

## Case Report

## Enhancing adsorptive removal of diclofenac from aqueous solution: Evaluating organic and inorganic acid treatment of zeolite

María E. Peñafiel<sup>a,\*</sup>, Lourdes Jara-Cobos<sup>a</sup>, Damián Flores<sup>b</sup>, Carola Jerves<sup>a</sup>, Miguel Menendez<sup>c</sup>

<sup>a</sup> Grupo de Ingeniería de las Reacciones Químicas, Catálisis y Tecnologías del Medio Ambiente (IRCMA), Departamento de Biociencias, Universidad de Cuenca, Cuenca, Ecuador

<sup>b</sup> Facultad de Ciencias Químicas, Universidad de Cuenca, Cuenca, Ecuador

<sup>c</sup> Catalysis, Molecular Separations and Reactor Engineering Group (CREG), Aragon Institute of Engineering Research (I3A), Universidad Zaragoza, 50018, Zaragoza, Spain

## ARTICLE INFO

## Keywords:

Acidic treatment

Adsorption

Diclofenac

Modification

Zeolite

## ABSTRACT

This study examined the adsorption capacity of natural zeolite (ZN) and zeolite treated with citric acid (ZCA) and nitric acid (ZNA) to evaluate their effectiveness in removing the pharmaceutical compound diclofenac (DCF) from water in batch experiments. Fourier Transform Infrared Spectroscopy (FTIR) and textural properties (BET) were used to investigate the changes in zeolite resulting from chemical modifications. The findings demonstrate a significant enhancement in surface area, pore volume, and the presence of acidic sites, resulting in an improved adsorption capacity for DCF. The observed increase in the Si/Al ratio following acid treatment suggests the dealumination of the zeolite. Results have shown an increase in the percentage of DCF adsorbed to 76.8 % from 11.2 % using nitric acid-treated and untreated zeolites, respectively. In comparison, citric acid zeolite achieves 48.9 %. The adsorption kinetic was assessed using pseudo-first and pseudo-second-order models, and it was observed that the pseudo-second-order provided the best fit for all adsorbents. Furthermore, the BET model exhibited the best fit for the adsorption isotherm data. The maximum adsorption capacities were found to follow the order: ZNA (85.9 mg/g) > ZCA (33.6 mg/g) > ZN (14.4 mg/g). These results indicate that the acidic treatment enhances the adsorption capacity of the zeolite, and nitric acid treatment shows the most significant improvement.

### 1. Introduction

Events like the pandemic of COVID-19, the seasonal flu, and some diseases let grow the use of some medicaments. This increase, therefore, leads to an increase in the quantity of these drugs in water and an increase in the environmental consequences. For example, Cooper et al., 2022 warned that, while the world struggled to face the challenges of the pandemic, another problem arose as a consequence of the same in wastewater. Several investigations warn about the quality of water, since it has been overloaded by various types of contaminants, especially pharmaceuticals products [1,2]. These contaminants reach water sources mainly after consumption since the body is not able to assimilate all of the drugs, excreting a significant amount without alterations [3–5]. Therefore, this contamination problem becomes chronic as these contaminants are constantly introduced into the environment. In addition, conventional wastewater treatments are not capable of removing them

from water [6].

The variety of drugs is wide, but generic medications are the most consumed due to their availability without a prescription, and their consumption continues to increase every year. According to IMS-Health, it is projected that the global market for generic drugs will grow from \$411.6 billion in 2020 to \$650.3 billion in 2025 [7]. Among generic medicaments, diclofenac is one the most consumed since 1970 [8]. It is a non-steroidal anti-inflammatory drug (NSAID) with the ability to block or inhibit cyclooxygenase, which is the enzyme responsible for producing inflammation and pain. Therefore, along with other anti-inflammatory drugs, it is commonly used to relieve pain and inflammation. DCF is prescribed in oral tablets or topical gel forms.

Diclofenac primarily gets into wastewater after consumption, as approximately 6–30 % of this medication is excreted in its original form [9]. Vieno and Sillanpää (2014) [10] demonstrate that diclofenac has low degradability and a low elimination rate in treatment plants. It is

\* Corresponding author.

E-mail address: [maria.penafiel@ucuenca.edu.ec](mailto:maria.penafiel@ucuenca.edu.ec) (M.E. Peñafiel).

<https://doi.org/10.1016/j.cscee.2023.100575>

Received 3 October 2023; Received in revised form 29 November 2023; Accepted 30 November 2023

Available online 5 December 2023

2666-0164/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

also, among the most frequently detected in the effluents of treatment plants [11–14]. Additionally, numerous studies have provided for the detrimental effect of DCF on aquatic organisms. For instance, research conducted by Refs. [9,14] has demonstrated that DCF can induce alterations in fish behavior, disrupt their development, and negatively impact their reproductive capabilities. For this reason, the presence of DCF in wastewater and surface water is of global concern, leading to the search for various methods to remove it from water. Furthermore, the review conducted by Ref. [2] about the presence of various drugs in the environment warned of a potential increase in environmental effects and suggested the need to seek efficient and economically viable processes to remove these compounds.

Although many techniques have been tried for DCF degradation and removal from water [15–18], adsorption is the most attractive technique due to its simplicity and efficiency. The search is focused on efficient [19,20] and low-cost adsorbent materials [18,21]. Clays are low-cost natural materials used to remove contaminants such as oil, chemicals, heavy metals [22,23], and other industrial uses [24]. Zeolite is a clay widely distributed in the Earth's crust, with significant deposits found in sedimentary and volcanic rocks. It is composed of crystalline aluminosilicates, characterized by a three-dimensional network of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedral, linked by oxygen bonds. This structure forms channels and cavities of uniform size, resulting in a high specific surface area and regular pore distribution. Its abundance makes it one of the most common minerals and its wide geographic distribution makes it accessible for use in various scientific and industrial applications [18].

Pérez-Botella et al. (2022) [25] affirm that a well-established trend can be seen where zeolitic adsorbents are kept for industrial processes, and new zeolitic materials are studied for emerging separations. Several studies have reported DCF adsorption in natural zeolites and in zeolites with treatments such as plasma, the use of surfactants, and others. García et al. (2019) [26] used plasma treatment of zeolites to increase the capacity of adsorbing DCF in aqueous medium. Zhang et al. (2020) [27] used coated zeolites with layers of Zn double hydroxides to remove cadmium in water. Vargas et al. (2020) [28]; Khaksarfard et al. (2023) [29], and Sun et al. (2017) [30] used zeolite in the presence of surfactants to remove DCF, showing that the drug adsorption was on the external surface of the adsorbent with a rapid removal rate and that the interactions were due to the functional groups present. In this study, 35 mg/g of diclofenac was adsorbed. Chauhan et al., 2020 [31] tried pillared clays to adsorb diclofenac and other drugs achieving a maximum adsorption capacity of 23.05 mg/g of DCF. Furthermore, the effect of sulfuric acid treatment on the physicochemical properties of kaolin was investigated by Ref. [32], observing an increase in surface area.

Chemical activation of carbons is widely employed [33,34]. However, the chemical activation of clays with acids to use as adsorbents has been less explored. Few studies have tested the effect of acidic modification, Hosseipour et al. (2023) [35] modified NaY zeolite with sulfuric acid. It is a simple technique and does not introduce additional compounds into the stream to be treated. Therefore, the results in this article will be novel and provide relevant information regarding the treatment of currents with DCF.

Considering, first, the effects of DCF on aquatic organisms and the need to eliminate it from water, and second, that the chemical activation of clays to remove drugs has not been performed so far, it will be effective to study the acid activation of clays to remove DCF from water. Therefore, this work focused on the adsorption of DCF by natural and modified zeolite using treatment with HNO<sub>3</sub> y C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> to increase adsorption capacity. The aims are to: 1) determine the differences in characteristics between natural and acid-modified zeolites; 2) compare the adsorption of DCF on the unmodified substrate and the substrate modified with different acids; 3) explore the adsorption mechanisms of DCF on the substrates; 4) select the optimal modified form.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Diclofenac (99 % DCF) supplied by Sigma Aldrich was used. Nitric acid (HNO<sub>3</sub> 78 %) and citric acid (CH<sub>2</sub>COOH)<sub>2</sub>C(OH)COOH were acquired from Merck. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to regulate the pH. All the above-mentioned chemicals were analytic grade. DCF solutions were prepared using ultrapure water. The physicochemical properties of DCF are detailed in Table 1.

### 2.2. Preparation and characterization of adsorbent

The zeolite used in this study is type Y, and it was sourced from Ecuaminerales, MINMETEC in Ecuador, and possessed a particle size ranging between 20 and 40 nm.

The objective of the chemical activation process using different types of acids was to compare and evaluate the changes in the adsorption capacity of zeolite when subjected to an inorganic acid (strong acid) and an organic acid (weak acid).

In the acid modification, the zeolite was treated with nitric acid and citric acid solution (1 N) at a ratio 1g/10 mL. The acid-zeolite mixtures were shaken at 80 °C for 3 hours. Then, the zeolites were washed thoroughly with ultrapure water three times before drying them in an oven at 50 °C for 24 hours. The zeolites were denoted by ZNA (zeolite with nitric acid) and ZCA (zeolite with citric acid).

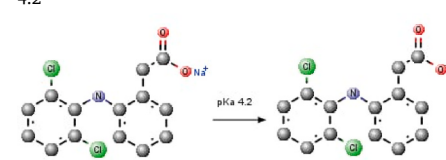
The characterization was used to verify possible changes in the properties and solid structure of the zeolite due to the acid treatment, through the following methods:

- Fourier Transform Infrared Spectroscopy (FTIR) was employed using a Thermo Scientific spectrometer Nicolet iS5 to gather information on chemical bonds and identification of functional groups. The analysis was conducted within the range of 4000 to 500 cm<sup>-1</sup>.
- The determination of specific area was carried out through nitrogen physisorption using an ASAP 2020 Micromeritics instrument, employing the Brunauer-Emmett-Teller method (BET) following ISO 9277.
- The potential of zero charges (pH<sub>ZPC</sub>) of adsorbents was measured following the method described by Antunes et al. (2021) [36].
- The chemical composition of the natural and treated adsorbents was analyzed.

### 2.3. Adsorption experiments

Solutions containing selected concentrations of DCF (5–50 mg/L) for the adsorption experiments were prepared by diluting a pre-made stock solution (100 mg/L). In order to find the optimal dosage of adsorbents required to achieve the maximum percentage of adsorption, a specific quantity of each adsorbent (0.01–0.4 g) was added to 50 mL of DCF

**Table 1**  
The physicochemical properties of diclofenac.

Parameter	Description
Molecular formula	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> NNaO <sub>2</sub>
Particle size (nm)	0.97 × 0.96
Molecular weight (mol.g <sup>-1</sup> )	318.1
pK <sub>a</sub>	4.2
pH dependence of DCF speciation	

solution with a concentration of 20 mg/L. The mixtures were stirred at a constant rate of 150 rpm and maintained at a temperature of 20 °C. The suspensions were agitated for 120 min, except for the kinetics, which involved varying times ranging from 2 to 120 min. Subsequently, the solutions were collected and filtered.

The residual concentrations were evaluated using a UV spectrometer at 273 nm (Thermo Scientific Genesys™ 10S spectrophotometer, USA). The effect of solution pH on the adsorption percentage of natural and modified zeolites was determined by adjusting the pH values (ranging from 2 to 10) of 20 mg/L DCF solutions with 0.1 N NaOH and HCl solutions. The reported results in this study represent the average value obtained from three experimental replicates, which was considered the standard.

The amount of DCF adsorbed (mg/g) at time  $t$ , and the percentage of CIP removal (%R) by ZN, ZNA, and ZCA were calculated by:

$$q = \frac{(C_o - C_t)V}{m} \quad (1)$$

$$\%R = \frac{100(C_o - C_t)}{C_o} \quad (2)$$

where,  $C_o$  y  $C_t$  are the concentration (mg/L) of DCF at initial and at time  $t$  (min), respectively.  $V$  is the volume of solution (L).  $m$  is the adsorbent mass (g).

To analyze the experimental results and gain insights into the adsorption process, various kinetic model such as the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, as well as isotherm models including Langmuir, Freundlich, and BET were employed.

### 2.3.1. Kinetic models

The pseudo-first-order model is expressed by linearized equation

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (3)$$

where  $q_t$  and  $q_e$  are the amount of DCF adsorbed per zeolites (mg/g) at time  $t$  (min) and at equilibrium respectively;  $K_1$  is the rate constant of equation (1/min).

Pseudo-second-order is expressed by linearized equation

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where  $K_2$  is the rate constant of equation (g/mg.min).

The intraparticle diffusion model (Weber and Morris model) is expressed by

$$q_t = K_d t^{0.5} + C \quad (5)$$

$$R_i = 1 - \left( \frac{C}{q_{ref}} \right) \quad (6)$$

$K_d$  is the constants of the intraparticle diffusion model (mg/g min<sup>1/2</sup>);  $C$  is the intersection of the graph with the vertical axis (mg/g).  $R_i$  is defined as the initial adsorption factor and it is represented as the ratio of the initial adsorption amount ( $C$ ) to the final adsorption amount  $q_{ref}$ .  $q_{ref}$  (mg/g) is the solid phase concentration at time  $t = t_{ref}$  for an adsorption system;  $t_{ref}$  is the longest time in the adsorption process.  $R_i$

values have four zones, as show in Table 2 [37].

### 2.3.2. Isotherms models

The linearized Langmuir equation is

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (7)$$

$$R_L = \frac{1}{1 + K_L C_o} \quad (8)$$

where  $q_e$  is the equilibrium amount of DCF adsorbed by zeolites (mg/g),  $C_e$  and  $C_o$  are the equilibrium and initial concentration of DCF solution (mg/L),  $q_m$  is maximum adsorption capacity (mg/g) and  $K_F$  is the Langmuir constant.

The Freundlich model can be expressed as:

$$\log q_e = \log K_F + \frac{1}{N} \log C_e \quad (9)$$

where  $K_F$  is the Freundlich constant (mg/L) (mg/g)<sup>-1/n</sup>;  $N$  refers to the adsorption intensity (dimensionless).

The Brunauer-Emmet-Teller (BET) equation model is

$$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e) \left[ 1 + (C_{BET} - 1) \left( \frac{C_e}{C_s} \right) \right]} \quad (10)$$

$q_e$  and  $C_e$  have the same meaning indicated above,  $q_s$  is the theoretical saturation capacity in the first layer (mg/g),  $C_{BET}$  is the BET constant (L/mg),  $C_s$  is the adsorbent monolayer saturation concentration (mg/L).

Dubinin-Radushkevich model (D-R) was applied to distinguish the physical and chemical adsorption by its mean free energy,  $E$ .

$$\ln q_e = \ln q_m + K_{ad} \varepsilon^2$$

$K_{ad}$  is a constant related to free energy (mg<sup>2</sup>/J<sup>2</sup>),  $\varepsilon$  is the Polanyi potential (J/mol).  $q_m$  is the theoretical maximum adsorption capacity (mg/g)  $E$  can be calculated using the following relation

$$E = \frac{1}{\sqrt{2K_{ad}}} \quad (11)$$

### 2.3.3. Assessment of model fit

To mitigate the inherent bias caused by linearization, a nonlinear error function was employed to determine the optimal fit of kinetic and isotherm models to experimental data. Marquand percent standard deviation (MPSD) function was calculated using the equation provide (Eq. (12)).

$$MPSD = \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left( \frac{q_e - q_i}{q_e} \right)^2} \quad (12)$$

## 3. Results and discussion

### 3.1. Characterization of adsorbents

#### 3.1.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrums of both the natural and acid-treated zeolites are presented in Fig. 1. Notably, the acidic treated zeolites, particularly the HNO<sub>3</sub> treated zeolite (ZNA), exhibit distinct variations in the FTIR spectra. Peaks corresponding to stretching vibrations of OH groups appeared at approximately 3200 cm<sup>-1</sup>, indicating the presence of hydroxyls within the mesopores. The IR peaks observed at 1022 cm<sup>-1</sup> and 793 cm<sup>-1</sup> can be attributed to the vibrations Al–Al–OH, Al–Mg–OH, and Si–O–Si bonds. The enhanced relative intensity of the peaks around 3200 cm<sup>-1</sup> in the ZNA samples suggests an elevated presence of hydroxyl groups, possibly resulting in an increase in acid groups. Chen and

**Table 2**  
Initial adsorption factor ( $R_i$ ).

$R_i$	Initial adsorption behavior
$R_i = 1$	No initial adsorption
$1 > R_i > 0.9$	Weakly initial adsorption
$0.9 > R_i > 0.5$	Intermediately initial adsorption
$0.5 > R_i > 0.1$	Strongly initial adsorption
$R_i < 0.1$	Completely initial adsorption

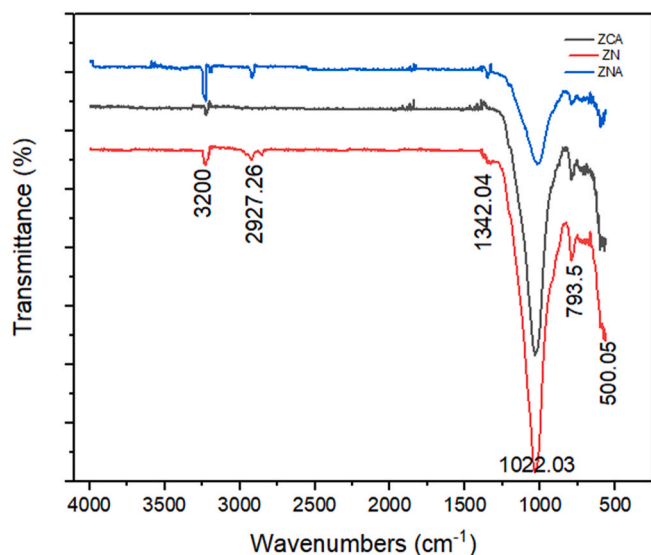


Fig. 1. FTIR spectrum.

Wu (2004) [38] postulated that the introduction of oxygen and nitrogen functional groups occurs in the adsorbent material through nitric acid oxidation. As a result, the appearance of a peak at  $1342\text{ cm}^{-1}$  in ZNA spectrum can be attributed to nitric acid treatment, which would introduce nitrate groups. It was observed that the intensity of the peaks at  $1022\text{ cm}^{-1}$  decreases as the acid strength increases in the acid treated zeolite. This suggests that the process of de-alumination is accelerated with nitric acid [39].

The ZN and ZCA samples exhibit a band around  $3200\text{ cm}^{-1}$ , which corresponds to the stretching vibrations of O–H bonds. Upon treatment of the zeolite with citric acid, a weak acid, there were minimal alterations in the peak pattern in  $3200\text{ cm}^{-1}$ . However, as the acid strength increased (using nitric acid), the intensity of peak significantly increased. This observation aligns with the findings of [39] during the acid treatment of kaolin.

### 3.1.2. Textural properties

The  $\text{N}_2$  adsorption–desorption isotherms of all adsorbents are presented in Fig. 2. Table 3 shows the specific surface area ( $S_{\text{BET}}$ ), size of pores and micropore volume of the adsorbents obtained before and after acid treatment.

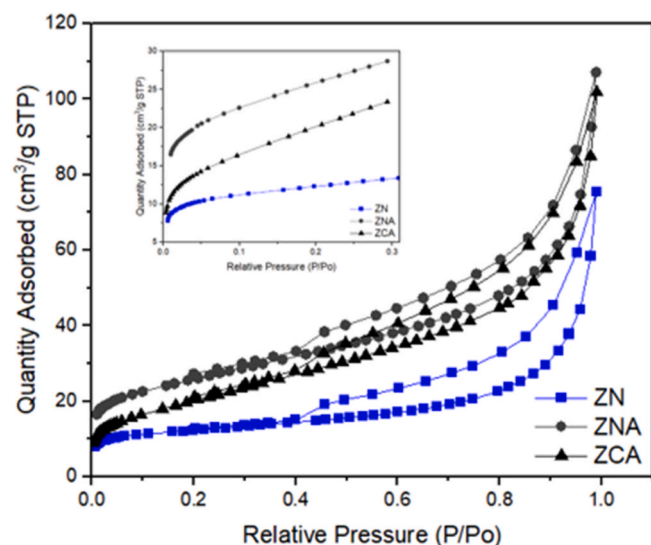


Fig. 2. The adsorption/desorption isotherms of  $\text{N}_2$ .

Table 3

The physicochemical properties adsorbents.

Material	Specific Surface $\text{m}^2\cdot\text{g}^{-1}$	Pore Volume $\text{cm}^3\cdot\text{g}^{-1}$	Pore size nm	$\text{pH}_{\text{ZPC}}$
ZN	41	0.07	6.50	7.6
ZNA	89	0.27	2.15	4.2
ZCA	61	0.09	3.16	4.9

The isotherms obtained for ZN, ZCA, and ZNA can be classified as type IV, indicating the presence of meso and micropores and multilayer adsorption. All three isotherms exhibit hysteresis loops, confirming the presence of mesoporous structures. The observed hysteresis loop type, H3 suggests the presence of non-rigid platy particles.

The H3 loop is observed when there are aggregates of plate-like particles, resulting in the formation of slit-shaped pores [40]. According to Ref. [32] the relative pressure ( $P/P_0$ ) at which the adsorption reaches the plateau shifts to higher values for samples with larger pore diameters. This parameter, ( $P/P_0$ ) at 0.2, is commonly used to qualitatively compare the pore dimensions among different samples, with higher values indicating large mesopore sizes. Acid treated zeolites exhibit higher ( $P_0/P$ ) values, indicating the presence of mesoporous structures.

According to the International Union of Pure and Applied Chemistry, mesoporous materials typically have diameters ranging from 2 nm to 50 nm and surface areas between 10 and  $200\text{ m}^2/\text{g}$ . Based on the data presented in Table 3, the acid treatment improves the surface area and increases the pore volume, thereby improving the mesoporous characteristic of zeolite. In comparison to the parent zeolite (ZN), both ZNA and ZCA can be classified as high surface area mesoporous adsorbents.

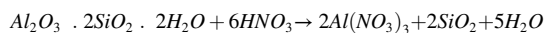
The obtained results demonstrate that nitric acid treatment enhanced the surface area more effectively than citric acid treatment. This can be explained by the intensity of de-alumination, which was more considerable than citric acid treatment. The results (Table 3) indicate that the total pore volume increased after acid treatment, while the average pore diameter decreased, as reported [41].

The decrease in  $\text{pH}_{\text{ZPC}}$  (point of zero charge) observed after the acid treatment of the zeolite suggests that ZAN and ZCA exhibit higher acidity compared to the natural material.

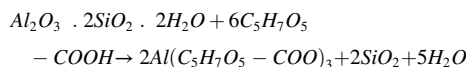
### 3.1.3. Chemical composition

The chemical analysis was carried out to know the chemical composition of zeolites before and after acid treatment. Table 4 shows the results obtained for the chemical composition of ZN, ZNA, and ZCA expressed as oxides percentage. Raw zeolite sample contains  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in high quantities whereas other oxides are present in low percentages.

The reaction between zeolite and nitric acid can be described by



While, the chemical equation between zeolite and citric acid is described by



The acid treatment induces compositional changes in the natural zeolite. According to chemical analysis, in nitric acid treatment, the contents of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  decrease, this decrease is lower with citric acid treatment, which suggests that the greater de-alumination depends on the strength of the acid. Conversely, the  $\text{SiO}_2$  content increases, resulting in an increased  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. The reduction in  $\text{Al}_2\text{O}_3$  content after acid treatment can be attributed to the leaching of  $\text{AlO}^+$ ,  $\text{Al}^{3+}$  ions from the octahedral layer, which occurs due to hydrolysis under acidic conditions. The de-alumination requires partial rearrangement of aluminosilicate framework may be formulated

**Table 4**

Chemical composition of the natural and treated adsorbents.

	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	MgO%	CaO%	Na <sub>2</sub> O%	K <sub>2</sub> O%	SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>
ZN	57.61	15.55	4.25	1.49	0.45	6.76	1.15	3.70
ZNA	64.38	12.32	2.24	1.15	0.56	3.68	0.85	5.22
ZCA	60.91	13.62	3.29	1.25	0.25	4.15	1.02	4.47

as depicted in Fig. 3 [39].

The cation ( $Mg^{2+}$ ,  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ )/Al ratio should be maintained at values close to 1 in order to achieve charge balance within the zeolite structure. The reduction of this ratio subsequent to acid treatment is believed to be indicative of the protonation level of the zeolites [42].

### 3.2. Adsorption studies of diclofenac

#### 3.2.1. Maximum removal percentage by adsorbents

To determine the dosage of each adsorbent for achieving the maximum percentage removal of DCF, adsorption experiments were conducted using a concentration of DCF solution of 20 mg/L and pH 6. The performance of ZN, ZNA, and ZCA was evaluated.

The effect of dosage on DCF adsorption capacities and removal percentage is shown in Fig. 4. As can be seen, with increasing dosage, the DCF removal increased for each adsorbent. Removal efficiency increases with the adsorbent dosage increasing as a result of the availability of more active sites and more surface area. This adsorption on ZCA and ZNA was significantly higher compared to ZN. The zeolite treated with the nitric acid sample was able to remove 76.8 % DCF compared to the citric acid treated zeolite sample which was able to remove only 48.9 % DCF, using the same dose (Fig. 4b). The doses required to achieve the maximum adsorption percentage were determined to be 2 g/L para ZN (48.5 %;  $q_e = 5.1$  mg/g), 1 g/L for ZCA (75.1;  $q_e = 17.1$ ), and 0.4 g/L for ZNA (76.8 %;  $q_e = 39.3$  mg/g) (Fig. 4a). The increase in adsorption capacity is due to the increase principally at the increase of surface area. It is evident that nitric acid treatment significantly improves the adsorption of DCF on the zeolite.

The adsorption capacity exhibited an increase with the augmentation of the surface areas ( $S_{BET}$ ) of the adsorbents, where a higher  $S_{BET}$  of the adsorbent (ZN < ZCA < ZNA) resulted in a greater adsorption capacity ( $q_e$ ). In order to understand the relationship between surface area and the increase in adsorption capacity, the experimental values of  $q_e$  were compared with the values of  $q_e$  estimated solely based on the surface areas.

The surface area of the zeolite increased by 2.17 times with nitric acid treatment (ZNA), which was expected to result in an increase in adsorption capacity from approximately 5.1 to 11.0 mg/g. However, the experimentally obtained adsorption capacity was 39 mg/g. With ZCA, an increase in adsorption capacity from 5.1 to 7.5 mg/g was expected,

but the experimental capacity obtained was 16.0 mg/g. The experimental  $q_e$  values showed a greater increase than expected solely based on the increase in surface area, indicating other interactions in the adsorption of DCF on modified zeolites (Fig. 4c).

The treatment with nitric acid caused the particle and pore size of zeolite to become smaller and have a higher surface area, which enabled it to have more active sites for adsorption. Previous studies using hierarchical ZSM-5 zeolite, in which mesopores were created by means of alkaline treatment, showed improvement over the non-treated zeolite [43]. The acid treatment employed in our case also causes the creation of mesopores, improving the accessibility of DFC to the zeolite surface. The lack of mass transfer contribution to the adsorption rate confirms this hypothesis. This effect, combined with the more acidic surface, may explain the great improvement in DFC adsorption in the treated zeolite.

The optimal dosage of zeolites to achieve maximum removal percentage in each case is lower than those used with other materials for DCF adsorption. For instance Ref. [44], used 1.5 g/L of the graphene to remove DCF. In a study conducted by Ref. [45], a dosage of 2 g/L of carbon nanotube-based beads was used, all with removal percentages lower than those found in the acid treated zeolites in this work.

#### 3.2.2. Effect of pH on the adsorption of DCF

The pH can influence the ionization state of functional groups on the adsorbent surface, altering its charge and surface properties. Additionally, the pH can also affect the degree of ionization of the adsorbate molecules, influencing their affinity for the adsorbent surface. Therefore, controlling and adjusting the pH of the solution is essential in optimizing adsorption processes, as it can significantly affect the efficiency and selectivity of the adsorption process.

Adsorption experiments were carried out at different pH values. Fig. 5 shows the effect of solution pH on the DCF adsorption capacity on ZN, ZCA, and ZNA.

At low pH values, the three adsorbent materials exhibit maximum adsorption capacity and percentage of DCF removal, which decreases as pH increases. The adsorption percentage for each adsorbent, based on the DCF dissociation percentage, is illustrated in Fig. S1.

As illustrated in Fig. 5, the adsorption capacity of DCF on the three adsorbents is higher at lower pH values and decreases with increasing pH values. This behavior was also described by Refs. [30,46,47]. The low solubility of DCF at pH values lower than its  $pK_a$  may partly explain

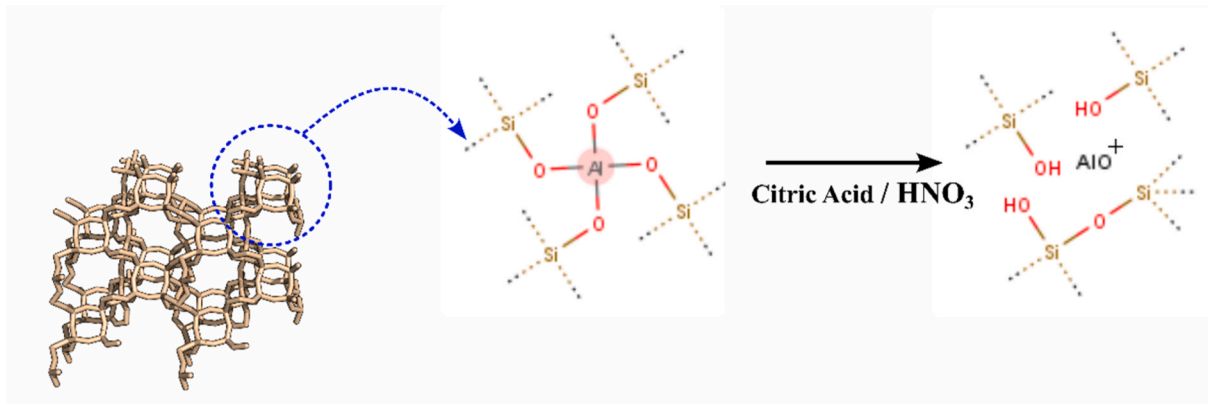
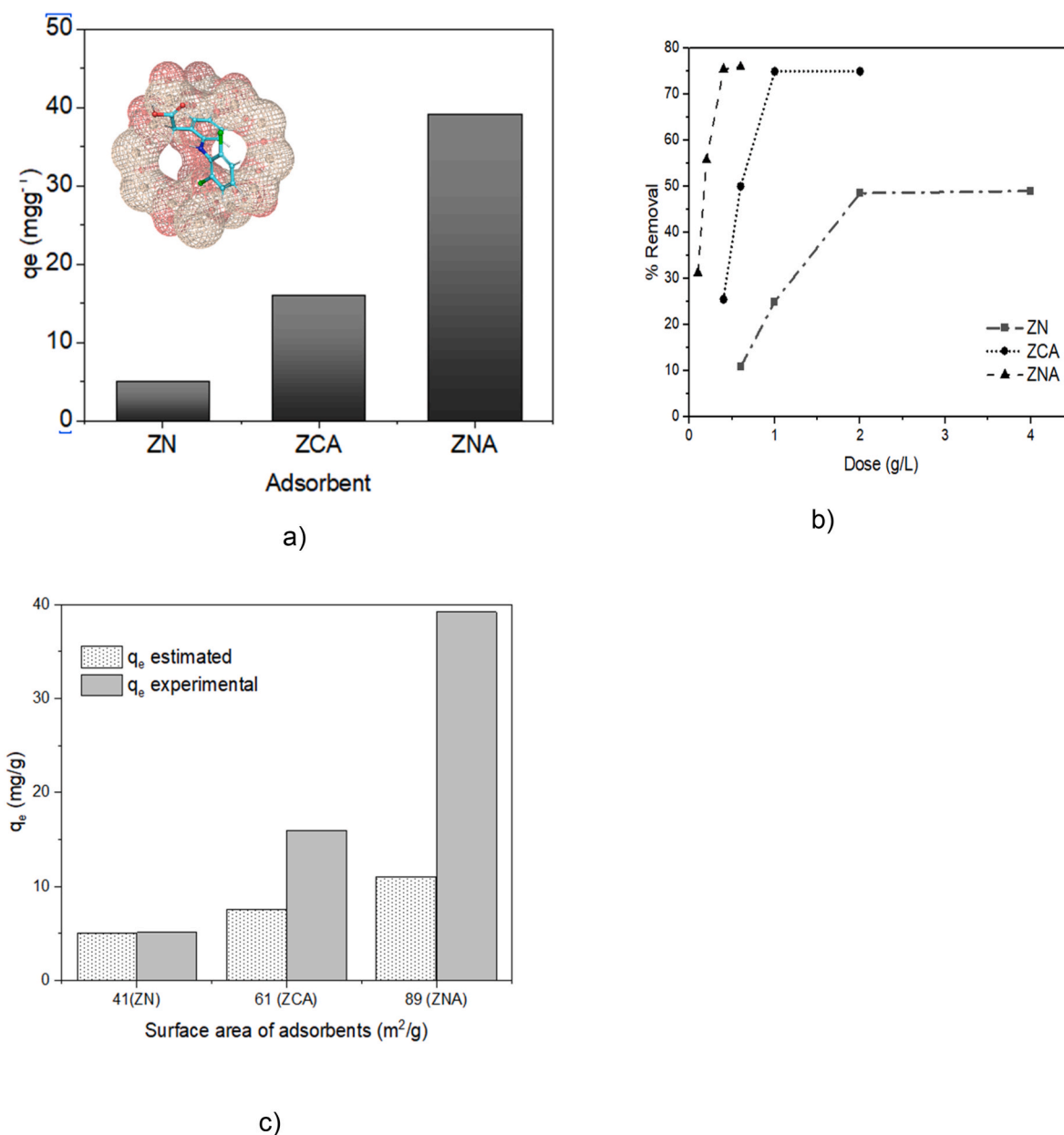


Fig. 3. Equation of de-alumination of zeolite.



**Fig. 4.** (a). The adsorption capacity achieved by each adsorbent with the optimal dosage (pH = 6, 20 °C). (b) Influence of dosage on the removal percentage of DCF from aqueous solution. (c) Comparing the estimated adsorption capacity based on increasing surface area with experimental adsorption capacity.

this trend. Bhadra et al. (2016) [48] demonstrated that the degree of adsorption depends on the amount of acid functional groups. The  $pH_{ZPC}$  of modified zeolites (Table 1) shows a higher acidity, which may explain the increased adsorption capacity. The decrease in adsorption capacity with increasing pH can be explained by electrostatic repulsion due to the increase in negative charge of both zeolites and DCF. The electrostatic interactions between functional groups on DCF and zeolites have been illustrated in Scheme 1.

According to  $pH_{ZPC}$ , the surface of ZN carries a positive charge when the pH is below 7.6, and a negative charge when the pH is above 7.6. The charge of DCF molecule is determined by its dissociation constant values. Since DCF has a  $pK_a$  of 4.2, it exists in its non-ionized form at a pH below 4.2 but carries a negative charge at a pH above 4.2. At pH 6, DCF is negative, as shown in Table 1, while ZN is positive, which favors electrostatic attractions. At pH less than 6, as indicated above, the low solubility of DCF favors adsorption. The increase in the removal of DCF over ZCA and ZNA recorded at pH 4 and 6 could be attributed to the

dissociation of  $-COO$  groups on DCF, resulting in increased negative charges over it; while at pH 4 ZCA is positive, and ZNA is neutral [31]. It was noticed that DCF had no affinity to the zeolites at pH below 7.

### 3.2.3. Adsorption kinetic studies

The adsorption kinetic study provides essential information about the adsorption rate and mechanism, the controlling step, and the overall efficiency of the process. Analyzing the kinetic can determine how quickly solutes are being adsorbed onto the solid surface and the factors that influence this process.

In this study, the aim was to ascertain the time required to achieve equilibrium by evaluating the adsorption capacity of DCF on both raw and acid treated zeolites within the time frame of 5–120 minutes. The adsorption kinetic was examined under a pH of 6 and a temperature of 20 °C for all adsorbents. To analyze the experimental data, the pseudo first order, pseudo second order, and intraparticle diffusion models were employed. The obtained data and the corresponding best fit plots are

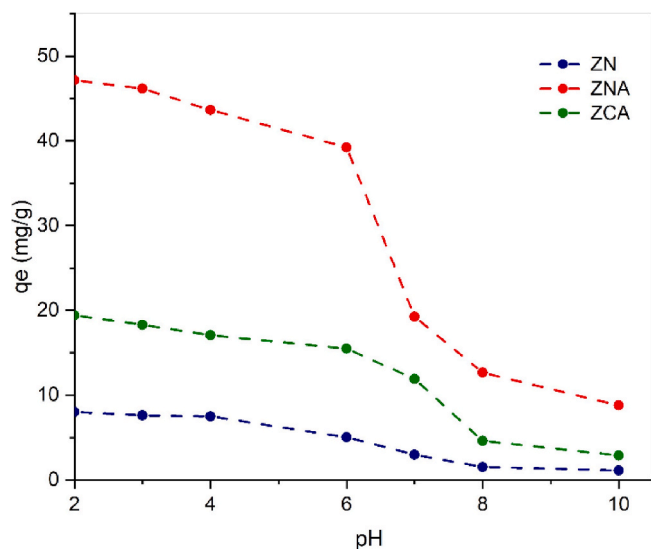


Fig. 5. Influence of pH on the adsorption of DCF ( $C_0 = 20\text{ mg/L}$ ,  $20^\circ\text{C}$ ), ZN (dosage =  $2\text{ g/L}$ ), ZCA (dosage =  $1\text{ g/L}$ ), ZNA (dosage =  $0.4\text{ g/L}$ ).

presented in Fig. 6, while the calculated parameters of the model are provided in Table 5.

As show in Fig. 6, uptake rate was rapid within the first 20 min. After 60 min to ZN and ZCA and 90 min to ZNA there was no significant increase observed in the adsorption capacity, indicating that equilibrium can be assumed to have been reached. Thus, the adsorption equilibrium time for ZN and ZCA was reached within 60 minutes, whereas for ZNA, it took 90 minutes. These equilibrium times are lower than the reported values for DCF adsorption [30].

In the plots present in Fig. 6, the lines represent the linear models, while the symbols correspond to the experimental data. Upon fitting both the pseudo first order and pseudo second order models, the pseudo second order exhibited the best fit for both raw and treated zeolites. This conclusion is supported by the correlation coefficient ( $R^2 = 0.99$ ).

The kinetic constant  $K_2$  was found to be higher for ZN compared to ZNA, indicating a faster adsorption process and shorter time required for ZN to reach adsorption equilibrium. The pseudo second order plot

reveals that the adsorption of DCF follows  $ZNA > ZCA > ZN$ .

Upon analyzing the adjusted experimental data to the intraparticle diffusion model, it was observed that for ZN, a  $C$  value of  $3.45\text{ mg/g}$ , and a  $R_i$  value of approximately 0.3 were obtained. This value of  $R_i$  suggests strong initial adsorption. For ZCA and ZNA, the  $R_i$  values were 0.51 and 0.59 respectively, indicating intermediately initial adsorption [36].

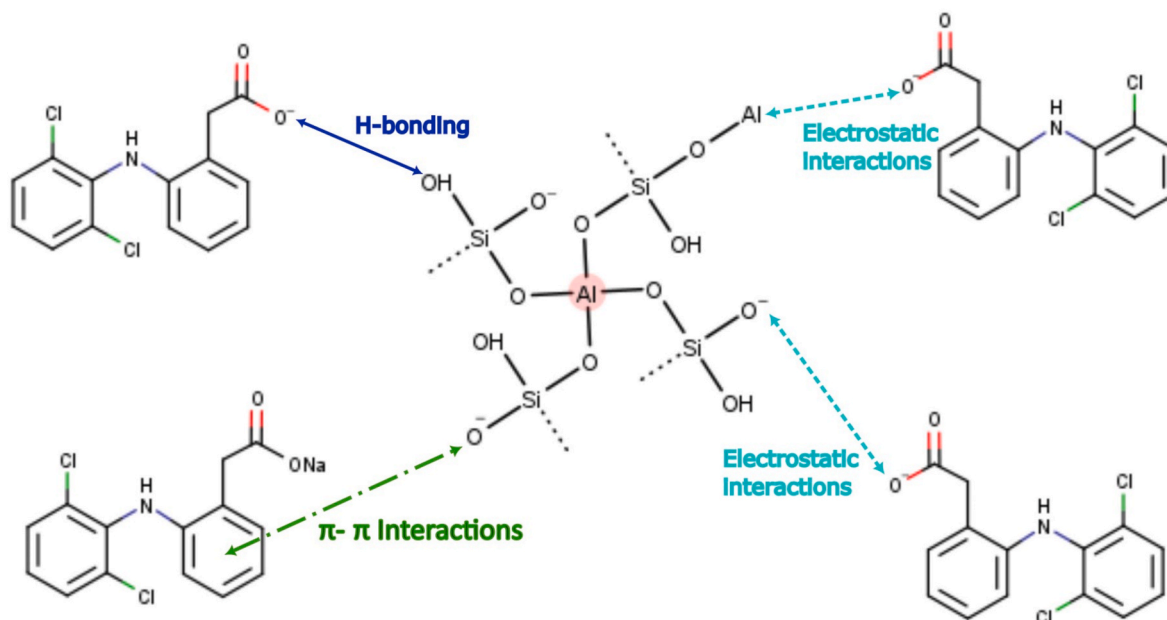
In the case of the two acidic treated zeolites, the intraparticle diffusion model exhibited two linear regions that did not intersect the origin, implying that intraparticle diffusion is not the rate-controlling step. The first linear portion corresponds to rapid external mass transfer, while the second region is associated with adsorption on the external surface [49]. These results are in accordance with the textural properties obtained for all the adsorbents, where ZN is mesoporous material, while ZCA and ZNA possess more microporous and higher surface area  $S_{BET}$  [50].

### 3.2.4. Adsorption equilibrium studies

Equilibrium models, known as adsorption isotherms, describe the equilibrium relationship between the concentration of the adsorbate in the bulk solution and the quantity of adsorbate adsorbed at adsorbent while maintaining constant pH and temperature conditions.

The isotherms presented in Fig. 7 were derived from a concentration range of DCF between 5 and 50 mg/L, under conditions of pH 6 and  $20^\circ\text{C}$ . Although the adsorption processes were almost nearly complete within 60 minutes for ZN and ZCA, and within 90 minutes for ZNA (Fig. 6), the adsorption period was extended to 120 minutes to ensure that equilibrium was reached. The obtained experimental data were fitted to various models, and the corresponding parameters are summarized in Table 6. The best fits of the models and D-R plots are shown in Fig. 7.

The adsorption isotherm of ZN can be classified as type L-3 isotherm according to the classification by Giles [51], indicating favorable and multilayer adsorption. This type of isotherm is commonly observed in mesoporous solids. Within the studied concentration range, the best fit for ZN was obtained using the BET model, which supports the occurrence of multilayer adsorption. The DCF adsorption on the surface of ZN is likely facilitated by van der Waals interactions between the two entities. The fit to the D-R model suggests physical adsorption, as evidenced by the adsorption energy values of  $6.9\text{ kJ/mol}$ . Additionally, the BET model adequately describes the observed multilayer physical



Scheme 1. Possible mechanisms of adsorption of DCF given interactions of their functional groups with zeolites.

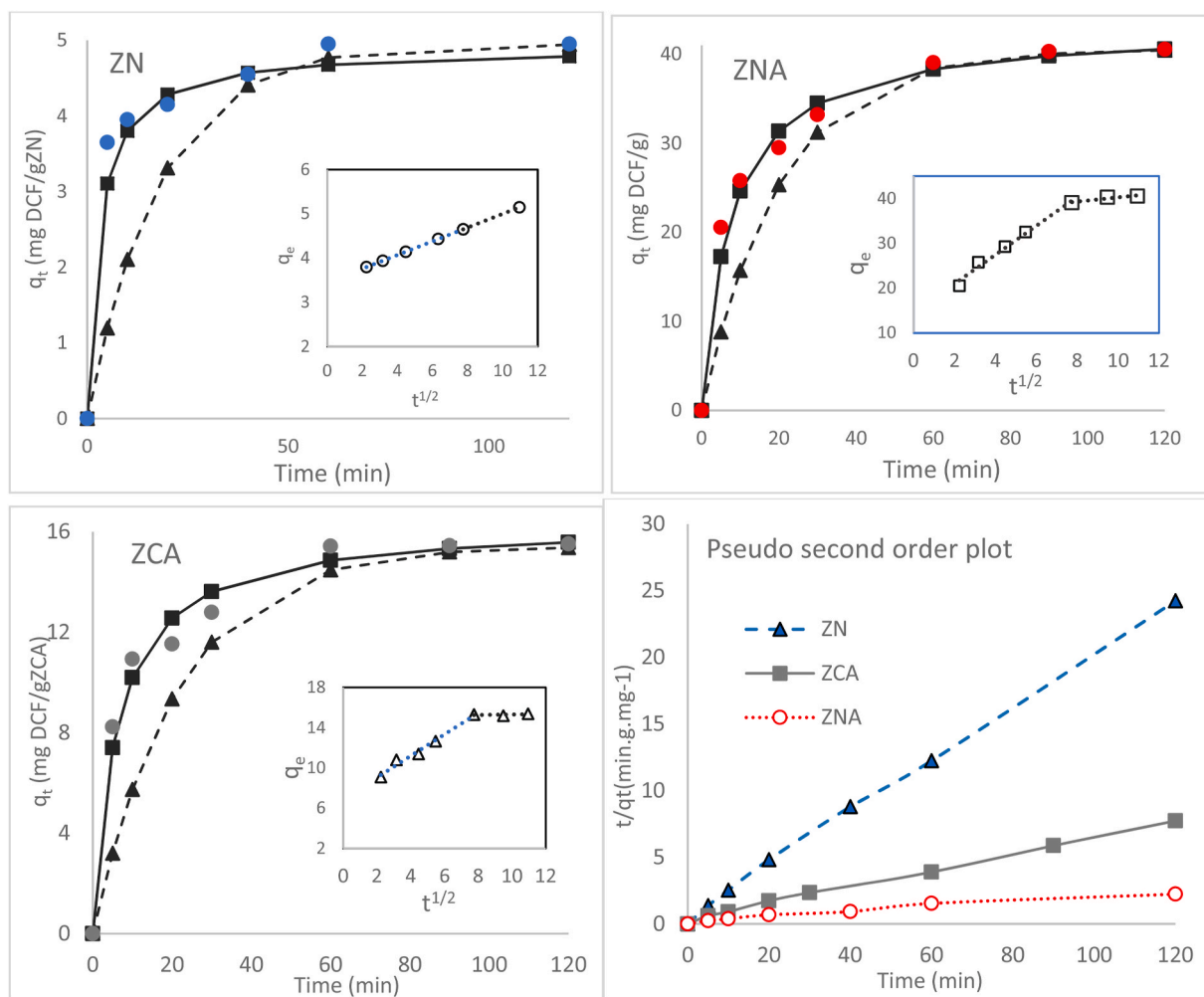


Fig. 6. Curve-fitting plot of studies kinetic models. Pseudo first order (—) and pseudo second order (- - -). Intraparticle diffusion model. Pseudo second order plot.

**Table 5**  
Parameters of the pseudo first order and pseudo second order models.

Model	Parameters	ZN	ZNA	ZCA
Pseudo first order	$q_e$ (mg g <sup>-1</sup> )	4.95 ± 0.8	40.55 ± 2.2	15.43 ± 2.0
	$K_1$ (min <sup>-1</sup> )	0.055	0.042	0.046
	$R^2$	0.91	0.96	0.95
Pseudo second order	$q_e$ (mg g <sup>-1</sup> )	4.50 ± 0.6	42.19 ± 1.8	16.36 ± 1.2
	$K_2$ (g.mg <sup>-1</sup> .min <sup>-1</sup> )	0.005	0.010	0.008
	$R^2$	0.99	0.99	0.99

adsorption.

The adsorption isotherms of the acidic treated zeolites (ZNA and ZCA) exhibit a type L behavior. These zeolites demonstrate a better fit to the BET model and the Freundlich model. Following the acid treatment, the theoretical adsorption capacity in the first layer ( $q_s$ ) increases from 5.5 mg/g in ZN to 16.4 mg/g for ZCA and up to 45.05 mg/g for ZNA. This enhancement in adsorption capacity in the monolayer suggests an increase in the number of active sites due to the increase in the specific surface area. The mean adsorption energy ( $E$ ) values obtained from the D-R model were 7.45 and 7.14 KJ/mol for ZNA and ZCA respectively, indicating physical adsorption.

The  $q_{max}$  values from the Langmuir model for ZCA and ZNA are 2 and 6 times higher than that of ZN, respectively. These results confirm that

the ZNA is the most effective adsorbent among those studied for the removal of DCF from water. The values of  $R_L$  parameter, as shown in Fig. S2, further support the favorable adsorption of DCF onto the adsorbents. The lower  $R_L$  values and higher  $K_L$  values observed onto ZNA compared to ZCA are in agreement with the more favorable adsorption of DCF onto ZNA.

### 3.2.5. Adsorption mechanism

In general, the quantity of adsorbate adsorbed onto any adsorbent increases as the surface area increases, particularly with the increase of activated sites. The results obtained demonstrated a significant increase in the surface area of zeolite after acid treatment, resulting in an increase in adsorption capacity. However, this increase was greater adsorption capacity was observed. However, this increase was higher than expected due to the increase in surface area.

To understand the possible interaction mechanism for the adsorption of DCF over all adsorbents, adsorption over ZN was studied, and then investigations were performed for both ZCA and ZNA.

The solution pH is a crucial parameter in the mechanism of adsorption in the aqueous phase, as it influences the properties of both the adsorbates and adsorbents. In the case being studied, the electrostatic attraction and repulsion are influenced by the pH of the study solution, as described above. Therefore, electrostatic interactions alone are insufficient to explain the observed adsorption capacities.

Several authors have provided explanations for the adsorption of DCF through the formation of hydrogen bonds,  $\pi$ - $\pi$  bonding, and hydrophobic attraction [48,52]. The increase of hydroxyl groups in zeolite



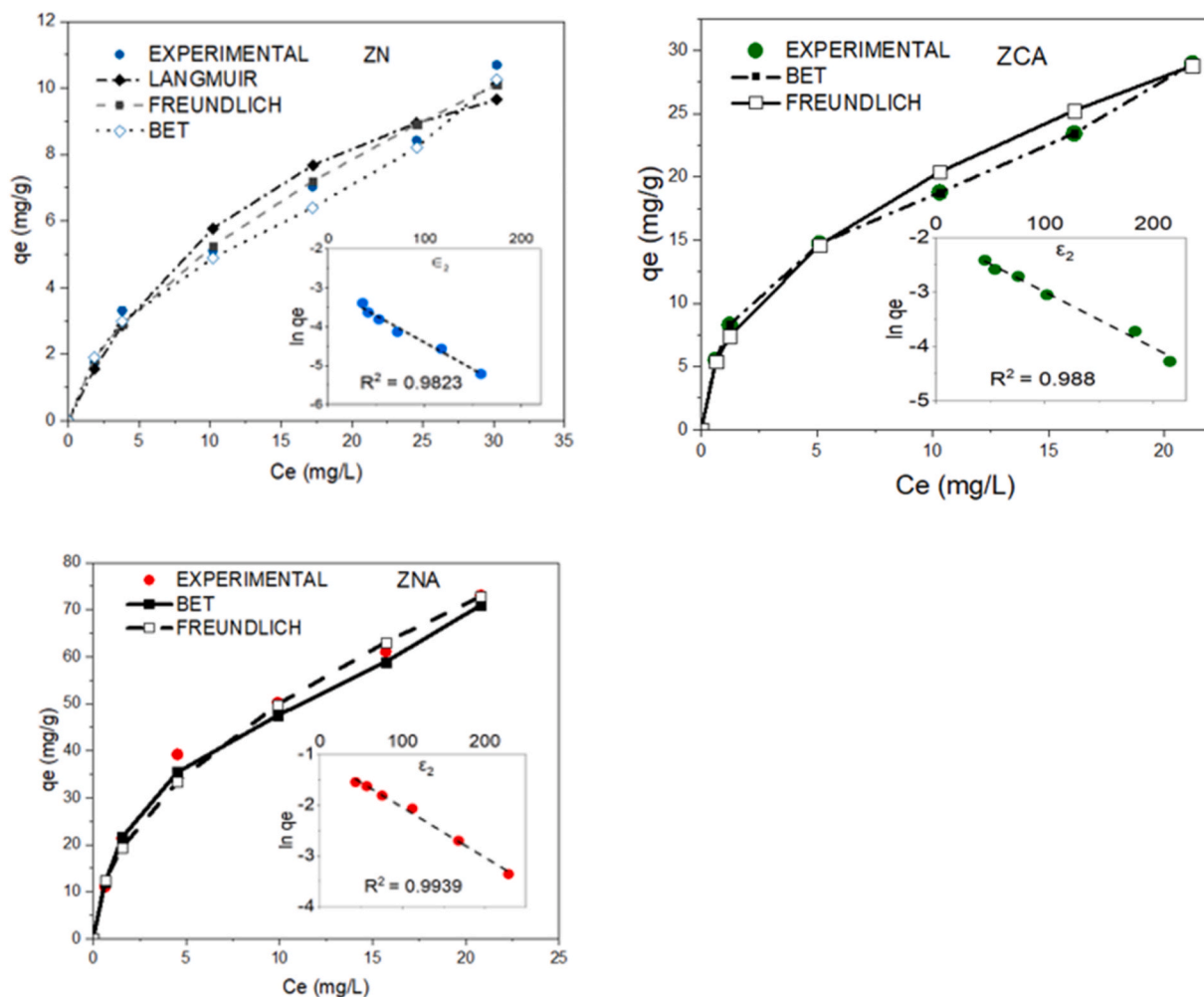


Fig. 7. Curve-fitting plot of studies isotherm models. Plot of the D-R model is presented in the small box.

**Table 6**  
Equilibrium parameters of DCF adsorption onto natural and acid treated zeolites.

Adsorbent	Langmuir Parameters				Freundlich parameters				BET parameters			
	$q_{\max}$ (mg/g)	$K_L$	$R^2$	MPSD	$K_F$	$n$	$R^2$	MPSD	$q_s$ (mg/g)	$C_{BET}$	$R^2$	MPSD
ZN	$14.4 \pm 1.2$	0.063	0.91	0.081	1.3	1.65	0.98	0.055	5.5	15.91	0.99	0.032
ZNA	$85.9 \pm 3.3$	0.192	0.96	0.091	15.2	1.97	0.98	0.041	45.0	27.25	0.99	0.017
ZCA	$33.6 \pm 2.3$	0.215	0.95	0.045	6.7	1.96	0.97	0.058	16.4	36.26	0.99	0.024

after acid treatment increases the possibility of hydrogen bond formation. Hydrogen bonding is a possible mechanism for the adsorption of DCF, as the electronegative species in DCF (O and N) can form hydrogen bonds with protons on ZNA and ZCA, thereby explaining the increase in adsorption capacity. The increase in hydroxyl functional groups is greater in the zeolite treated with nitric acid, which explains the greater adsorption capacity achieved by this zeolite sample. Furthermore, the presence of nitrogen in ZNA is one of the main differences between ZCA and ZN, which possibly improves the adsorption capacity of ZNA. The functional groups present in DCF such as carboxyl group (-COOH) and phenyl group (-C<sub>6</sub>H<sub>4</sub>-) can interact with zeolite, which also has suitable sites for hydrogen bonding (H<sup>+</sup>). Hydrogen bonds are weak partial intermolecular bonds and are a special type of dipole-dipole moment. They exist between hydrogen and some atoms such as oxygen, nitrogen, and fluorine. For this reason, the presence of N in the ZNA favors adsorption at different pH values. These interactions are despite in [Scheme 1](#).

In [Scheme 1](#), the interactions between the hydrogen atoms of the hydrogen atoms of diclofenac and the oxygen or nitrogen atoms present in the zeolite are represented. These interactions are shown as lines or bridges between the involved atoms. In addition to hydrogen bonds,  $\pi$ - $\pi$  interactions between the phenyl group of DCF and zeolite are represented. These interactions would be shown as a superposition of the electron clouds of the aromatic ring.

On the other hand, the zeolite treated with nitric acid exhibited a higher degree of protonation, due to the decrease in the content of Al<sub>2</sub>O<sub>3</sub> and other oxides, suggesting an increase in the quantity of H<sup>+</sup> cations present. This greater protonation improves the adsorption capacity of ZNA by attracting the negative charges of DCF.

[Table 7](#) presents a comparison of the adsorption performance of DFS with other modified zeolites in terms of their maximum adsorption capacity ( $q_{\max}$ ) using the Langmuir isotherm. Despite the fact that anionic adsorbents are not effective at adsorbing anionic adsorbents such as DCF, acid treatment improves the surface area in contrast to cationic

**Table 7**

Comparison of the DCF adsorption by some modified zeolites from previous literature.

Treatment	Q <sub>max</sub>	Reference
Surfactant-modified	18.16 (mg/g)	[29]
Cationic surfactant-modified	70.2 (mmol/Kg)	[29]
Cationic surfactant-modified	14.8 (mg/g)	[53]
Plasma-activated	4.2 (mg/g)	[26]
Sulfuric-acid treatment	117.7 (mg/g)	[35]

treatment [51]. The acid treatment promotes the de-alumination of the zeolite, which in turn enhances hydrogen bonding and  $\pi$ - $\pi$  interactions. As a result, the adsorption capacity of DCF is significantly improved. Based on this, it was concluded that ZNA could potentially be a promising adsorbent.

On the other hand, the use of clays as adsorbent materials offers a significant advantage in terms of their ability to be regenerated and reused in multiple cycles after adsorption. This is made possible through various methods, such as thermal treatment, which involves subjecting the clay to high temperatures. Chemical regeneration has also been extensively studied and proven effective, especially for removing organic contaminants. Additionally, alternative methods like solvent-based regeneration and electrochemical regeneration can be employed. Notably, studies carried out by Refs. [29,54] successfully achieved clay regeneration through acid treatment, allowing for up to 5 adsorption/desorption cycles with a reduction in adsorption capacity of up to 40 %.

#### 4. Conclusions

In this study, a simple acid treatment method was found to be capable of improving the adsorption of zeolite capacity. Nitric acid showed superior performance in improving DCF adsorption compared to citric acid. Chemical analysis, FTIR, and BET were utilized to further understand the impact of acid treatment on the surface and structure characteristics of both raw and treated zeolites. The acid treatment resulted in the de-alumination of the zeolite, an increased surface area, a decreased Si/Al ratio, and enhanced surface acidity. It was approved that nitric acid causes a more effective de-alumination of zeolite than citric acid and, consequently higher surface area and higher adsorption capacity.

Batch adsorption experiments were conducted to determine the optimal adsorbent dosage, contact time for equilibrium, and effect of pH, on D F adsorption capacity. The results showed that a lower adsorbent dosage was required with ZNA (0.4 g/L) compared to ZN (2 g/L) to achieve the maximum removal efficiency. The pH study revealed a good adsorption capacity and high percentage of adsorption at pH 6 on the acid treated zeolites. According to the results of pH study, the main mechanism of DCF adsorption on raw and acid treated zeolites was hydrogen bond. Zeolites treated with acid, especially nitric acid, have a greater number of functional groups that allow the formation of these bonds. According to the results, nitric acid treatment is more effective in improving the adsorption properties of zeolite and enhancing the adsorption capacity of DCF than citric acid treatment.

The adsorption kinetic study followed the pseudo second order model. For treated zeolites, the intraparticle diffusion model exhibited that intraparticle diffusion is not the rate-controlling step. The adsorption equilibrium data were best fitted with the BET isotherm, confirming the multilayer adsorption. The D-R model indicates physisorption. According to the results, nitric acid treatment is more effective in improving the adsorption properties of zeolite and enhancing the adsorption capacity of DCF than citric acid treatment. Accordingly, the modification of zeolite with nitric acid can be considered an excellent and effective method for adsorption of pharmaceuticals on zeolites.

#### Credit author statement

Lourdes Jara: Formal analysis, Funding acquisition, Investigation, Methodology, Resources, Writing – original draft. Damián Flores: Data curation, Formal analysis, Software, Validation. Maria Eulalia Peñafiel: Conceptualization, Formal analysis, Methodology, Supervision, Visualization, Writing – original draft, Writing – review & editing. Carola Jerves: Project administration, Software. Miguel Menendez: Supervision, Writing – review & editing

#### 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.

#### Data availability

The authors are unable or have chosen not to specify which data has been used.

#### Acknowledgments

The authors would like to acknowledge the Vicerrectorado de Investigación de la Universidad de Cuenca (VIUC).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cscee.2023.100575>.

#### References

- [1] E.F.D. Januário, Y.J. Fachina, G. Wernke, G.M.M. Demiti, L.B. Beltran, R. Bergamasco, A.M.S. Vieira, Application of activated carbon functionalized with graphene oxide for efficient removal of COVID-19 treatment-related pharmaceuticals from water, *Chemosphere* 289 (2022), 133213.
- [2] R.P. Nippes, P.D. Macruz, G.N. da Silva, M.H.N.O. Scaliante, A critical review on environmental presence of pharmaceutical drugs tested for the covid-19 treatment, *Process Saf. Environ. Protect.* 152 (2021) 568–582.
- [3] P. Guerra, M. Kim, A. Shah, M. Alaee, S.A. Smyth, Occurrence and fate of antibiotic, analgesic/anti-inflammatory, and antifungal compounds in five wastewater treatment processes, *Sci. Total Environ.* 473 (2014) 235–243.
- [4] R.A. Hamza, O.T. Iorhemen, J.H. Tay, Occurrence, impacts and removal of emerging substances of concern from wastewater, *Environ. Technol. Innovat.* 5 (2016) 161–175.
- [5] C. Song, C. Zhang, L. Fan, L. Qiu, W. Wu, S. Meng, J. Chen, Occurrence of antibiotics and their impacts to primary productivity in fishponds around Tai Lake, China, *Chemosphere* 161 (2016) 127–135.
- [6] X. Chen, L. Lei, S. Liu, J. Han, R. Li, J. Men, L. Zhu, Occurrence and risk assessment of pharmaceuticals and personal care products (PPCPs) against COVID-19 in lakes and WWTP-river-estuary system in Wuhan, China, *Sci. Total Environ.* 792 (2021), 148352.
- [7] Generic Drugs Market - Growth, trends, COVID-19 impact, and forecasts (2023–2028) <https://www.researchandmarkets.com/reports/5318624/generic-drugs-market-growth-trends-covid-19#rela2-5328624>. (Accessed 24 may 2023).
- [8] V. Acuña, A. Ginebreda, J.R. Mor, M. Petrovic, S. Sabater, J. Sumpter, D. Barceló, Balancing the health benefits and environmental risks of pharmaceuticals: diclofenac as an example, *Environ. Int.* 85 (2015) 327–333.
- [9] J. Wilkinson, P.S. Hooda, J. Barker, S. Barton, J. Swinden, Occurrence, fate and transformation of emerging contaminants in water: an overarching review of the field, *Environ. Pollut.* 231 (2017) 954–970.
- [10] N. Vieno, M. Sillanpää, Fate of diclofenac in municipal wastewater treatment plant—a review, *Environ. Int.* 69 (2014) 28–39.
- [11] R.N. Coimbra, C. Escapa, S. Paniagua, M. Otero, Adsorptive removal of diclofenac from ultrapure and wastewater: a comparative assessment on the performance of a polymeric resin and activated carbons, *Desalination Water Treat.* 57 (57) (2016) 27914–27923.
- [12] M. de Oliveira, B.E.F. Frihling, J. Velasques, F.J.C. Magalhães Filho, P.S. Cavalheri, L. Migliolo, Pharmaceuticals residues and xenobiotics contaminants: occurrence, analytical techniques and sustainable alternatives for wastewater treatment, *Sci. Total Environ.* 705 (2020), 135568.
- [13] M. Dubey, S. Mohapatra, V.K. Tyagi, S. Suthar, A.A. Kazmi, Occurrence, fate, and persistence of emerging micropollutants in sewage sludge treatment, *Environ. Pollut.* 273 (2021), 116515.

- [14] Q. Sui, X. Cao, S. Lu, W. Zhao, Z. Qiu, G. Yu, Occurrence, sources and fate of pharmaceuticals and personal care products in the groundwater: a review, *Emerging Contam.* 1 (1) (2015) 14–24.
- [15] T.S. Alkhouraji, Advanced oxidation process based on water radiolysis to degrade and mineralize diclofenac in aqueous solutions, *Sci. Total Environ.* 688 (2019) 708–717.
- [16] L. He, L. Lv, S.C. Pillai, H. Wang, J. Xue, Y. Ma, L. Yang, Efficient degradation of diclofenac sodium by periodate activation using Fe/Cu bimetallic modified sewage sludge biochar/UV system, *Sci. Total Environ.* 783 (2021), 146974.
- [17] V. Muelas-Ramos, M.J. Sampaio, C.G. Silva, J. Bedia, J.J. Rodriguez, J.L. Faria, C. Belver, Degradation of diclofenac in water under LED irradiation using combined g-C<sub>3</sub>N<sub>4</sub>/NH<sub>2</sub>-MIL-125 photocatalysts, *J. Hazard Mater.* 416 (2021), 126199.
- [18] F. Fadzail, M. Hasan, N. Ibrahim, Z. Mokhtar, A.Y.P. Asih, A. Syafuddin, Adsorption of diclofenac sodium using low-cost activated carbon in a fixed-bed column, *Biointerface Research in Applied Chemistry* 12 (6) (2022) 8042–8056. <http://repository.unusa.ac.id/id/eprint/8716>.
- [19] J. Xie, M. Liu, M. He, Y. Liu, J. Li, F. Yu, Y. Lv, C. Lin, X. Ye, Ultra-efficient adsorption of diclofenac sodium on fish-scale biochar functionalized with H<sub>3</sub>PO<sub>4</sub> via synergistic mechanisms, *Environ. Pollut.* 322 (2023), 121226, <https://doi.org/10.1016/j.envpol.2023.121226>.
- [20] S. Zhuang, R. Cheng, J. Wang, Adsorption of diclofenac from aqueous solution using UiO-66-type metal-organic frameworks, *Chem. Eng. J.* 359 (2019) 354–362.
- [21] L. Wu, C. Du, J. He, Z. Yang, H. Li, Effective adsorption of diclofenac sodium from neutral aqueous solution by low-cost lignite activated cokes, *J. Hazard Mater.* 384 (2020), 121284.
- [22] L.V. Baia, W.C. Souza, R.J. De Souza, C.O. Veloso, S.S. Chiaro, M.A.G. Figueiredo, Removal of sulfur and nitrogen compounds from diesel oil by adsorption using clays as adsorbents, *Energy Fuels* 31 (11) (2017) 11731–11742.
- [23] H. Najafi, S. Farajfaed, S. Zolgharnian, S.H.M. Mirak, N. Asasian-Kolur, S. Sharifian, A comprehensive study on modified-pillared clays as an adsorbent in wastewater treatment processes, *Process Saf. Environ. Protect.* 147 (2021) 8–36.
- [24] G. Rytwo, R. Lavi, Y. Rytwo, H. Monchase, S. Dultz, T.N. König, Clarification of olive mill and winery wastewater by means of clay-polymer nanocomposites, *Sci. Total Environ.* 442 (2013) 134–142.
- [25] E. Pérez-Botella, S. Valencia, F. Rey, Zeolites in adsorption processes: state of the art and future prospects, *Chem. Rev.* 122 (24) (2022) 17647–17695.
- [26] J.J.M. Garcia, J.A.P. Nuñez, H.S. Salapare, M.R. Vasquez, Adsorption of diclofenac sodium in aqueous solution using plasma-activated natural zeolites, *Results Phys.* 15 (2019), 102629.
- [27] X. Zhang, Y. Xue, J. Gao, C. He, Y. Ji, Y. Dou, Comparison of adsorption mechanisms for cadmium removal by modified zeolites and sands coated with Zn-layered double hydroxides, *Chem. Eng. J.* 380 (2020), 122578.
- [28] A.M. Vargas, C.C. Cipagauta-Ardila, D.R. Molina-Velasco, C.A. Ríos-Reyes, Surfactant-modified natural zeolites as carriers for diclofenac sodium release: a preliminary feasibility study for pharmaceutical applications, *Mater. Chem. Phys.* 256 (2020), 123644.
- [29] Y. Khaksarfard, A. Bagheri, A.A. Rafati, Synergistic effects of binary surfactant mixtures in the adsorption of diclofenac sodium drug from aqueous solution by modified zeolite, *J. Colloid Interface Sci.* 644 (2023) 186–199.
- [30] K. Sun, Y. Shi, X. Wang, Z. Li, Sorption and retention of diclofenac on zeolite in the presence of cationic surfactant, *J. Hazard Mater.* 323 (2017) 584–592.
- [31] M. Chauhan, V.K. Saini, S. Suthar, Ti-pillared montmorillonite clay for adsorptive removal of amoxicillin, imipramine, diclofenac-sodium, and paracetamol from water, *J. Hazard Mater.* 399 (2020), 122832.
- [32] X. Pu, N.W. Liu, L. Shi, Acid properties and catalysis of USY zeolite with different extra-framework aluminum concentration, *Microporous Mesoporous Mater.* 201 (2015) 17–23.
- [33] Q. Han, J. Wang, B.A. Goodman, J. Xie, Z. Liu, High adsorption of methylene blue by activated carbon prepared from phosphoric acid treated eucalyptus residue, *Powder Technol.* 366 (2020) 239–248.
- [34] A.F. Streit, G.C. Collazzo, S.P. Druzian, R.S. Verdi, E.L. Foletto, L.F. Oliveira, G. L. Dotto, Adsorption of ibuprofen, ketoprofen, and paracetamol onto activated carbon prepared from effluent treatment plant sludge of the beverage industry, *Chemosphere* 262 (2021), 128322.
- [35] E. Hosseinpour, A. Rahbar-Kelishami, M.S. Nabavi, Evaluation of alkaline and acidic modification of NaY zeolite for enhancing adsorptive removal of diclofenac sodium from aqueous solution, *Surface. Interfac.* 39 (2023), 102917.
- [36] M. Antunes, V.I. Esteves, R. Guégan, J.S. Crespo, A.N. Fernandes, M. Giovanela, Removal of diclofenac sodium from aqueous solution by Isabel grape bagasse, *Chem. Eng. J.* 192 (2012) 114–121, <https://doi.org/10.1016/j.cej.2012.03.062>.
- [37] F.C. Wu, R.L. Tseng, R.S. Juang, Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics, *Chem. Eng. J.* 153 (1–3) (2009) 1–8.
- [38] J.P. Chen, S. Wu, Acid/base-treated activated carbons: characterization of functional groups and metal adsorptive properties, *Langmuir* 20 (6) (2004) 2233–2242.
- [39] A.K. Panda, B.G. Mishra, D.K. Mishra, R.K. Singh, Effect of sulphuric acid treatment on the physico-chemical characteristics of kaolin clay, *Colloids Surf. A Physicochem. Eng. Asp.* 363 (1–3) (2010) 98–104.
- [40] J.B. Condon, *Surface Area and Porosity Determinations by Physisorption: Measurement, Classical Theories and Quantum Theory*, Elsevier Science, 2019, <https://doi.org/10.1016/C2018-0-00544-7>.
- [41] C. Wang, S. Leng, H. Guo, L. Cao, J. Huang, Acid and alkali treatments for regulation of hydrophilicity/hydrophobicity of natural zeolite, *Appl. Surf. Sci.* 478 (2019) 319–326.
- [42] E. Díez, C. Redondo, J.M. Gómez, R. Miranda, A. Rodríguez, Zeolite adsorbents for selective removal of Co (II) and Li (I) from aqueous solutions, *Water* 15 (2) (2023) 270.
- [43] V. Rac, V. Rakić, D. Stojić, V. Pavlović, S. Bosnar, A. Auroux, Enhanced accessibility of active sites in hierarchical ZSM-5 zeolite for removal of pharmaceutically active substances: adsorption and microcalorimetric study, *Arab. J. Chem.* 13 (1) (2020) 1945–1954.
- [44] I.M. Jauris, C.F. Matos, C. Saucier, E.C. Lima, A.J.G. Zarbin, S.B. Fagan, F. M. Machado, I. Zanella, Adsorption of sodium diclofenac on graphene: a combined experimental and theoretical study, *Phys. Chem. Chem. Phys.* 18 (3) (2016) 1526–1536, <https://doi.org/10.1039/C5CP05940B>.
- [45] C.V.T. Rigueto, M. Rosseto, M.T. Nazari, B.E.P. Ostwald, I. Alessandretti, C. Manera, J.S. Piccin, A. Dettmer, Adsorption of diclofenac sodium by composite beads prepared from tannery wastes-derived gelatin and carbon nanotubes, *J. Environ. Chem. Eng.* 9 (1) (2021), 105030.
- [46] L. Zhang, Y. Fu, Z. Wang, G. Zhou, R. Zhou, Y. Liu, Removal of diclofenac in water using peracetic acid activated by zero valent copper, *Separ. Purif. Technol.* 276 (2021), 119319.
- [47] H. Xu, S. Zhu, M. Xia, F. Wang, Rapid and efficient removal of diclofenac sodium from aqueous solution via ternary core-shell CS@ PANI@ LDH composite: experimental and adsorption mechanism study, *J. Hazard Mater.* 402 (2021), 123815.
- [48] B.N. Bhadra, P.W. Seo, S.H. Jhung, Adsorption of diclofenac sodium from water using oxidized activated carbon, *Chem. Eng. J.* 301 (2016) 27–34.
- [49] B. Chekmane, F. Zermene, M. Baudu, O. Bouras, J.P. Basly, Sorption of basic dyes onto granulated pillared clays: thermodynamic and kinetic studies, *J. Colloid Interface Sci.* 381 (2012) 158–163.
- [50] A.A. Maggio, M.E.R. Jalil, J. Villarreal-Rocha, K. Sapag, M.T. Baschini, Fe-and SiFe-pillared clays from a mineralogical waste as adsorbents of ciprofloxacin from water, *Appl. Clay Sci.* 220 (2022), 106458, <https://doi.org/10.1016/j.clay.2022.106458>.
- [51] C.H. Giles, D. Smith, A. Huitson, A general treatment and classification of the solute adsorption isotherm. I. Theoretical, *J. Colloid Interface Sci.* 47 (3) (1974) 755–765.
- [52] B.Y.Z. Hiew, L.Y. Lee, X.J. Lee, S. Gan, S. Thangalazhy-Gopakumar, S.S. Lim, T.C. K. Yang, Adsorptive removal of diclofenac by graphene oxide: optimization, equilibrium, kinetic and thermodynamic studies, *J. Taiwan Inst. Chem. Eng.* 98 (2019) 150–162.
- [53] D. Krajišnik, A. Daković, M. Milojević, A. Malenović, M. Kragović, D. B. Bogdanović, J. Milić, Properties of diclofenac sodium sorption onto natural zeolite modified with cetylpyridinium chloride, *Colloids Surf. B Biointerfaces* 83 (1) (2011) 165–172.
- [54] A. Maged, S. Kharbish, I.S. Ismael, A. Bhatnagar, Characterization of activated bentonite clay mineral and the mechanisms underlying its sorption for ciprofloxacin from aqueous solution, *Environ. Sci. Pollut. Control Ser.* 27 (2020) 32980–32997.

### Further reading

- [55] D. Smiljanić, B. de Gennaro, F. Izzo, A. Langella, A. Daković, C. Germinario, M. Mercurio, Removal of emerging contaminants from water by zeolite-rich composites: a first approach aiming at diclofenac and ketoprofen, *Microporous Mesoporous Mater.* 298 (2020) 110057.