Enhanced adsorptive removal of diclofenac sodium from aqueous solution by bentonite-supported nanoscale zero-valent iron

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ABSTRACT
Nano zero-valent iron-bentonite (B-nZVI) is an excellent composite for treating recalcitrant organic pollutants. In this study, B-nZVI was prepared via NaBH₄ reduction method and characterized using different instruments including X-ray diffraction apparatus (XRD), Fourier-transform infrared spectroscopy (FTIR), Field emission scanning electron microscope (SEM), Transmission electron microscope (TEM), and UV–Vis spectrophotometry. Also, the efficiency of B-nZVI as an adsorbent to remove diclofenac sodium (DCF) from aqueous solution was investigated, and compared with activated carbon (AC) under different experimental conditions such as pH, adsorbent dose, DCF initial concentration, temperature, and contact time. The B-nZVI has successfully removed a high percentage of DCF from aqueous solution (~80%) within 50 min, 25 °C, and pH = 3. The maximum adsorption capacity of B-nZVI at equilibrium was 140.8 mg g⁻¹ compared to 107.5 mg g⁻¹ via AC. Furthermore, it was found that the DCF adsorption best fitted the Langmuir isotherm and pseudo-second-order kinetic models (R² > 0.987). Also, the thermodynamic parameters of adsorption were estimated and the average values showed that the adsorption of DCF via B-nZVI is an endothermic process (∆H° = 29.8 ± 5.2 kJ mol⁻¹), and spontaneous with a positive value of entropy (∆S° = 175.4 ± 11.3 mol⁻¹ K⁻¹) at 25 °C. The point of zero charge (PZC) was determined (7.0 ± 0.1) using a salt addition method. Finally, column filtration was demonstrated using a mixture of sand and B-nZVI composite, which showed a significant advantage in comparison with that activated carbon/sand mixture.

1. Introduction
Pharmaceutical compounds (PhACs) have been detected in different aquatic environment compartments (Daughton, 2004; Daughton & Ternes, 1999; Kümmeter, 2001; Ternes, 1998). The presence of such nonbiodegradable stable substances even at very low concentrations have been related to bacterial resistance, chronic toxicity, and endocrine disruption (Castiglioni et al., 2006; Halling-Sørensen et al., 1998).

Diclofenac sodium (DCF) (Figure 1), a 2-[(2, 6-dichlorophenyl) amino] benzene acetic acid, monosodium salt, is widely used as a nonsteroidal anti-inflammatory pharmaceutical drug (Beltrán, Pocostales, Alvarez, & Oropeza, 2009; Kormosh, Hunka, & Bazel, 2008; Kumar, Shankar, & Singh, 2011; Patil & Chaudhari, 2012). Additionally, DCF has been detected in water resources and wastewater treatment plant effluents in concentrations up to μg L⁻¹ (Zuccato, Calamari, Natangelo, & Fanelli, 2000). Therefore, the removal of DCF from wastewater and polluted water is of high importance.

Removing pharmaceutical residues from water have limitations, such as energy consumption and operation cost. In contrast, adsorption is a simple, rapid, low cost, high adsorption capacity, and an efficient method for removing organic residues (Al-Jabari, Khalid, Sulaiman, Alawi, & Shilo, 2018; Al-Jabari et al., 2019; Sulaiman & Al-Jabari, 2020).

Adsorption using activated carbon is one of the best methods suggested to eliminate recalcitrant organic compounds, heavy metals, and dyes (Jasim, Baban, & Jasim, 2013; Noreen, Bhatti, Iqbal, Hussain, & Sarim, 2020; Pehlivan, Kahraman, & Pehlivan, 2011; Roivas & Neuvonen, 1994). Despite its low cost and high adsorption capacity, the regeneration failure of used activated charcoal restricts its applicability (AbdulRahim, Zaharaddeen, & Garba, 2016; Miyah et al., 2017; Yaneva & Koumanova, 2006).

The presence of nZVI particles in the adsorption environment is reactive and prone to agglomeration, resulting in a substantial reduction in their reactivity (Li, Elliott, & Zhang, 2006; Theron, Walker, & Cloete, 2008). Composites of nZVI have been extensively...
synthesized to stabilize the nZVI particles in the adsorption of residual pollutants from aqueous solutions. In addition to the increased number of active inherent surface sites, the specific surface area, and reducing the reaction time (Bhatti, Safa, et al., 2020; Li et al., 2006; Mahmood et al., 2013; Pasinszki & Krebsz, 2020; Sana, Haq Nawaz, Khalid, Jan, & Munawar, 2020; Tam et al., 2020; Theron et al., 2008; Toli, Varouxaki, Mystrioti, Xenidis, & Papassiopi, 2018).

Low-cost bentonite (B) could be used as a carrier material for nZVI particles to improve the adsorption efficiency, by reducing agglomeration, and thus enhancing the degradation of organic pollutants on the surface of composite (B-nZVI) in aqueous solutions (Bhatti, Safa, et al., 2020; Ternes, 1998).

Removal of DCF sodium from aqueous solution using advanced oxidation processes such as ozonation or photocatalysis has a limitation due to dimerization of carboxylic acid rather than going mineralization (Jabbari, Eslami, & Mahmoudian, 2020; Sulaiman & Shahwan, 2017). The adsorption method has been recently considered for removing DCF from an aqueous environment (Ponder, Darab, & Mallouk, 2000; Urooj, Bhatti, Munawar, Saba, & Muhammad, 2019; Üzüm et al., 2009). However, there are limited studies about pharmaceutical drug adsorption using B-nZVI (Sulaiman & Al-Jabari, 2020; Sulaiman & Shahwan, 2017).

In this article, the adsorption parameters and the potential removal of DCF via the surface of B-nZVI and AC were investigated. First, the B-nZVI was synthesized using the NaBH4 reduction method and characterized using different characterization techniques to confirm its physical and chemical properties. After that, the adsorption efficiency of B-nZVI and AC for the removal of DCF from an aqueous solution was evaluated. The effect of experimental conditions such as pH, adsorbent dose, temperature, adsorbate concentration, and contact time on the removal efficiency was studied. To investigate the adsorption mechanism of DCF onto the surface of B-nZVI composite and AC, Langmuir isotherm and pseudo-second-order kinetic models were applied, and thermodynamic parameters were calculated to interpret the adsorption mechanism. Finally, the removal efficiency was ascertained using a column filtration filled with a mixture of sand and B-nZVI composite and compared with that activated carbon/sand mixture.

2. Materials and methods

2.1. Chemicals

Bentonite (cation exchange capacity (CEC): 32.4 meq/100 g, a montmorillonite content (wt) <40%, chemical contents: 62.5% SiO2, 1.75% Fe2O3, 18.5% Al2O3, 4.25% MgO, 2.75% Na2O, and 0.95% CaO). Iron chloride hexahydrate (FeCl3.6H2O ≥ 97%), Sodium borohydride (NaBH4 ≥ 96%), DCF sodium (>99%) was obtained from Jerusalem Pharmaceutical Company (Palestine). Fine powder activated carbon (FAC) (particle size ≤ 60 μm), granular activated carbon (GAC) (particle size ≤ 700 μm).

All chemicals used in this study were purchased from Sigma Chemical Company Co. Ltd. (Munich, Germany), and they were used without further treatment. Bentonite was sieved to 200 size and was dried before use overnight at 25 °C. FAC and GAC were used in batch and column adsorption experiments, respectively. DCF sodium solution used was prepared by dissolving the required amount of the DCF sodium drug inappropriate volume of deionized water.

2.2. Wastewater treatment plant (WWTP) and DCF stability in Birzeit University (BZU) sludge

2.2.1. WWTP

BZU WWTP’s was constructed from the stabilization system, which is used to treat the domestic sewage of 16,000 staff and students. Daily, the system collects about 190 m³ of slightly diluted sewage. Students and staff spend almost 10 h of active works. Therefore, the typical wastewater of the University does not represent rural domestic sewage (Sulaiman & Shahwan, 2017).

2.2.2. Active quality parameters of BZU WWTP sludge

According to the standard chemical methods, physical, chemical, and biological wastewater parameters were reviewed and evaluated before any experiment, the parameters were listed in Table 1 (Federation, 2005).

2.2.3. Stability analysis for DCF

A stability study of DCF was performed using 100 mg L⁻¹ solutions in pure water, or Activated sludge was taken from the WWTP installed at BZU. Samples at specific time intervals (0–30 days) were collected from the stability solutions (maintained under continuous orbital shaking), then the samples
were filtered and analyzed using HPLC. Finally, the degradation of by-products of DCF was investigated using liquid chromatography/Fourier-transform ion cyclotron resonance mass spectrometry.

### 2.3. Methods

#### 2.3.1. Synthesis of nZVI and bentonite-supported nZVI

The nZVI sample was synthesized according to the previously reported method (Federation, 2005; Matias, Vilela, Becegato, & Paulino, 2019; Urooj et al., 2019; Uzum et al., 2009). The 9.68 g of FeCl₃·6H₂O was dissolved in 100 mL of bi-distilled water and pure ethanol (4:1, v/v). Using a three-necked flask, the solution was kept under an inert nitrogen atmosphere with continuously mixing for 15 min. Then, 200 mL of 0.47 M NaBH₄ was added to the mixture gradually at the flow rate of 2 mL min⁻¹. The mixture was continued under an inert atmosphere until the color of the mixture was gradually changed to black and completely consuming NaBH₄ and the color of the mixture was gradually changed to black and completely consuming NaBH₄ and FeCl₃·6H₂O (Bhatti, Safa, et al., 2020; Kim, Hong, Lee, Shin, & Yang, 2008; Sulaiman & Shahwan, 2017).

\[
4\text{Fe}^{3+} + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow 4\text{Fe}^{0} + 3\text{H}_2\text{BO}_3^- + 12\text{H}^+ + 2\text{H}_2\text{O}
\]

Afterward, particles were collected using vacuum filtration, and then the particles were washed and rinsed using absolute ethanol at least 3 times. To avoid oxidation the produced particles were dehydrated overnight under a vacuum at 333 K, and then the samples produced were kept in an inert atmosphere for further study (Kim et al., 2008; Matias et al., 2019).

#### 2.3.2. Characterization

Fourier transform infrared spectrometer (FTIR-Nicolet 5700, Thermo Corp., USA) was used to record the vibrational spectra of the samples, and each sample was directly analyzed and scanned 4 times in the range of (400–4000 cm⁻¹)(Sulaiman & Shahwan, 2017). Morphology and distribution of B, n-ZVI, B-nZVI were characterized using a scanning electron microscope (SEM, Philips-FeI XL30, operating voltage 20 kV, Philips Electronics Co., Netherlands), and Transmission electron microscope (TEM, JEM-2100F).

The X-ray diffraction (XRD) patterns were measured on Philips-X’Pert Pro MPD (the Netherlands, 40 kV, and 40 mA, a high-power Cu Kα), and all samples were measured at a scan rate of 3° min⁻¹ with scanning angle range from 5° to 80° of 2θ (Sulaiman & Shahwan, 2017).

The concentrations of DCF in aqueous solutions were measured by Perkin Elmer (Lambda 5 ultraviolet-visible spectrophotometer). The samples were stirred vigorously to establish the adsorption equilibrium using a water bath shaker. A Shimadzu high-performance liquid chromatography-mass spectrometry HPLC–MS/MS system (Shimadzu Corp., Japan) was used for degradation stability analysis of the samples.

The analytes were separated using two conjugate columns (BXridge™ C18 guard column 4.6 mm × 20 μm, and 4.6 mm × 150 mm C18 XBridge@column, particle size 5 μm).

#### 2.3.3. Adsorption experiments

The adsorption experiments were carried out in triplicate (using a batch technique) by shaking DCF adsorption solution at 250 rpm for 3 h. The calibration curve was prepared by appropriate dilution (5–200 mg L⁻¹) from a stock solution of 1000 mg L⁻¹. Also, 100 mL with a proper initial concentration of DCF solution was prepared and mixed with a specified adsorbent mass in a brown amber bottle. After equilibrium was established, the residual DCF was separated using a syringe filter (Millipore Millex-G, Hydrophilic PVDF 0.45 μm pore size). Then the concentrations of DCF solutions were measured at a maximum wavelength of λ = 276 nm.

To study the effect of adsorbent dose, 100 mg L⁻¹ (pH~ 5.6) of DCF solution was mixed with 0.1, 0.25, 0.5, 0.75, and 1.0 g of B-nZVI composite at 25 °C for 3 h, then the removal efficiency was calculated using Eq. (1). At 25 °C, the kinetic and isotherm parameters were evaluated over intervals of time using 0.200 g adsorbent in 100 mL of different initial DCF.
concentrations (5, 10, 20, 50, 100, and 180 mg L\(^{-1}\)). Also, the effect of heat on the adsorption of DCF via B-nZVI was evaluated in the range of (15–55 °C). The thermodynamic adsorption parameters of DCF via B-nZVI were calculated over two different temperatures (25 and 55 °C).

The effect of pH was studied at different values (3.0, 5.0, 7.0, and 9.0), and the removal efficiency was investigated using Eq. (1). The point of zero charge (PZC) of the B-nZVI composite was evaluated by adding 0.05 g to 40 mL 0.01 M NaCl at different initial pH (2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, and 12.0). Subsequently, the solution was set for 24 h to attain the final pH, and the difference between the final and initial pH was plotted versus the initial pH to determine the PZC (Fürstner, Murphy, & Rulkens, 1995; Larous & Meniai, 2016).

\[
R = \frac{C_0 - C_t}{C_0} \times 100\%
\]  

(1)

Where \(C_0\) is the initial DCF concentration (mg L\(^{-1}\)), and \(C_t\) is the DFC concentration at a time \(t\) (min), and \(R\) (%) is the percentage removal of DCF.

### 2.3.4. Column experiments

Mixtures of 20 cm layer quartz sand and B-nZVI/GAC were prepared in the ratio of (49:1, w/w) and filled in columns of 25 cm length and 5 cm diameter. Besides, a 3 cm layer of treated quartz sand covered the bottom of the columns. Before using, the used quartz sand was treated carefully by washing with distilled water and dehydrated at 110 °C for 24 h. DCF solutions were prepared in different initial concentrations (0.01, 0.1, 10, 100 mg L\(^{-1}\)), and these solutions were allowed to pass through the columns separately with the 2.0 mL min\(^{-1}\) flow rate, and the eluted fractions elute were collected to measure the DCF concentrations solution.

### 3. Results and discussion

#### 3.1. Wastewater characteristics and stability of DCF

The biological, chemical, and physical parameters of wastewater collected from BZU’s WWTP aeration chamber are shown in Table 2. Those parameters show that the nutrient contents in the sludge. The contents included the total dissolved solids (TDS), biological oxygen demand (BOD), chemical oxygen demand (COD), settable solids, and bacteria were very high. These results were reproducible and predictable within the expected range because the test samples were collected from the same WWTP aeration chamber unit (Sulaiman & Shahwan, 2017).

The wastewater samples used in this experiment contained a large number of bacteria and a moderate amount of suspended solids. Activated sludge from BZU, which was analyzed in a previous study which reported the presence of Enterobacter: E. coli, Enterobacter sakazakii, Enterococcus faecalis, Pseudomonas aeruginosa, Enterobacter aerogenes, Enterococcus, Leptospira, Klebsiella pneumonia, Staphylococcus aureus, Enterobacter cloacae Salmonella, Staphylococcus aureus, powdery bacilli, Streptococcus, and Neisseria (Bhatti, Safa, et al., 2020). TDS values and electrical conductivity (EC) of the test samples were found lower than the expected values of municipal wastewater.

The DCF stability was tested for both purified water and sludge of BZU. The data obtained from both media indicated that the DCF had resisted the degradation for more than one month at ambient temperature. These results confirm that the DCF is stable against both bacterial degradation and water hydrolysis (Tam et al., 2020).

#### 3.2. Characterization of adsorbents particles

Forms of iron oxide are chemically stable, whereas nZVI exhibits a high chemical reactivity and could be easily oxidized in the presence of oxygen. The presence of metallic iron particles in the lattice structure of nZVI enables to convert different pollutants into less toxic forms (Sulaiman & Al-Jabari, 2020; Sulaiman & Shahwan, 2017).

As well-known, nZVI has a characteristic core-shell structure, the core distinct by metallic iron or zero-valent (Fe\(^0\)), whereas the shell is distinct having the mixture of different iron oxides [Fe(II) and Fe(III)] as a result of the oxidation of Fe\(^0\) nanoparticles. The previous studies showed that nZVI has special electron-donating properties, making it an ingenious material.
used for pollutant treatment (Carpenter, Calvin, Stroud, & Harris, 2003; Ponder et al., 2001; Wang et al., 2009). The proposed mechanism suggests that the nZVI uses the center shell characteristic structure to fix the organic contaminants through the adsorption leading to the redox process. The core of nZVI particles acts as an electron source for the redox reactions, while the oxide shell provides destination sites for chemisorbed organic and inorganic contaminants (Sulaiman & Shahwan, 2017).

NZVI particles form a chain-like aggregates structure due to the presence of strong magnetic dipoles on their surface. However, when the nZVI particles agglomerate, they give rise to a permanent oxide shell, while the thinner interface of iron oxide shells separates the Fe⁰ cores. Additionally, the produced amorphous thinner iron oxide shell prevents further iron oxide crystals, and the earlier oxidation of the core of iron nanoparticles (Carpenter et al., 2003; Shi, Zhang, & Chen, 2011; Sulaiman & Shahwan, 2017; Zhang, Lin, Lu, & Chen, 2010).

The Fe⁰ core plays a significant role in charge migration from the core to the chelated contaminant that is adsorbed on the nanoparticle surface (Sulaiman & Shahwan, 2017). Although Fe⁰ has semiconductor characteristics (Beltrán et al., 2009; Carpenter et al., 2003; Shi et al., 2011; Tabak, Afsin, Caglar, & Koksal, 2007; Yuan et al., 2008; Zhang et al., 2010), the charge transfer was weak due to the small core thickness and its relatively low working sites, which could be a reason for the decreased pollutants adsorption (Carpenter et al., 2003; Förstner et al., 1995; Larous & Meniai, 2016; Ponder et al., 2001; Wang et al., 2009).

Different techniques were used such as SEM, TEM, XRD, and FTIR to characterize and analyze the adsorbent particles in the present research. In Figure 2(B), the XRD spectrum shows a reflection montmorillonite (M) peak almost at 5°, which is the distinct part of bentonite.

The quartz (Q) peaks at (18°, 25°, 37°, 40°, 44°, 54°, 60°, and 70°) are impurities existing with bentonite tested sample. Figure 2 (1) and (2) are the XRD spectra of B-nZVI composite before and after the adsorption, respectively. The spectrum in Figure 2 (1) shows a basic reflection at 45°, which is a characteristic peak for nZVI in the analyzed sample. Also, the spectrum shows a lower crystallinity of nZVI due to the existence of produced boron from the reducing agent (NaBH₄) in the crystalline lattice of iron nanoparticles. The XRD pattern of B-nZVI particles after removal DCF from the aqueous solution is shown in Figure 2 (2). The spectrum indicates that the montmorillonite and Fe⁰ reflection peaks vanished. This suggests that the clay experienced an exfoliation when Fe nanoparticles were incorporated into the adsorbate layer. Also, the sample had undergone large-scale oxidation, which is realized from the Fe⁰ reflection peak’s disappearance and appearance of the Fe₃O₄ (magnetite) reflection peak.

The morphology of bentonite, nZVI, and B-nZVI after adsorption were characterized using SEM and TEM as shown in Figure 3. Figure 3(a,b) show the SEM images of unprocessed natural bentonite and nZVI, respectively. The bentonite morphology seems like bulky flocs with leaf-like flakes, with many small gullies between different layers. While the synthesized nZVI particles have a typical spherical structure and consist of chain-like aggregates, as shown in Figure 3(b). The Composite of B-nZVI after adsorption is shown in Figure 3(c,d). The spherical nZVI particles seem more dispersed and less aggregated on the upper layer. On the other hand, the aggregated nZVI particles seem to be accumulated on the internal layers of clay. The TEM image clearly shows a limited diffusion of these particles between the bentonite sheets (Sulaiman & Shahwan, 2017). Comparing the morphology of nZVI particles before and after adsorption indicates significant morphological changes. The nanoparticles suffered from a large amount of oxidation after the adsorption of contaminants, which has been confirmed by the given XRD spectrum (Sulaiman & Shahwan, 2017). The average diameter of nZVI particle distributed on the bentonite structure varies between 40 and 100 nm (Sulaiman & Shahwan, 2017).

The FTIR spectra of DCF, natural bentonite, nZVI, and B-nZVI-DCF were recorded in the range of 400–4000 cm⁻¹ (Figure 4). In Figure 4(a), the spectrum shows vibrational bands of diclofenac are located at 3383 cm⁻¹ for (N–H), 3072 cm⁻¹ (C–H arom), 3256 cm⁻¹
(N–H···O), 1571 cm\(^{-1}\), 1503 cm\(^{-1}\) (C=\(\text{C}_{\text{arom}}\)), 1453 and 1400 cm\(^{-1}\) (V\(_s\) COO), 1289 cm\(^{-1}\) (C–N\(_{\text{arom}}\)), and 748 cm\(^{-1}\) (\(\delta\) C–H\(_{\text{arom}}\)), while the band at 448 cm\(^{-1}\) belongs to the C–Cl stretching vibration (Sun et al., 2017; Yuan et al., 2008; Zhao et al., 2017).

The bentonite IR-spectrum, shown in Figure 4(b), indicates that Al–O and Al–O–H vibrational groups occur at 915 cm\(^{-1}\) and 3447 cm\(^{-1}\), respectively. The vibrational modes at 533 and 458 cm\(^{-1}\) are scribed to Si–O–Al and Si–O–Si vibrations, respectively. While the Si–O vibrational feature appears at 1020 cm\(^{-1}\) (Sulaiman & Shahwan, 2017; Zhao et al., 2017). The sharp peak of the Si-O bond in the tetrahedral plane of Si-O-Si group appears at 1020 cm\(^{-1}\). While the peak at 1631 cm\(^{-1}\) belongs to the H–O–H stretching vibration of water species and hydrogen-bonding of Si–O–H in bentonite.

The IR absorbance bands of nZVI are illustrated in Figure 4(c). The stretching bands of Fe–O on the iron oxide thin layer occur at 470, 533, 794, 920, and 1.040 cm\(^{-1}\) (Beltrán et al., 2009; Yuan et al., 2008). Therefore, these results are compatible with the oxidation bands appearing in the spectrum of B-nZVI after adsorption of DCF. This supports the partial oxidation of nZVI on the composite’s surface, as shown in Figure 4(d). Additionally, the same characteristic peaks of DCF are observed in the spectrum but with lower intensity, e.g., (V\(_{\text{as}}\) COO) at 1571 cm\(^{-1}\). Furthermore, some peaks have shifted like C–Cl stretching vibration to 468 cm\(^{-1}\), indicating that the Cl atom participates in the adsorption process. These changes indicate that the oxygen atoms of the carboxylate group (-COO-) were merged into the
interaction between DCF and B-nZVI composite after adsorption. Consequently, complexation may occur between metal iron ions on the surface of the B-nZVI composite and the carboxyl group of DCF. Additionally, the presence of hydrogen acceptors like (-NH) and a hydrogen donor (OH groups) on the surface of B-nZVI composite favors the formation of H bonds.

3.3. Removal efficiency of DCF

3.3.1. Effect of pH

The adsorption process is highly affected by the solution’s acidity and basicity (Özcan, Ömeroğlu, Erdoğan, & Özcan, 2007; Sun et al., 2017). To investigate the effect of pH on the adsorption efficiency of B-nZVI composite, the PZC experiment was conducted.

As shown in Figure 5, the DCF adsorption decreases with increasing pH value, which indicates that the adsorption capacity is greatly reliant on the pH of the solution. The pH values of the solution can change the charges on the surface of the adsorbent, its morphology, and the degree of adsorbate dissociation. The highest DCF removal rate with B-nZVI composite was in acidic media of pH 3.

The zeta potential measurements give us information about the charges of the outer surface of the material. PZC is the pH at which the net positive and negative charges on the material surface are equivalent. Figure 6 shows that the zeta potential of B-nZVI in an aqueous solution at different pH. The results indicate that the PZC was around 7.0, and sorbent net charge was positive over a range of pH < pH\text{PZC}, while it was negative over a range of pH > pH\text{PZC} (Förstner et al., 1995; Yetilmsezoy, Özçimen, & Koçer, 2020).

Electrostatic attraction forces can explain these results. As pH decreases, more protons will be available, and the presence of H\textsuperscript{+} promotes the formation of Fe(II)-DCF complex or hydrogen bond through the positive ionization of B-nZVI surface and de-protonation of DCF (-COO-) (Bhattacharyya & Sharma, 2004; Bhatti, Safa, et al., 2020; Fito, Abrham, & Angassa, 2020; Mittal, Kurup, & Gupta, 2005; Venkatapathy, Bessingpas, Canonica, & Perlinger, 2000; Zhao et al., 2017). At pH > 4.12, DCF (pK\text{a} = 4.2) is almost negatively charged and the net charge of B-nZVI is positive till pH = 7.0. Thus, the high adsorption capacity in the pH range of (3.0–7.0) is due to the strong electrostatic attraction between the DCF and B-nZVI. As pH goes higher than 7.0, the adsorption capacity decreases with increasing the pH due to the repulsion forces of similar negative charges for both adsorbent and adsorbate. A similar finding was reported in earlier studies (Zhao et al., 2017). Other factors that could lead to a decrease in the adsorption efficiency are the precipitation, and iron oxide formation observed at high pH values. It is observed that the DCF was precipitated from the solution at pH lower than its pKa. Also, the hydroxide ions cause clogging of the active surface sites by forming shells around B-nZVI particles (Venkatapathy et al., 2002). This result is also consistent with a previous XRD and SEM analysis work showing that hematite (γ-Fe\textsubscript{2}O\textsubscript{3}) and magnetite (Fe\textsubscript{3}O\textsubscript{4}) are formed during the preparation of B-nZVI composite (Zhao et al., 2017).

3.3.2. Effect of adsorbent dose

The effect of B-nZVI amount was investigated and plotted in Figure 7. The data indicates that by increasing the adsorption dosage up to 0.25 g and higher, the removal amount of DCF has maximized, which could be due to increasing the adsorbent surface area confirmed by the DCF elimination (Mittal et al., 2005).
3.3.3. Adsorption kinetic

Adsorption kinetic parameters at different contact times of DCF and B-nZVI were investigated. Three types of adsorbents: 0.2 g of bentonite, activated carbon, and B-nZVI composite were used separately with 100 mg L\(^{-1}\) of DCF at pH = 5.6. The results are represented in Figure 8. The data indicate that at the initial time of the adsorption process the rate of DCF adsorption was rapid. The adsorption of DCF via B-nZVI composite almost reached the equilibrium after 100 min.

The high removal efficiency of B-nZVI composite for DCF(R\(_R\) % = 80%) confirms that bentonite has established good dispersibility for nZVI on bentonite layers, enhancing the DCF adsorption efficiency using B-nZVI, compared with AC (R\(_R\) % ≈ 55%) and B (R\(_R\) % ≈ 12%) (Beltrán et al., 2009; Jabbari et al., 2020).

A modified pseudo-second-order rate equation was investigated, and its parameters were applied to study the kinetic adsorption process of DCF using activated carbon and B-nZVI composite as given below (Celebi, Üzüm, Shahwan, & Erten, 2007; Shahwan, 2014):

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}
\]

Where \(C_0\); initial concentration, \(Q_e\) (mg g\(^{-1}\)); equilibrium mass of DCF adsorbed per gram of adsorbent, \(Q_t\); amount of adsorbate at time \(t\), and \(k_2\) is the rate constant. The plot of \(t/Q\) vs. \(t\) is presented in Figure 9. The second-order kinetic model is well fitted for both adsorbents, with a linear regression correlation coefficient \(R^2 > 0.98\). In contrast, the applied pseudo-first-order model has a bad correlation between adsorption values \(R^2 < 0.78\).

3.3.4. Adsorption isotherm

The influence of the initial concentration of DCF on the adsorption isotherm process using activated carbon, bentonite, and B-nZVI composite was investigated. The percentage of removal is shown in Table 3. It is obvious that as the initial concentration of DCF increases, the elimination percentage increases. Under the specified conditions, the B-nZVI composite showed better removal efficiency than bentonite and AC at various initial concentrations. Also, the bentonite showed less performance in the removal process of DCF, indicating that the nZVI is pragmatically responsible for removing the major DCF components (Beltrán et al., 2009).

The isotherm parameters were evaluated using both activated carbon and B-nZVI composite, and the Langmuir isotherm was applied using Eq. (3):

\[
\frac{C_e}{Q_e} = \frac{1}{(KQ_{\text{max}})} + \frac{C_e}{Q_{\text{max}}}
\]

Where \(Q_e\) (mg g\(^{-1}\)); equilibrium mass of DCF adsorbed per g of adsorbent, \(C_e\) (mg L\(^{-1}\)); equilibrium concentration of DCF, \(Q_{\text{max}}\) (mg g\(^{-1}\)); maximum
mass of the drug removed by the adsorbent, and \( k \) (L mg\(^{-1}\)C\(_0\)) is the Langmuir binding constant.

Experimental data showed that the elimination process of DCF via B-nZVI composite and activated carbon obeys the Langmuir isotherm model, as shown in Figure 10. The \( R^2 \) values estimated for both models are found as higher than 0.987, as shown in Table 4. Furthermore, the values of the Langmuir parameters, \( Q_{\text{max}} \) and \( K \) showed that B-nZVI composite has been more effective in terms of adsorption affinity and removal capacity than the other previously established adsorbents for elimination of DCF (Beltrán et al., 2009).

### 3.3.5. Thermodynamic parameters

The effect of temperature on the removal of DCF by B-nZVI was studied in the range of (15–55\(^\circ\)C) using 0.25 g B-nZVI and 100 mg L\(^{-1}\) of DCF; the results are shown in Figure 11. The data illustrates that the removal rate increased as the temperature increased. Also, the removal percentage of DCF was found as 70.0% at 15\(^\circ\)C, and 100.0% at 25\(^\circ\)C. However, as the temperature increased above that, the adsorption efficiency did not change, and the removal was almost completed.

The following equations were used to calculate thermodynamic parameters of the adsorption process of DCF, \( \Delta H^0 \), \( \Delta S^0 \), and \( \Delta G^0 \):

\[
\Delta H^0 = R \ln \left( \frac{Rd_{2}}{Rd_{1}} \right) \frac{T_2 - T_1}{T_2} \quad (4)
\]

\[
\Delta G^0 = -RT \ln Rd \quad (5)
\]

\[
\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (6)
\]

In a sorption study, the precise estimation of the parameters is subject to several limitations; the \( Rd \) is simply an empirical constant rather than a thermodynamic equilibrium constant and is operative under a specific set of reaction conditions. Thus, from a thermodynamic perspective, assuming that the values of \( \Delta H^0 \), \( \Delta S^0 \), and \( \Delta G^0 \) are only temperature-dependent, the calculated value of \( Rd \) is varying with initial concentration and reveals in their values (Boparai, Joseph, & O’Carroll, 2011; Hameed, Rahim, Dewayanto, & Nordin, 2019; Shahwan, Erten, & Unugur, 2006).

Thermodynamic parameters of adsorption were estimated after attainment of the equilibrium table:  

| Adsorbents | \( K \) (L mg\(^{-1}\)) | \( Q_{\text{max}} \) (mg g\(^{-1}\)) | \( R^2 \)  |
|-----------|----------------|----------------|------|
| B-nZVI    | 0.104117       | 140.8 mg g\(^{-1}\) | 0.9953 |
| AC        | 0.09287        | 107.5 mg g\(^{-1}\) | 0.9872 |

The contact time is 3 h at a temperature of 25 \(^\circ\)C and a dose equal to 0.2 g L\(^{-1}\).
between different initial concentrations of DCF solution, with 0.25 g from B-nZVI composite, at 25 and 55 °C. The values of \( \Delta H^\circ \), \( \Delta S^\circ \), and \( \Delta G^\circ \) were obtained and tabulated in Table 5.

The positive value of standard enthalpy change \( \Delta H^\circ \) indicates the occurrence of an endothermic process supported by the favorable adsorption of DCF at higher temperatures.

Increasing the temperature in the endothermic process causes increasing the kinetic and potential energy of the DCF molecules in the solution, thereby increasing their mobility and ability to contact the adsorbent surface.

The \( R_d \) values obtained at different temperatures were used to evaluate the standard change Gibb’s free energy (\( \Delta G^\circ \)) of adsorption at each concentration. As shown in Table 5, the negative \( \Delta G^\circ \), means that the adsorption process of DCF is spontaneous on the surface of the B-nZVI composite, and the DCF adsorption equilibrium is preferable to products over reactants. However, these values are less than the associated values of chemical bond formation, indicating physisorption rather than chemisorption process (Boparai et al., 2011; Hameed et al., 2019). The standard entropy of the sorption process was calculated using the values of \( \Delta G^\circ \) and \( \Delta H^\circ \) via Eq. (6). The positive sign of \( \Delta S^\circ \) illustrates that the degree of freedom increases at the liquid-solid interface as the adsorption progresses.

3.4. Filtration results

The DCF solutions were passed through a filter containing a mixture of excess sand and either granulated activated carbon (GAC) or B-nZVI at a ratio of (49:1, w/w). As shown in Table 6, the filter composed of B-nZVI composite has a significant advantage in removing DCF over the activated carbon mixture. These results are inconsistent with the adsorption parameters obtained and clearly demonstrate that B-nZVI acts more efficiently than GAC on removing the DCF.

4. Conclusion

In this research, the adsorption efficiency of bentonite, B-nZVI, and AC was investigated for removing DCF from an aqueous solution. The bentonite prevents nZVI aggregation and increases nZVI adsorption activity. Therefore, the B-nZVI has better removal efficiency than other adsorbents in an aqueous solution. Based on the batch adsorption experiments, the pH effect has a major impact on the adsorption process in the range of pH (3.0 – 7.0), the removal capacity was sharply decreased as pH increased. The pZC (7.0 ± 0.1) was evaluated using the salt addition method. The FTIR and XRD have been used to confirm the DCF adsorption and to investigate the adsorption interactions. The equilibrium data well fit the Langmuir isothermal model for both B-nZVI and AC with \( q_{\text{max}} \) equal to 140.8 mg g\(^{-1}\) and 107.5 mg g\(^{-1}\), respectively.

Thermodynamic parameters were estimated at 25 °C, and the average values show that the adsorption process is endothermic (\( \Delta H^\circ = 29.8 \pm 5.2 \text{kJ mol}^{-1} \)), and spontaneous with a positive value of entropy (\( \Delta S^\circ = 175.4 \pm 11.3 \text{kJ mol}^{-1} \text{K}^{-1} \)) within the range of specified temperature (25–55 °C). Finally, column filtration results showed a significant advantage for B-
nZVI/sand mixture compared to GAC/sand mixture column for DCF removal in an aqueous solution.

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