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Fabrication of HKUST-1/ZnO/SA nanocomposite for Doxycycline and Naproxen adsorption from contaminated water

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ABSTRACT

Doxycycline and Naproxen are among the most widely used drugs in the therapy of CoVID 19 disease found in surface water. Water scarcity in recent years has led to research to treat polluted water. One of the easy and low-cost methods for treatment is adsorption. The utilize of Metal-Organic Frameworks (MOFs) to evacuate pharmaceutical contaminants from water sources has been considered by researchers in the last decade. In this research, HKUST-1/ZnO/SA composite with high adsorption capacity, chemical and water stability, recovery, and reuse properties has been synthesized and investigated. By adding 10 wt% of ZnO and 50 wt% of sodium alginate to HKUST-1, at 25 °C and pH = 7, the specific surface area is reduced by 60%. The parameters of drugs concentration C₀ = (5,80) mg/L, time = (15,240) min, and pH = (2,12) were investigated, and the results showed that the HKUST-1/ZnO/SA is stable in water for 14 days and it can be used in 10 cycles with 80% removal efficiency. The maximum Adsorption loading of doxycycline and Naproxen upon HKUST-1/ZnO/SA is 97.58 and 80.04 mg/g, respectively. Based on the correlation coefficient (R²), the pseudo-second-order and the Langmuir isotherm models were selected for drug adsorption. The proposed mechanism of drug uptake is by MOFs, hydrogen bonding, electrostatic bonding, and acid-base interaction.

1. Introduction

Water shortage is one of the greatest challenges of the present century and the crisis of the coming decades, especially in water-scarce countries. A crisis that can lead to many changes in the world. Pollution of existing water resources is another problem. Also, organic, metal and porous frameworks can be used for synthesis and reduction of waste materials from different sources (Feng.
Cycline is 15900 and 50000 the second most widely used drug after antibiotics. Naproxen is used to relieve mild to moderate pain caused by various conditions. It is essential to discover effective treatments (Ray and Shaw, 2019). Given the global outbreak of COVID-19 in 2020, and the lack of effective antiviral drugs and vaccines, it is essential to discover effective treatments (Lai, 2020, 2021; Sun and Ostrivko, 2020). Doxycycline and Naproxen are some of the drugs that were studied in connection with the treatment of this disease (Wurtz et al., 2020). Doxycycline is a tetracycline antibiotic that stops the activity of bacteria in some infections of the chest, skin, and around the mouth. The rest of the antibiotics enter the sewage and the environment through human urine and faeces. These materials cause resistance to microbial agents, causing resistant strains (strains) in pathogens. Elimination of isolates resistant to common antibiotics will be very costly (Khanday et al., 2021). Analgesics are essential to discover effective treatments (Lai, 2020, 2021; Sun and Ostrikov, 2020). Doxycycline and Naproxen are some of the drugs used after antibiotics. Naproxen is used to relieve mild to moderate pain caused by various conditions. It is also used to reduce pain, swelling, and stiffness in joints caused by osteoarthritis (Pap et al., 2021). This group of drugs is found within the sewer and most aquatic environments and different soil levels (Czech et al., 2021). The water solubility of Naproxen and doxycycline is 15900 and 50000 μg/L, respectively (Mora and Martínez, 2007; Isidori et al., 2005; Bogardus and Blackwood, 1979; Shen et al., 2020). However, The WHO has confirmed the presence of the remaining 15–25 μg/L high-dose drugs in drinking water (Organization, 2012). This low concentration in water causes diseases and drug resistance in the human body (Housman et al., 2014; Laxminarayan et al., 2011). The removal of these substances in the low concentration in drinking water and even in high concentrations in wastewaters is essential (Li and Li, 2015; Wilkinson et al., 2022; Wee et al., 2022). Studies show that biological treatment is insufficient to decompose this compound, and new methods such as advanced oxidation or adsorption must be used to prevent contamination of natural waters (Ahmed et al., 2017; Deng and Zhao, 2015; Ribeiro et al., 2015; Sillanpää et al., 2018). The design and operation of the adsorption method are very simple and do not produce toxic substances, nor is it expensive. Therefore, the adsorption method is used as an viable and inexpensive method (Seo et al., 2016). The use of surface adsorbents for porous nanostructures, called Metal-Organic Frameworks (MOF), to remove pharmaceutical contaminants from water sources has been considered by researchers over the past decade (Hooriabad Saboor et al., 2022; Beydaghdari et al., 2022). MOFs owing to high porosity, and special surface attractiveness in removing pollutants. These materials absorb pollutants under various mechanisms such as electrostatic forces, hydrophobicity, hydrogen bonding, and π-π bonding (Gao et al., 2018; Canivet et al., 2014). Cu-BTC or HKUST-1, is a MOF including copper ions and 1,3,5-benzene tricarboxylic acid (BTC) (Azhar et al., 2017). Pores of varying size, shape, and polarity have voids promising for the specific adsorption of distinctive gasses (Domann et al., 2019). The slight chemical and water stability of HKUST-1, the low adsorption capacity, and the difficulty of recycling this adsorbent are some of the challenges that scientists face in using this MOF in aqueous media (Burcht et al., 2014). So, HKUST-1 has been used extensively to adsorb pollutants in gaseous environments (Borfecchia et al., 2012; Hulvey et al., 2013; Ló pez-Monreal and Loera-Serna, 2022; Ebrahim and Bandosz, 2022). The results of researches indicate that the adsorption capacity increases by using their proper combination with polymers (Kang et al., 2011; Safy et al., 2020; Perry et al., 2014). Sodium alginate (SA) is a linear polysaccharide derived from alginic acid (Karthik and Meenakshi, 2015). Alginate is used in many foods and therapeutic applications due to its biocompatibility, low harmfulness, low priced, and mellow gelation (Gao et al., 2020). In 2017, Zhuo et al. (2017) combined MIL-101 with SA and polymer beads and investigated the Adsorption loading of MIL-101/SA, MIL-101/CS for ibuprofen, and ketoprofen. The Adsorption loading was expanded by combining MIL-101 with sodium alginate. The adsorption capacity of ibuprofen and ketoprofen were equal to 80 and 140 mg/g. Owing to the adsorption mechanism and the hydrophilicity of sodium alginate (its low water stability), this adsorbent has been used in only one cycle. As a result, by combining MOFs with metal oxides, a stable adsorbent can be achieved in aqueous and chemical environments (Emam et al., 2020; Mahmoody et al., 2019). Also, By increasing the adsorbent stability, the adsorbent can be recovered and used in many cycles with a low removal efficiency percentage. Researchers including Hu (Hu et al., 2020), Wang (Wang et al., 2019), and Gupta (Gupta et al., 2021) show that combining MOFs with zinc oxide increases chemical and aqueous stability. Zinc oxide (ZnO) is mineral material that does not dissolve in water and is widely used in many industries. Researchers have considered this compound because of its chemical stability, high catalytic attributes, cheap price, high adhesion and coating strength, recoverability, and non-toxicity (Di Mauro et al., 2017). In the adsorption process by MOFs, various parameters such as pH, temperature, pollutant concentration, adsorbent mass, etc., affect the performance of the process (Ahmed et al., 2015). For example, Xu et al. (2015) used the HKUST-1 to adsorb Congo red dye. The adsorption capacity is 49.5 mg/g. The mechanism is the pi-pi stacking electrostatic forces. Ma et al. (2022) used the HKUST-1 for adsorption of humic acid. The adsorption capacity is 14.42 mg/g. By expanding the introductory methods, with the aim of increasing the adsorption capacity, and chemical and water stability, and it was used in the adsorption of naproxen and doxycycline drugs. Also, the main factors influence the equilibrium adsorption rate, like pH and adsorption concentration, are studied.

2. Material & methods

2.1. Materials

Zinc acetate dihydrate (CAS NO: 5970-45-6), Copper (II) nitrate trihydrate (CAS NO: 10031-43-3), 1,3,5-Benzene tricarboxylic acid (CAS NO: 554-95-0), Sodium alginate (CAS NO: 9005-38-3), Potassium Hydroxide (CAS NO: 1310-58-3), Triethylamine (CAS NO: 121-44-8), Ethanol (CAS NO: 64-17-5), Methanol (CAS NO: 67-56-1), N, N-Dimethylformamide (DMF) (CAS NO: 68-12-2), Hydrochloric acid (CAS NO: 7647-01-0), and Sodium hydroxide (CAS NO: 1310-73-2) with a purity of more than 99% were procured from Sigma Aldrich. Doxycycline and Naproxen were procured from Iran Daru Pharmaceutical Company of Iran with a purity of 98%. Table 1
reports the physical and chemical attributes of the drugs studied.

2.2. Methods

2.2.1. Preparation of ZnO

Zinc oxide were synthesized according to previous research (Bhakat and Singh, 2012). 195.2 g of Zinc acetate dihydrate was added to 100 ml of water and ethanol solution (80:20) and stirred. 12.1 g of KOH is dissolved in 10 ml of distilled water, and drop by drop is added to the initial solution. The resulting solution was set down in an oven at a temperature of between 80 °C for 3 h. The powder was washed several times with methanol and water. At long last, the suspension was centrifuged, and the resulting gel was dried at room temperature.

2.2.2. Preparation of HKUST-1

HKUST-1 was synthesized by the method reported in the previous study (Azad et al., 2016). In summary, 5 g Cu(NO$_3$)$_3$.3H$_2$O and 1.05 g of benzene tricarboxylic acid were dissolved in 100 ml of a dimethylformamide solution, ethanol, and distilled water (40:40:20), separately. The resulting solutions are then mixed, and 0.5 ml of triethylamine is quickly added to it, and then the solution is transferred to an ultrasonic homogenizer for 20 min. At long last, the powder was dried in a vacuum oven at 120 °C overnight and then transferred to a desiccator.

2.2.3. Preparation of HKUST-1/ZnO

0.15 g of ZnO nanoparticles and 1.6 g of 1,3,5-Benzenetricarboxylic acid were dissolved in 50 ml ethanol. Further, 0.73 g Cu(NO$_3$)$_3$.3H$_2$O was dissolved in 50 ml methanol. Once 30 min, each suspension was mixed and directly transferred to an ultrasonic homogenizer for 5 min. The obtained powder was washed and eventually placed in a vacuum oven at 80 °C for 12 h.

2.2.4. Preparation of composite HKUST-1/ZnO/SA

1.35 g of Cu(NO$_3$)$_3$.3H$_2$O and 0.337 g of 1,3,5-Benzenetricarboxylic acid dissolved in 100 ml of water, ethanol, and dimethylformamide (20:40:40). 1 g of zinc oxide and 0.5 g of sodium alginate dissolved in water. All solutions were combined. After 30 min, 1 ml of triethylamine solution is added and transferred to the ultrasonic homogenizer for 1 h. The resulting powder was washed twice with methanol and placed in a vacuum oven at 80 °C for 12 h.

2.3. Characterization

The X-Ray Diffraction (XRD) was fulfilled via an advanced D8 device (Bruker Co. Germany). In addition, Fourier transforms spectrometer model FT/IR 6300 with the resolution of 4 cm$^{-1}$ manufactured by (JASCO Co. Japan) was used for FTIR analysis. The specific surface area was measured using BELSORP-mini 2 devices (BEL Japan Inc., Japan), with the particle size distribution determined by the SZ-100 device (Horiba Co., Japan). The Field Emission Scanning Electron Microscope (FESEM) analysis was fulfilled using (MIRA III of TESCAN Co., Czech Republic). Also, the drug concentration was measured via spectrophotometric analysis using UV/Vis spectrophotometer DR-5000 device manufactured by (JASCO Co. Japan).

3. Results and discussion

3.1. Characterization

3.1.1. XRD analysis

According to Fig. 1, a peak in the ZnO pattern at 2θ of 31.9, 34.5, 36 indicates the proper synthesis and its high crystal phase (JCPDS card No. 36–1451). In addition, the peaks are shown at 2θ, equaling 6.7, 9.6, and 11.7, demonstrating HKUST-1. Since sodium alginate is an amorphous polymer, its peaks can only be seen in 2θ, 20–25 ° (JCPDS card No. 37–1492). In the pattern (d), the presence of a peak at 2θ of 10.5, 12.6, 14.16 is related to HKUST-1. At the same time, 2θ equals 31.9, 34.5, 36 is associated with the ZnO band in the HKUST-1/ZnO/SA composite, suggesting proper adsorbent synthesis.

3.1.2. FTIR analysis

The FTIR band is captured for HKUST-1 at 400-4000 cm$^{-1}$, where carboxylic and hydroxyl functional group is observed in the

| Table 1 |
|---|
| The attributes of Doxycycline and Naproxen (Damiani et al., 2002; Papich et al., 2013). |
| Drugs | Doxycycline | Naproxen |
|---|---|---|
| Chemical Formula | C$_{22}$H$_{24}$N$_{2}$O$_{8}$ | C$_{14}$H$_{14}$O$_{3}$ |
| Molecular weight (g/mol) | 444.4 | 230.26 |
| Water solubility (μg/L) | 50000 | 15900 |
| pk$_{a}$ | 3.09 | 4.15 |
| λ$_{max}$ (nm) | 360 | 432 |

![Drug structure](image)
structure (Fig. 2a). The band related to C–H is seen at 600-900 cm$^{-1}$. The vibration at the 489 cm$^{-1}$ regions is pertaining with Cu–O vibrations. The C=O band is observed in the 1708 cm$^{-1}$, and vibrations in the 1322-1615 cm$^{-1}$ region pertain to C=C vibrations of the benzene ring. In addition, the vibrancy in the 1230 cm$^{-1}$ region is related to C=O stretching vibrations of carboxylic groups, where an increase in the intensity of these bands is observed upon the binding of the metal to the carboxyl group. According to Fig. 2b, C=O stretch vibrations have been observed at the wavelength of 570–447 cm$^{-1}$. R–COO stretch vibrations are observed at 1496 and 1520 cm$^{-1}$, respectively. At 1640, 2900, and 3410 cm$^{-1}$ wavelengths, vibrations related to C=C (aromatic ring), CO–OH, and O–H can be observed, respectively. In the FTIR band for Zn–O nanoparticles (Fig. 2c), the Zn–O band at 420 cm$^{-1}$ is consistent with the references (Bhakat and Singh, 2012). According to Fig. 2d, the composite strip is synthesized correctly and contains all the strips associated with HKUST-1 and SA plus ZnO.

3.1.3. BET analysis

To determine the specific surface area (SSA), the BET method is used. Fig. 3 shows the BET and the BJH diagram. Consistent with the IUPAC classification (Muttakin et al., 2018), the isotherm kind IV is determined alongside a hysteresis loop, shown in diagrams (a, d). According to diagrams of Fig. 3 (b, c) for HKUST-1/ZnO/SA and HKUST-1, a lower within the specific surface area and isotherm kind III in addition to hysteresis kind III has been identified. Due to the existence of the hysteresis curve, the adsorbent nevertheless has mesopores in which pores are corrugated, resilient, and expansible. BJH diagrams show that adsorbents have meso- and micropores, and the proportions’ distribution of pores is heterogeneous.

According to Table 2, the SSA of SA, ZnO, HKUST-1, and HKUST-1/ZnO/SA is 10.17, 85.37, 847.1, 589.8, and 83.375 m$^{2}$/g, respectively. Due to the synergistic effects and the metal oxide particle size, which is smaller than the HKUST-1, the SSA is reduced (Azhar et al., 2017). Past research has shown that the specific surface area diminishes by adding metal oxide nanoparticles while these adsorbents still have high adsorption capacity (Azhar et al., 2017; Zhuo et al., 2017; Li et al., 2014).
3.1.4. Analysis of FESEM

The FE-SEM images of samples at the scale of 1 μm shows in Fig. 4. According to these images, SA-shaped spherical particles and zinc oxide nanorods are identifiable, similar to those published in previous studies (Karthik and Meenakshi, 2015; Bhakat and Singh, 2012). Moreover, in the image related to the composite adsorbent, the distribution of particles is uniform, and all the particles are observed.

3.2. Adsorption examinations

3.2.1. Isotherm models

For Naproxen via SA, ZnO, HKUST-1/ZnO/SA, and HKUST-1, the highest adsorption capacity (qmax) in the Langmuir model was 126.4, 60.03, 80.04, 45.06 mg/g, respectively. The adsorption amount for doxycycline applying SA, ZnO, HKUST-1/ZnO/SA, and HKUST-1 was 23.37, 78.59, 97.58, and 150.6 mg/g, respectively. According to the results of Table 3 and the correlation coefficients (R²), the Redlich-Peterson and Langmuir isotherm models are more compatible with the experimental data. The adsorption of drugs on the adsorbents is restricted to one layer on the plane because of the predominance of electrostatic interaction among the adsorbent and drugs or the stability of the adsorption surface in opposition to the adsorbate molecules. The fixed Kₐ value shows the adsorption ability of the adsorbent in the Langmuir isotherm (Langmuir, 1916). The highest value for HKUST-1 and SA adsorbents was 0.16 L/mg and 0.078 L/mg. The high value of Kᵢ in the Freundlich model indicates a high adsorption rate of pollutants because this value is dependent on the adsorption rate. This model considers that adsorption occurs on heterogeneous and multilayered surfaces, so the results verify the uniform adsorbent structure related to obtained correlation coefficients. Within the Freundlich model, the parameter (n) appears

| adsorbant     | aₛ,BET(m²/g) | aₛ,Lang(m²/g) | Total pore volume(cm³/g) | Mean pore diameter (nm) |
|---------------|--------------|---------------|--------------------------|-------------------------|
| SA            | 4.16         | 10.17         | 0.017                    | 23.74                   |
| ZnO           | 65.39        | 85.37         | 0.51                     | 30.01                   |
| HKUST-1       | 742.3        | 847.1         | 0.36                     | 1.68                    |
| HKUST-1/ZnO/SA| 289.7        | 354.2         | 0.5                      | 3.64                    |

Fig. 3. The BET and BJH results of a) HKUST-1, b) SA, c) ZnO, d) HKUST-1/ZnO/SA.
Table 3

| Isotherm models       | parameter | Doxycycline | Naproxen |
|-----------------------|-----------|-------------|----------|
|                       |           | HKUST-1     | HKU/ZnO/SA | ZnO | SA | HKUST-1 | HKU/ZnO/SA | ZnO | HKUST-1 |
| Langmuir              | $q_{\text{max}}$ (mg.g$^{-1}$) | 150.6 | 97.58 | 78.59 | 23.37 | 126.40 | 80.04 | 60.03 | 45.06 |
|                       | $K_L$ (L.mg$^{-1}$) | 0.16 | 0.069 | 0.038 | 0.12 | 0.078 | 0.036 | 0.022 | 0.053 |
|                       | $R^2$     | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 |
| Freundlich            | $K_F$ (mg$^{1-n}$.L$^n$.g$^{-1}$) | 30.58 | 21.02 | 11.31 | 11 | 23.76 | 15.23 | 5.12 | 7.681 |
|                       | $n$       | 4.1 | 3.32 | 2.74 | 6.5 | 3.22 | 2.24 | 2.15 | 2.586 |
|                       | $R^2$     | 0.85 | 0.95 | 0.96 | 0.95 | 0.98 | 0.93 | 0.95 | 0.96 |
| Temkin                | $B_T$ (kJ.mol$^{-1}$) | 18.15 | 19.35 | 17.04 | 4.05 | 70.33 | 61.15 | 12.63 | 25.93 |
|                       | $K_T$ (L.mg$^{-1}$) | 8.01 | 0.81 | 0.37 | 15.36 | 0.71 | 0.64 | 0.25 | 0.71 |
|                       | $R^2$     | 0.85 | 0.96 | 0.96 | 0.83 | 0.96 | 0.97 | 0.97 | 0.94 |
| Redlich-peterson      | $K_{AIP}$ (L.mg$^{-1}$) | 32.05 | 5.38 | 2.43 | 6.28 | 3.41 | 3.60 | 2.21 | 1.29 |
|                       | $n_{AIP}$ (L.mg$^{-1}$) | 0.12 | 0.028 | 0.014 | 0.19 | 0.016 | 0.018 | 0.014 | 0.013 |
|                       | $R^2$     | 1.08 | 1.13 | 1.15 | 1.05 | 1.19 | 1.39 | 1.34 | 1.24 |
| Hill                  | $q_H$ (mg.g$^{-1}$) | 151.3 | 60.47 | 38.28 | 24.1 | 123.6 | 76.95 | 59.43 | 48.12 |
|                       | $K_H$     | 36.07 | 44.49 | 47.32 | 78.74 | 13.44 | 95.48 | 95.47 | 43.32 |
|                       | $n_H$     | 1.3 | 1.37 | 1.36 | 1.3 | 1.16 | 1.36 | 1.54 | 1.41 |
|                       | $R^2$     | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.98 |
| Duinin-Radushkevich   | $q_{\text{max}}$ (mg.g$^{-1}$) | 146.6 | 58.27 | 38.77 | 22.49 | 128 | 78.99 | 58.87 | 47.88 |
|                       | $K^*10^7$ (mol$^2$.kJ$^2$) | 7.11 | 7.37 | 7.87 | 1.24 | 6.3 | 11.1 | 10.8 | 7.45 |
|                       | $E$ (kJ.mol$^{-1}$) | 0.9 | 0.82 | 0.79 | 0.67 | 0.8 | 0.65 | 0.68 | 0.86 |
|                       | $R^2$     | 0.99 | 0.96 | 0.96 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 |

Fig. 5. Curve fitting of Langmuir isotherm a) Doxycycline adsorption, b) Naproxen adsorption (at 25 °C, V:25 mL, m:5 mg, time:240 m.)
the desirability of adsorption. This coefficient requirement lies inside the range of 1–10 for desirable adsorption; therefore, due to the coefficient (n) received in the Freundlich equation, the adsorption of drugs on the research adsorbents is of good desirability (Freundlich, 1906). The mechanism of adsorption (physical and chemical) is investigated by Temkin model. Founded upon the \( R^2 \) in the Temkin model, the adsorption mechanism was determined to be hydrogen bands; however, it was not significant. The adsorption of pollutants on the adsorbent surface was exothermic, and it’s related to the positive value of \( A_T \) and \( B_T \) (Temkin, 1940). The high value of \( B_T \) for adsorbents demonstrates the creation of a strong hydrogen band among molecules of pollutants and adsorbents. Dubinin-Radushkevich presented another isotherm (Dubinin). It is used to calculate the free adsorption energy (E). It can assume that chemical adsorption is included within the adsorption prepare if the value of E is inside the range of 8–61 kJ/mol. According to the (E) values, the adsorption of doxycycline is physical, and the adsorption of Naproxen is physical and chemical. The Hill isotherm equation expresses the binding of different species onto homogeneous substrates (Hill, 1910). For the Hill model, \( R^2 \) is nearly 0.99 for all adsorbates. Founded on what has been presented, the adsorption of drugs on the adsorbents was single-layered, and the adsorbent structure was homogeneous; adsorption occurred both chemically and physically. According to Fig. 5, the Langmuir model fits the experimental equilibrium data well.

3.2.2. Effect of pH

The pH is one of the foremost vital variables affecting the absorption process and the mechanism of electrostatic interaction. Using the pHZpc test, the type of charge on the adsorbent surface can be well determined. pHZpc was measured by the drift method (Nasiruddin Khan and Sarwar, 2007) and for SA and ZnO, HKUST-1, HKUST-1/ZnO/SA are equal to 7, 9, 4, 6,5, respectively. Also, \( pK_a \) is doxycycline and Naproxen, equal to 3.9 and 4. According to the mentioned values, the surface charge of the pollutant is less than \( pK_a \).
positive at pH and negative at more pH. Also, the surface charge at pH is less positive than PZC and less negative for adsorbents. As a result, at pHs between the pollutant $pK_a$ and the adsorbent PZC, the adsorbent and surface charge are unnamed. Due to the influence of electrostatic forces, the highest Adsorption loading occurs. According to Fig. 6, (a) the Adsorption loading of doxycycline on the SA, ZnO, HKUST-1/ZnO/SA adsorbents at pH = 6 are 25.36, 80.3, 95.2 mg/g, while that of HKUST-1 at pH = 4 is 148.3 mg/g; (b) the maximum Adsorption loading of Naproxen on the SA, ZnO, HKUST-1/ZnO/SA adsorbents at pH = 6 are 130.2, 60, 84.2 mg/g while that of HKUST-1 at pH = 4 is 47.2 mg/g;

According to Fig. 7, due to the effect of pH to change the Adsorption loading, the adsorption mechanism of Naproxen and doxycycline are electrostatic forces. Due to benzene rings in the drug and adsorbent, the adsorption mechanism is the $\pi-\pi$ interaction. The adsorbent can also adsorb the contaminant through hydrogen bonding. Also, the carboxylic acid group (acidic) functional group in the adsorbent and the OH and NH functional group in the drug, Naproxen, and doxycycline can be adsorbed under the mechanism of acid-base.

3.2.3. Adsorption kinetics

Contact time is one of the foremost basic factors within the adsorption process for removing drug contaminants from an aqueous solution. Because when the time of the adsorbent contact with the future is long enough, the drug will have ample opportunity to be on active sites. Therefore, the elimination efficiency of drugs increases with increasing contact time. The impact of time changes on the efficiency of the drug removal process is shown in Fig. 8. The gotten data were coordinated with pseudo-first-order kinetic, pseudo-second-order kinetic models and intra-particle diffusion model and Boyd model. As maintained by Table 4 and the $R^2$ values, the pseudo-second-order kinetic model is admissible for the uptake of doxycycline and Naproxen. $K_2$ and $K_1$ are velocity constants. The value of C in the model is the penetration of mass transfer resistance particles caused by the boundary layer thickness. Also, a larger C indicates the presence of both adsorption species and intracelluluar diffusion mechanism. The Boyd model was examined to dissect the mechanism of intraparticle diffusion further. The values of $R^2$ show adsorption velocity controled by intraparticle and film diffusion. As appeared in Fig. 8, because of the lacuna of the active sites and the high initial concentration of drugs, the adsorption rate was higher and the slope of the graph is exceptionally spicy, within the early times. Over time, active sites are slowly possessed; the rate is moderated down (the slope of the graph is decreased to zero) until the equilibrium befallies and the adsorption chart is settled. Moreover, the slope of graph is settled, after approximately 30 min, and the equilibrium arise. In any case, the perusal period kept going up to 2 h to guarantee full equilibrium.

3.3. Water stability of adsorbent

According to the XRD pattern of SA, ZnO, HKUST-1/ZnO/SA adsorbents in Fig. 9, taken after placing the adsorbents in water for 2 weeks, the adsorbents were relatively stable. Still, due to ligand hydrolysis, HKUST-1 was destroyed in water and found to have an unfavourable XRD pattern. Combining HKUST-1 with SA, ZnO is to build a stable adsorbent in aqueous media.
3.4. Recycling the MOFs

Adsorbents recovery is one of the foremost imperative features. According to Fig. 10, after each wash and reduction step, the adsorbent adsorption capacity decreases slightly, and even after 5 reduction steps, the adsorbent maintained its adsorption capacity. As a result, a small amount of this adsorbent can absorb more pollutants and reduce operating costs.

Table 5 compares the synthesized adsorbent with other adsorbents for the adsorption of Naproxen and doxycycline. According to the results, the adsorbent is eco-friendly and water-stable in aqueous environments. It can be used in various cycles with high adsorption capacity and recoverability.
4. Conclusion

HKUST-1, ZnO, and HKUST-1/ZnO/SA were synthesized. The results of characterization analysis showed the successful synthesis of adsorbents. The summary of the results is as follows:

- By adding 10 wt% of ZnO and 50 wt% of SA to HKUST-1 at 25 °C and pH = 7, the specific surface area is reduced by 60%.
- By concentration increments from 5 to 80 ppm, the adsorption capacity increases so that the adsorbents reach equilibrium. The maximum adsorption capacity of doxycycline and Naproxen on HKUST-1/ZnO/SA is 97.58 and 80.04 mg/g, respectively.
The adsorption capacity increases and then decreases by changing the pH from 2 to 12. The maximum adsorption capacity befalls at pH = 6 for SA, ZnO, HKUST-1/ZnO/SA and at pH = 4 for HKUST-1.

Mechanisms involved in adsorption include hydrogen bonding, electrostatic forces, acid-base interplay, and pi stacking.

The water stability of the HKUST-1 is 7 days, and by combining the adsorbent with ZnO and SA, the water stability is 14 days.

Although the price of MOFs is higher than natural adsorbents and activated carbon, due to their very high adsorption capacity, they can be used in smaller quantities than the other adsorbents mentioned in terms of economics and will have a higher value. Given that the synthesis of MOF has been considered in recent years, and the company has succeeded in mass production of one of the types of MOF, the method of green synthesis in this article can be helpful. Because the adsorbent is used in this paper in the batch system and its stability is acceptable, this adsorbent can be used in adsorption tower systems and Continuous systems in future studies. It is recommended to study the simultaneous removal of drugs from real samples of wastewaters.

Table 5

| Adsorbent             | qe (mg/g) | Isotherm | Kinetics | pH | Cycle | Ref          |
|-----------------------|-----------|----------|----------|----|-------|--------------|
| Naproxen              | For each adsorbent | For each adsorbent | For each adsorbent | For each adsorbent | For each adsorbent | For each adsorbent |
| Activated carbon (F-400) | 3.2       | Freundlich | –        | –  | –     | Yu et al. (2008) |
| Peanut shells-derived biochars | 88.7      | Langmuir | p-second order | 6  | 2     | Tomul et al. (2020) |
| bone char             | 4.6       | Langmuir | p-second order | 6  | –     | Reynej-Avila et al. (2015) |
| Ethylenediamine (ED)/MIL101 | 154      | Langmuir | p-second order | 4  | 3     | Hasan et al. (2013) |
| MIL101(Cr)            | 92.1      | Langmuir | p-second order | 4  | –     | Hasan et al. (2012) |
| MIL-100(Fe)           | 88        | Langmuir | –        | 4  | –     | Hasan et al. (2012) |
| Activated carbon      | 44        | Langmuir | p-second order | 6  | –     | Hasan et al. (2012) |
| UO-66                 | 33.6      | Langmuir | p-second order | 4  | –     | Sun et al. (2019) |
| UiO66-NH2             | 9.16      | Langmuir | p-second order | 4  | –     | Sun et al. (2019) |
| Graphene Oxide Nanopowders | 21.91    | Langmuir | p-second order | –  | –     | Ci et al. (2020) |
| Chitosan-modified waste tire rubber | 2.3       | –        | p-second order | 6  | –     | Phasuphan et al. (2019) |
| HKUST-1               | 45.06     | Langmuir | p-second order | 6  | 3     | This work     |
| SA                    | 126.40    | Langmuir | p-second order | 6  | 3     | This work     |
| ZnO                   | 60.03     | Langmuir | p-second order | 6  | 4     | This work |
| HKUST-1/SA/ZnO        | 80.04     | Langmuir | p-second order | 6  | 6     | This work     |
| Doxycycline           | For each adsorbent | For each adsorbent | For each adsorbent | For each adsorbent | For each adsorbent | For each adsorbent |
| Magnetic FeO4@Chitosan Carbon Microbeads | 4.8       | Langmuir | p-second order | 6  | –     | Bai et al. (2018) |
| iron-loaded sludge biochar | 104.86   | Langmuir | p-second order | 6  | –     | Wei et al. (2019) |
| graphene nanosheet     | 84        | Hill     | p-second order | –  | –     | Rostamian and Behnejad (2018) |
| MIL53(Fe)             | 477       | Langmuir | p-second order | 6  | –     | Naeimi and Faghfihan (2017) |
| Ni-doped MIL-53(Fe)   | 397.22    | Langmuir | p-second order | 5.5 | –     | Xiong et al. (2019) |
| Activated carbon      | 36        | Langmuir | –        | 7  | 2     | Alsaedi et al. (2020) |
| Zeolite               | 75        | Langmuir | p-second order | 7  | 2     | Alsaedi et al. (2020) |
| UiO66                 | 156.25    | Langmuir | p-second order | 7  | 3     | Alsaedi et al. (2020) |
| HKUST-1               | 150.6     | Langmuir | p-second order | 4  | 3     | This work     |
| SA                    | 23.37     | Langmuir | p-second order | 6  | 3     | This work     |
| ZnO                   | 78.59     | Langmuir | p-second order | 6  | 4     | This work     |
| HKUST-1/SA/ZnO        | 97.58     | Langmuir | p-second order | 6  | 6     | This work     |

• The adsorption capacity increases and then decreases by changing the pH from 2 to 12. The maximum adsorption capacity befalls at pH = 6 for SA, ZnO, HKUST-1/ZnO/SA and at pH = 4 for HKUST-1.

• Mechanisms involved in adsorption include hydrogen bonding, electrostatic forces, acid-base interplay, and pi stacking.

• The equilibrium time of the adsorbers at 25 °C, concentration = 80 ppm, is 120 min.

• The water stability of the HKUST-1 is 7 days, and by combining the adsorbent with ZnO and SA, the water stability is 14 days.

• HKUST-1/ZnO/SA adsorbent was used in 10 cycles with 80% removal efficiency, while HKUST, ZnO, and SA can be used in 3 and 5 cycles.

Although the price of MOFs is higher than natural adsorbents and activated carbon, due to their very high adsorption capacity, they can be used in smaller quantities than the other adsorbents mentioned in terms of economics and will have a higher value. Given that the synthesis of MOF has been considered in recent years, and the company has succeeded in mass production of one of the types of MOF, the method of green synthesis in this article can be helpful. Because the adsorbent is used in this paper in the batch system and its stability is acceptable, this adsorbent can be used in adsorption tower systems and Continuous systems in future studies. It is recommended to study the simultaneous removal of drugs from real samples of wastewaters.

Author statement

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Declaration of competing interest

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

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