carried out using different scavengers. Figure 11 (e) displayed the utilization of HCOOH (for electrons), IPA (for hydroxyl radicals), KI (for holes and surface bound hydroxyl radicals) and NaCl (for holes) scavengers and correspondent degradation efficiencies for KTC after 60 min of reaction were found to be 41 %, 50.1 %, 51.2 % and 40.7 %, respectively. It was noticed that the quenching experiments verified the role of all employed scavengers i.e. electrons, holes and hydroxyl radicals. However, the major quenching effect was exhibited by electrons and holes in photocatalytic degradation of KTC using NH₂-UiO-66. Similarly, Fig. 11(f) unveiled 36.3 %, 50.3 % and 42.3 % degradation of TC upon addition of p-Bq (superoxide radicals), IPA and NaCl, respectively, within 280 min of solar illumination. This signified the dominating role of superoxide radicals, hydroxyl radicals and holes in the degradation of TC over the synthesized MOF.

Possible photocatalytic mechanism

Based on the aforementioned experimental results, Fig. 12 represents the possible photocatalytic mechanism for the degradation of KTC and TC over NH₂-UiO-66. The values of CB and VB edge potentials of MOF were calculated by the use of following mathematical equations:

$$E_{VB} = X - E_f + 0.5 \cdot E_g$$

$$E_{CB} = E_{VB} - E_g$$

where the term E_{VB} and E_{CB} represents the valence band and conduction band potential, respectively, and E_g is the band gap of NH₂-UiO-66 obtained by Fig. 3(c). E_f refers to the energy of free electrons (4.5 eV) and X is the electronegativity of NH₂-UiO-66 (5.3 eV) (Du et al. 2020). As such, the potentials of 2.05 eV and - 0.45 eV were attained as the VB and CB edge values, respectively, for NH₂-UiO-66. Illuminating the surface of catalyst with solar light resulted in the activation of catalyst leading to the creation of electrons and holes in CB and VB, respectively. The energy level of CB of NH₂-UiO-66 (-0.45 eV) was found

to be more negative than ($E^0(\text{O}_2/\cdot\text{O}_2^-) = -0.33 \text{ eV vs NHE}$) (Wang et al. 2020), indicating that the photogenerated electrons are capable to reduce O_2 , which can further oxidize the pollutants and form $\cdot\text{OH}$ upon reacting with water molecules. Meantime, the higher positive potential (2.05 eV) of $\text{NH}_2\text{-UiO-66}$ than ($E^0(\text{OH}/\cdot\text{OH}) = 1.99 \text{ eV vs NHE}$) (Zhao et al. 2016), was competent to execute the oxidation reaction of OH^- to $\cdot\text{OH}$. Therefore, the degradation of KTC and TC could be ascribed to the redox reactions occurring on the surface of the catalyst.

Recyclability

For practical applications, the usage of $\text{NH}_2\text{-UiO-66}$ as a photocatalyst as well as sensor in long runs can be analysed by determining its stability and reusability. The fabricated MOF was subjected to five cycles each for the detection and degradation of KTC and TC in optimal conditions (Fig. 13(a and b)). For detection, certain amount of MOF was dispersed in 10^{-4} M solution of KTC and TC for 10 min and afterwards struck for multiple washing with water and ethanol. For degradation, reusability was carried out by employing simple filtration method followed by drying. From Fig. 13 (a and b), excellent stability and recyclability of the prepared material can be observed for the simultaneous detection and photocatalytic removal of drugs after five cycles. Moreover, XRD and FTIR of the reused catalyst (after fifth cycle) was also carried out which confirmed the structural stability of the $\text{NH}_2\text{-UiO-66}$ by displaying no obvious changes (Fig. 13(c and d)). Thus, the fabricated MOF was highly stable and reusable making it suitable for realistic applications.

Conclusions

To conclude, synthesis of dual functional $\text{NH}_2\text{-UiO-66}$ and its utilization as sensor as well as photocatalyst for the simultaneous determination and removal of some pharmaceutical drugs has been reported. In particular, specific FL behaviour towards KTC and TC was observed with linear correlation ranging from 0–3 μM and lower detection limits. As a superb sensing platform, the prepared MOF was also validated for the reliable detection of KTC and TC in real water samples. Not only this, $\text{NH}_2\text{-UiO-66}$ also demonstrated high performance photoactivity for removal of KTC and TC under natural sunlight. Moreover, the fabricated bifunctional material exhibited excellent recyclability towards the recognition and degradation of KTC and TC over five cycles. These cumulative attributes of $\text{NH}_2\text{-UiO-66}$ endows unique potential for the efficacious treatment of pharmaceuticals in aqueous phase.

Declarations

Conflicts of interest

There are no conflicts of interest among authors.

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Data availability

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Ethical approval: Not applicable

Consent to participate: Informed consent was obtained from all individual participants included in the study.

Consent to publish: The participant has consented to the submission of the case report to the journal.

Author's contributions: **Manpreet Kaur:** Conceptualization, Methodology, Data curation, Writing-original draft. **Surinder Kumar Mehta:** Conceptualization, Resources, Data curation, Writing-original draft and Supervision. **Sushil Kumar Kansal:** Conceptualization, Resources, Data curation, Writing-original draft and Supervision.

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Figures

Figure 1

Typical (a) XRD pattern and (b) FTIR spectrum of as-prepared NH_2 -UiO-66

Figure 2

XPS spectrum (a) Full scan of NH₂-UiO-66, (b) Zr 3d, (c) C 1s, (d) O 1s and (e) N 1s

Figure 3

(a) N₂ adsorption-desorption isotherm, (b) BJH pore size distribution, (c) UV-DRS absorbance spectra (inset shows Tauc plot) and (d) TGA curve of NH₂-UiO-66

Figure 4

Typical (a-c) FESEM images and (d-f) HRTEM images of NH₂-UiO-66

Figure 5

Elemental mapping images of (a) Zr, (b) C, (c), O, (d) N, and (e) EDX spectrum of NH₂-UiO-66

Figure 6

Impact of (a) different excitation wavelengths, (b) varied NaCl concentrations, (c) pH and (d) photostability on the FL emission spectra of synthesized NH₂-UiO-66 at room temperature

Figure 7

(a) Extent of the FL response of NH₂-UiO-66 MOF in the presence of various drugs (10⁻³ M), (b) FL spectra of MOF in the presence and absence of KTC and TC (10⁻³ M), (c) Bar graph depicting FL behavior of MOF towards different cations and anions (10⁻³ M), and (d, e) FL emission intensities of NH₂-UiO-66 over mixed drugs each of 10⁻³ M concentration for KTC and TC, respectively

Figure 8

(a and c) FL emission spectra of NH₂-UiO-66 with addition of different concentrations of KTC and TC, (b and d) Stern-Volmer curve for FL quenching of NH₂-UiO-66 by KTC and TC, respectively

Figure 9

UV-vis absorption spectra of drugs and excitation spectrum of NH₂-UiO-66

Figure 10

Effect of various operational parameters (a, b) pH, (b, c) catalyst loading, (d, e) initial drug concentration on the photodegradation of KTC and TC, respectively in the presence of solar light

Figure 11

UV-vis absorbance spectra of (a) KTC (pH 6, 10 mg/L) and (b) TC (pH 4, 10 mg/L) with $\text{NH}_2\text{-Uio-66}$ loading 0.25 g/L, (c, d) Comparison between photolysis, adsorption and photocatalysis with $\text{NH}_2\text{-Uio-66}$ for KTC and TC both, (e, f) Role for different scavengers in the photodegradation of KTC and TC under optimized conditions

Figure 12

Plausible photocatalytic mechanism of $\text{NH}_2\text{-UiO-66}$ towards the degradation of KTC and TC under solar light irradiation

Figure 13

(a and b) Reusability of $\text{NH}_2\text{-UiO-66}$ towards the detection and decomposition of KTC and TC, respectively, over five cycles, (c) XRD and (d) FTIR of $\text{NH}_2\text{-UiO-66}$ after five runs

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