

Acid-salt-modified natural zeolite as a highly efficient adsorbent for pharmaceuticals from contaminated water

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ABSTRACT

Acetaminophen (ACT), commonly known as paracetamol, is a widely used nonprescription analgesic and antipyretic. However, its extensive presence in aquatic resources poses a significant threat to aquatic organisms because of its toxic characteristics. In this study, the removal of ACT using acid-salt modified Philippines natural zeolite (ASMPNZ) was investigated. ASMPNZ was chemically modified with nitric acid and sodium chloride. The morphological structure and functional groups of ASMPNZ were characterized using scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). The central composite design (CCD) of the response surface methodology (RSM) was used to determine the optimum values of parameters. The optimum conditions, 0.40 g of ASMPNZ, 60 min of reaction time, and pH 2, achieved a maximum removal efficiency of 94.3 % of ACT removal. These optimum values of parameters were validated by conducting an actual experiment, and the result showed that the removal efficiency (93.9 %) is within the 95 % confidence interval. The Langmuir isotherm model suggests that ACT adsorption onto ASMPNZ follows monolayer coverage on a homogeneous surface. Kinetic studies revealed that the pseudo-second order model provided the best fit, indicating chemisorption as the prevalent adsorption mechanism. This study demonstrates that ASMPNZ is an efficient adsorbent for the removal of ACT-contaminated water and offers a promising solution for mitigating pharmaceutical pollution in aquatic environments. Unlike prior studies that rely on single-step zeolite modification, we investigate a low-cost Philippine natural zeolite sequentially modified by acid and salt and, via RSM-guided optimization with experimental validation, achieve high ACT removal (94 % at 0.40 g, 60 min, pH 2; $q_{\max} = 237.5$ mg/g) while elucidating a Langmuir monolayer, pseudo-second-order chemisorption mechanism.

1. Introduction

Pharmaceuticals as contaminants in water bodies have raised significant environmental and health concerns because of their significant estrogenic and toxic effects [20]. With 3000 pharmaceutical compounds, including analgesics, antipyretics, antibiotics, antihistamines, antimicrobials, antivirals, and stimulants, they are considered a major group of emerging contaminants [21]. These pollutants reach aquatic systems through improper disposal, industrial and medical discharges and human excretion [22]. Once released into aquatic environments, they contribute to the growing problem of pharmaceutical contamination.

Recent global monitoring studies reveal the widespread presence of pharmaceuticals in aquatic environments. A systematic review by aus der Beek et al. [1] reported pharmaceutical residues in over 71 countries, with concentrations ranging from ng/L to several $\mu\text{g/L}$ in surface waters [1]. More recent surveys indicate that antibiotics, analgesics, and antipyretics remain among the most frequently detected contaminants, with average concentrations of acetaminophen, diclofenac, and ibuprofen reaching up to 5 $\mu\text{g/L}$ [2], in wastewater effluents and up to 297 $\mu\text{g/L}$ in rivers and lakes worldwide [3] [3]. Groundwater and even treated drinking water have also shown contamination, raising significant public health and ecological concerns. These findings emphasize that pharmaceutical pollution is a global issue requiring effective

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treatment strategies, particularly in low- and middle-income regions where wastewater treatment infrastructure is limited.

Acetaminophen (ACT) is one of the most widely used analgesics and antipyretics, prescribed for fever, headaches, and pain relief. It is estimated that global consumption is $1.45 \cdot 10^5$ tons per year. The solubility of ACT is 12.8 g L^{-1} ; hence, a significant fraction—between 58 % and 68 %—is excreted by humans and subsequently enters the water systems [23]. ACT has been detected at concentrations ranging from ng/L to $\mu\text{g/L}$ [24]. These levels of concentration pose significant effects on aquatic organisms and human health [24,25]. Consequently, it is crucial to develop effective treatment methods for its removal from wastewater.

Treatment technologies, including membrane separation process, adsorption, electro-dialysis, photolytic degradation, sonolysis, chemical oxidation, coagulation-flocculation, aerobic process, and anaerobic process, have been explored to mitigate the pharmaceutical contaminants [26]. Among these, adsorption has gained popularity because of its simplicity, reliability, and cost-effectiveness in removing organic pollutants from water. Zeolite, a naturally occurring aluminosilicate mineral, has shown promise as an adsorbent for wastewater treatment [27].

Natural zeolites are commonly used to reduce turbidity and remove ammonium, heavy metals, and cationic contaminants from wastewater. They possess a large surface area and high cation exchange capacity [28,29], enabling them to adsorb a wide range of contaminants. Thus, they are used to remove pharmaceutical pollutants such as diclofenac and ketoprofen [30]. To enhance their adsorption capacity, various modification techniques have been applied to natural zeolite. The modified zeolites for wastewater treatment are attracting new research interest because of their significant occurrence, characteristics, optimum performance, and inexpensive cost [31].

Acid and salt modifications have been shown to improve the adsorption properties of natural zeolites significantly. Acid treatment dissolves impurities and enlarges the pores by replacing H^+ with K^+ , Ca^{2+} , and Mg^{2+} , thereby increasing porosity and adsorption capacity [29,32]. Similarly, modification through salt enhances pore volume and diameter, improving ion-exchange capacity and creating more adsorption sites [33,34].

Although acid and salt modifications have individually demonstrated improvements in porosity, ion-exchange capacity, and adsorption performance, studies explicitly combining these two approaches remain limited. The combined modifications reported in literature involve acid-thermal or surfactant-salt treatments, which are better than the single treatments due to synergistic effects on surface area and functionality [4,34]. Hence, the present work addresses this gap by evaluating acid-salt modified Philippine natural zeolite (ASPNZ) for the removal of acetaminophen from aqueous solutions.

Despite the great advantage of acid-salt modified zeolite for pharmaceutical pollutant removal, its application in ACT removal has not been extensively explored. Thus, this study aims to investigate the removal efficiency of acid-salt modified Philippine natural zeolite (ASPNZ) for the removal of ACT from an aqueous solution. Zeolites were naturally acquired in the Philippines. The study utilizes the central composite design (CCD) of the response surface methodology (RSM) to optimize the parameters: ASPNZ loading, contact time, and pH. Furthermore, adsorption isotherms and kinetic models were also integrated in this study to determine the mechanisms of ACT onto ASPNZ. This study provides valuable insights into the potential of ASPNZ for pharmaceutical pollutant removal, contributing to wastewater treatment strategies and environmental protection.

2. Materials and methods

2.1. Modification of natural zeolites

The natural zeolite used in this study was purchased from LITHOS manufacturing OPC, Philippines. The material was crushed to a particle

size of 100–300 μm using a mortar and pestle to obtain a fine powder. The particle range of 100–300 μm was selected to balance adsorption performance and practical handling. Accordingly, zeolite sizes make sense because it offers a good balance: the particles are small enough to give high adsorption efficiency, thanks to their larger surface area and more active sites, but not so small that mass transfer through the pores becomes a major limitation [5,6] [5,6]. The chemical modification process for the zeolite was adapted from [35]. Acid-salt modification was employed to enhance the properties of the zeolite samples.

Before modification, the raw zeolite was rinsed four times with distilled water to remove contaminants and then dried at 150°C for six hours until a constant weight was achieved. Acid modification was performed by soaking the zeolite in 0.5 M nitric acid. The mixture was stirred at 200 rpm using a magnetic stirrer at room temperature for 12 h [36]. After soaking, the samples were repeatedly rinsed with distilled water until a neutral pH (pH 7) was reached, then filtered and oven-dried at 150°C until a constant weight was obtained.

For salt modification, the dried acid-treated zeolite was soaked in 1 M sodium chloride and stirred at 200 rpm at room temperature for 24 h (Li et al., 2011). Subsequently, the samples were rinsed with distilled water until pH 7 was reached, then filtered and oven-dried at 150°C until constant weight was achieved.

The choice of nitric acid and sodium chloride for modification was based on prior studies demonstrating their ability to enhance zeolite properties. Nitric acid effectively removes surface impurities and exchangeable cations, leading to higher porosity and additional active sites [7] [7]. Sodium chloride introduces Na^+ ions into the zeolite lattice, improving cation exchange and adsorption affinity [8] [8]. Their combined use was anticipated to provide synergistic improvements in adsorption performance.

2.2. Analytical methods

The surface morphology and functional groups of the ASPNZ adsorbent were investigated by Scanning Electron Microscope (Hitachi S-3400 N Type II) and Fourier Transform Infrared Spectroscopy (Thermo Scientific Nicolet 6700). The concentration of ACT was determined using the UV-vis spectrophotometer (UV-VIS 2800 model) at 430 nm wavelength.

2.3. UV-vis determination of ACT

Adsorption experiments were carried out to make a calibration curve using ACT solutions with concentrations ranging from 0 to 120 mg/L. ACT concentrations were determined following the procedure described by [9] [9], in which nitric acid was added to produce a characteristic yellow coloration [37]. The absorbance of the resulting solutions was measured using a UV-vis spectrophotometer at 430 nm [10] [10]. The calibration curve obtained yielded the regression equation shown in Eq. 1, with a correlation coefficient ($R^2 = 0.996$).

$$y = 0.0026x + 0.005 \quad (1)$$

2.4. ACT batch adsorption

Numerical optimization was carried out using response surface methodology (RSM) in Design Expert Version 7.0, applying central composite design (CCD) as described by Granada et al. [11]. RSM was selected because it is widely applied in adsorption studies for its ability to evaluate the combined influence of operating variables and their interaction with fewer experimental runs compared to one-factor-at-a-time approaches. The CCD framework allows estimation of linear, interaction, and quadratic effects, providing a comprehensive understanding of factor relationships while maintaining statistical robustness and experimental efficiencies. Analysis of variance (ANOVA) was used to validate the developed models, assess the significant terms, and

confirm model adequacies, ensuring reliable predictions of the adsorption performance of ASMPNZ. The experimental ranges and levels of the independent variables are presented in Table 1.

In each run, 100 mL of ACT solutions with a known initial concentration of 100 mg/L were treated with varying loading of ASMPNZ. The solution pH was adjusted to the desired value using 0.1 mol of HCl or 0.1 mol NaOH before each adsorption experiment. After agitation (100 rpm) under ambient temperature, the solution was filtered, and the filtrate was analyzed to obtain residual ACT concentration. The percentage of ACT removal (R_{ACT}) was calculated using Eq. 2:

$$R_{ACT}(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where C_i (mg/L) is the initial concentration of paracetamol and C_f (mg/L) is the final concentration of ACT.

2.5. Adsorption isotherm studies

The adsorption mechanism of ACT onto ASMPNZ was investigated by evaluating its adsorption equilibrium using Langmuir (Eq. 3) and the Freundlich (Eq. 4) isotherm models. The Langmuir model assumes monolayer adsorption on a uniform surface with a fixed number of identical sites [11]. On the other hand, the Freundlich model accounts for multilayer adsorption on a heterogeneous surface, considering variations in adsorption energies across different sites [38].

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (3)$$

where C_e (mg/L) represents the equilibrium concentration of ACT in the solution, q_e (mg/g) represents the amount of adsorbed ACT per unit weight of ASMPNZ, q_{max} (mg/g) is denoted as the amount of ACT absorbed at complete monolayer adsorption capacity, and K_L (L/mg) is the Langmuir equilibrium constant.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Where K_f (mg/g) (L/mg) $1/n$ and n are the Freundlich constants. The values of K_f define as the adsorption capability, and n denotes the adsorption intensity.

2.6. Kinetics of adsorption studies

The kinetic models are integrated in this study to describe the rate and mechanisms by which ACT molecules interact with the ASMPNZ surface. Pseudo-first-order and pseudo-second-order help to understand the adsorption process, optimize conditions, and predict the adsorption performance of ASMPNZ. The pseudo-first-order expressed in Eq. 5 assumes that the ASMPNZ adsorption dynamics is suitable for physisorption-dominated processes; while the pseudo-second-order depicted in Eq. 6 implies that the adsorption mechanism follows chemisorption as the rate-controlling step [39,40].

$$\ln q_e - q_t = \ln q_e - k_1 t \quad (5)$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacities at equilibrium and at time t (min), respectively, and k_1 is the rate constant for the pseudo-first order adsorption (min^{-1}).

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} - \frac{t}{q_e} \quad (6)$$

where k_2 is denoted as constants of pseudo-second-order rate equation (g/mg.min).

3. Results

3.1. ASMPNZ characterization

3.1.1. SEM analysis

The surface morphology analysis scanned in a 100 μm magnification SEM revealed that ASMPNZ has a rough surface, porous structure with well-defined channels and cavities (Fig. 1). The acid treatment enhanced the adsorption capacity of ASMPNZ by partially displacing H^+ with K^+ , Ca^{2+} , and Mg^{2+} from each layer of the surface to increase porosity, dissolve impurities in the pores, and dredge the ASMZ channels (Shi et al., 2017). Meanwhile, treatment of salt solutions improved the ASMPNZ pore volume and diameter, increasing ion exchange and adsorption activities. In comparison with the findings of Olegario-Sanchez and Pelicano, (2017), who characterized unmodified Philippine natural zeolite, the unmodified material has a smoother and less fractured surface morphology. This suggests that ASMPNZ modification resulted in the formation of a greater number of channels and cavities, increasing the surface area available for adsorption (Li et al., 2011).

3.2. Adsorption studies

3.2.1. Experimental results

The experimental runs were generated by the CCD of RSM, with operating variables including ASMPNZ loading, contact time, and pH. Table 2 shows the removal efficiency of ACT using ASMPNZ under varying experimental conditions. The highest removal efficiency of 90.9 % was recorded in run 20 with ASMPNZ of 0.60 g, reaction time of 90 min, and pH of 2. On the other hand, run 11 exhibits the lowest removal efficiency of 38.2 % under ASMPNZ loading of 0.60 g, reaction time of 90 min, and a pH value of 10.0 has the lowest removal efficiency of 38.2 %.

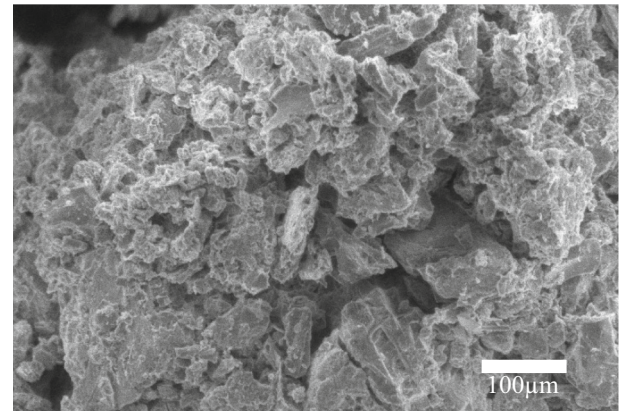


Fig. 1. SEM morphology of ASMPNZ.

Table 1
Coded Variables and Levels for Acetaminophen Removal.

Parameters	Units	Coded Symbol	Coded Level				
			−2	−1	0	+1	+2
ASMPNZ Loading	g	A	0.20	0.40	0.60	0.80	1.00
Contact Time	min	B	30	60	90	120	150
pH	–	C	2	4	6	8	10

Table 2

ACT removal by ASMPNZ from wastewater.

Run	ASMPNZ Loading (g)	Reaction Time (min)	pH	Removal Efficiency (%)
1	0.60	90	6.0	46.5
2	0.40	60	4.0	71.9
3	0.60	90	6.0	55.5
4	0.80	120	4.0	64.9
5	0.80	60	4.0	76.5
6	1.0	90	6.0	62.5
7	0.60	90	6.0	48.9
8	0.60	30	6.0	66.9
9	0.20	90	6.0	55.9
10	0.40	120	8.0	44.9
11	0.60	90	10.0	38.2
12	0.40	60	8.0	48.5
13	0.60	150	6.0	49.9
14	0.80	120	8.0	42.2
15	0.60	90	6.0	48.5
16	0.60	90	6.0	51.5
17	0.80	60	8.0	59.2
18	0.40	120	4.0	75.2
19	0.60	90	6.0	57.5
20	0.60	90	2.0	90.9

The effect of pH on ACT removal can be explained by both ACT speciation and the surface charge behavior of zeolites. ACT has a reported pK_a value of ≈ 9.38 ; therefore, it remains largely neutral under acidic conditions but becomes increasingly deprotonated at alkaline pH [41]. Natural and modified zeolites typically exhibit a point of zero (pHpzc) in the range of 5–7 [12] [12]. At pH values below the pHpzc, the zeolite surface is positively charged, favoring electrostatic attraction and hydrogen bonding with neutral or weakly charged ACT molecules, thereby enhancing adsorption efficiency. Conversely, ACT becomes increasingly ionized at higher pH as it reduces its affinity for the adsorption sites because of the electrostatic repulsion. Furthermore, zeolites have a rigid 3D structure made of Aluminum, silicon, and oxygen, with pores that hold H_2O and cations like potassium, sodium, and calcium. At lower pH, ACT interacts strongly with ASMPNZ because of the protonation of their carboxylic groups, facilitating the oxygen atom binding in the zeolite lattice [13] [13,42]. Although zeta potential measurements were not conducted in this study, the observed trends are consistent with reported literature on zeolite surface charge and pharmaceutical adsorption. Future investigations should include direct zeta potential analysis as SMPNZ to quantitatively confirm the relationship between surface charge and adsorption performance.

3.2.2. Statistical analysis

The adequacy of the model was validated using the Analysis of Variance (ANOVA). Table 3 presents the ANOVA results for the quadratic model of Act removal, showing the sum of squares, mean squares of each factor, F-value, and Prob > F values. The very low model p -value of <0.0001 confirms that the regression model is highly significant, indicating that the observed variability is ACT removal efficiency is reliably explained by selected factors rather than random errors. Model terms with “Prob > F” values less than 0.0500 (B, C, AB, A^2 , B^2 ,) The non-significant “Lack of Fit F-value” of 0.39 further demonstrate that the model error is attributable mainly to pure error rather than inadequate model form.

Importantly, the close agreement between the p “Pred R-Squared” of 0.8751 and “Adj R-Squared” value of 0.9277 suggests that the model has strong predicted capability without evidence of overfitting. The “Adeq Precision” value of 19.688, which is well above the threshold of 4, indicates an adequate signal-to-noise ratio and confirms the robustness of the model. Together, this diagnostic demonstrate that the CCD provided sufficient experimental points to estimate model terms reliability, while avoiding redundancy that could lead to overfitting.

The predicted reliability of the model is further supported by the

Table 3

Analysis of variance for the paracetamol removal efficiency.

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
Model	3257.31	9	361.92	28.08	< 0.0001 ^a
A – ASMPNZ Loading	15.31	1	15.31	1.19	0.3014
B – Contact time	247.98	1	247.98	19.24	0.0014
C - PH	2475.31	1	2475.31	192.02	< 0.0001
AB	100.32	1	100.32	7.78	0.0191
AC	23.36	1	23.36	1.81	0.2080
BC	19.00	1	19.00	1.47	0.2526
A^2	114.00	1	114.00	8.84	0.0140
B^2	92.86	1	92.86	7.20	0.0229
C^2	301.53	1	301.53	23.39	0.0007
Residual	128.91	10	12.89	–	–
Lack of Fit	35.91	5	7.18	0.39	0.8402 ^b
Pure Error	93.00	5	18.60	–	–
Cor Total	3386.22	19	–	–	–

$R^2 = 0.9619$, Adj $R^2 = 0.9277$, Pred $R^2 = 0.8751$, Adeq Precision = 19.668, C.V. % = 6.21.

predicted vs. actual plot shown in Fig. 2, in which most data points are closely aligned along 45° line. This clustering indicates a strong correlation between experimental and predicted values, validating the ability of the quadratic model to accurately predict ACT removal efficiency using ASMPNZ.

3.2.3. Mathematical model

According to the ANOVA results, the quadratic equations in terms of coded factors for the adsorption of ACT using ASMPNZ are shown in the following equation:

$$\begin{aligned} \text{Removal Efficiency (\%)} = & 51.79 + 0.98A - 3.94B - 12.44C - 3.54AB \\ & + 1.71AC - 1.54BC + 2.13A^2 + 1.92B^2 + 3.46C^2 \end{aligned} \quad (7)$$

The variables ASMPNZ loading in terms of g, reaction time in minutes, and pH are coded in terms of A, B, and C, respectively. The sign of the coefficient suggests valuable insights into how each variables influence the removal efficiency of ACT by ASMPNZ. Thus, the positive coefficient (A, AC, A^2 , B^2 , and C^2) suggests that the parameters enhance adsorption efficiency. On the other hand, parameters B, C, AB, and BC have negative coefficients, which lead to the decrease of ACT removal.

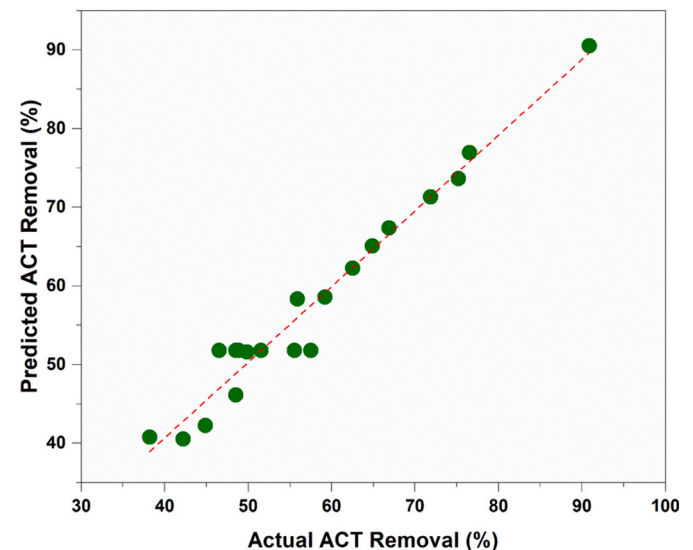


Fig. 2. Relationship between predicted vs. actual data for ACT removal using ASMPNZ.

3.3. Effects of parameters on paracetamol removal efficiency

The 3D response surface plot shown in Fig. 3 illustrates the relationship between contact time and ASMPNZ loading on ACT removal. The plot shows a concave relationship, where removal efficiently initially increases but then decreases beyond certain ASMPNZ loading and time values, with the highest efficiency of 65 % observed at the lower ranges of both factors. This non-monotonic trend can be attributed to equilibrium saturation and potential aggregation effects at higher adsorbent loading, which reduce the number of available active sites per unit mass and hinder effective adsorption [14] [14]. Similarly, extending the contact time beyond equilibrium does not enhance removal and may promote desorption or competitive redistribution of ACT molecules [15] [15]. The curvature of the surface further highlights the strong interaction between ASMPNZ loading and contact time, where changes in one parameter influence the effect of the other.

While pH (C) was also included as a factor in the CCD optimization, ANOVA results showed that its interactions with ASMPNZ loading and contact time were not statistically significant. Although, pH contributed significantly as a main effect and is discussed separately. This result is consistent with the study by Al-Rimawi et al. (2018) for zeolite adsorption of pharmaceuticals, where removal efficiency increased with ASMPNZ loading and time until equilibrium saturation was reached, after which efficiency declined. This suggests that the observed behavior is not anomalous, but rather consistent with adsorption theory under conditions of surface modification and saturation effects.

3.4. FTIR analysis

The FTIR spectra of ASMPNZ before adsorption (Fig. 4) showed the characteristic framework vibrations of zeolite, along with surface functional groups. Broad absorption around 3379 cm^{-1} and 2364 cm^{-1} correspond to H-bonding and O—H stretching, while bands at 1631 cm^{-1} and 1005 cm^{-1} were associated with carboxylate/quinonic groups and C—O stretching, respectively, indicating the presence of hydroxyl, and other functionalities. Framework-related Si—O and Al—O vibrations were also observed.

After ACT adsorption, most characteristic zeolite bands were retained, but several changes indicated interaction with ACT molecules. The O—H band shifted slightly (3365 cm^{-1}) with reduce intensity, suggesting hydrogen bonding with ACT's phenolic —OH group, where the result is isomorphic to the study of El-Gawad et al., (2025). (El-

Gawad et al., 2025) New or intensified bands at 1635 cm^{-1} , 1558 cm^{-1} , 1541 cm^{-1} , were attributed to amide N—H bending and C=O stretching, consistent with ACT's amide and carbonyl functional groups. A weak band 784 cm^{-1} confirmed the presence of aromatic C—H stretching, validating the adsorption of ACT's aromatic ring. In contrast, a peak at $\approx 2000\text{ cm}^{-1}$ previously assigned to N=C=S stretching, disappeared after adsorption, possibly due to surface coverage or chemical interactions with ACT [43–45].

These spectral changes indicate that adsorption occurred through hydrogen bonding between zeolite surface —OH groups and ACT's phenolic hydroxyl, as well as π - π interactions involving ACT's aromatic ring [46,47]. A comparative summary of the main bands and their changes before and after adsorption is presented in Table 4 for clarity.

3.5. Optimization and validation

To get the optimum values of the parameters, the criteria of these parameters were set according to the results from the adsorption studies. The ASMPNZ loading and contact time were set to a minimum, while pH 2 was targeted as it gives higher removal efficiency. Thus, the optimal values of the parameters suggested by CCD of RSM are 0.40 g of ASMPNZ loading, 60 min of reaction time, and pH 2, with a removal efficiency of 94.32 %. The RSM optimization using the desirability function yielded an overall desirability of 1.0, confirming that the proposed solution fully satisfied the set criteria. The optimum values were validated by conducting five replicate experiments. The result showed that the average removal efficiency is 93.86 % which is within the 95 % confidence interval, with a percentage error of 0.49 %. These findings confirmed that the model accurately predicts the optimal conditions for maximum removal efficiency, demonstrating its reliability and effectiveness of the ACT adsorption of ASMPNZ.

3.6. Adsorption isotherms study

Fig. 5 shows the nonlinearized plots of the Langmuir and the Freundlich isotherms for the removal of ACT by ASMPNZ. These were derived from the ACT concentration from 50 mg/L to 400 mg/L at pH 4 and contact time of 60 min. The corresponding parameters were reported in Table 5. For the Langmuir isotherm, was found an R^2 of 0.999, suggesting that the Langmuir model provides a reasonable description of the monolayer adsorption process onto the homogenous surface of ASMPNZ. It reveals that ASMPNZ has an adsorption capacity (q_{max}) of

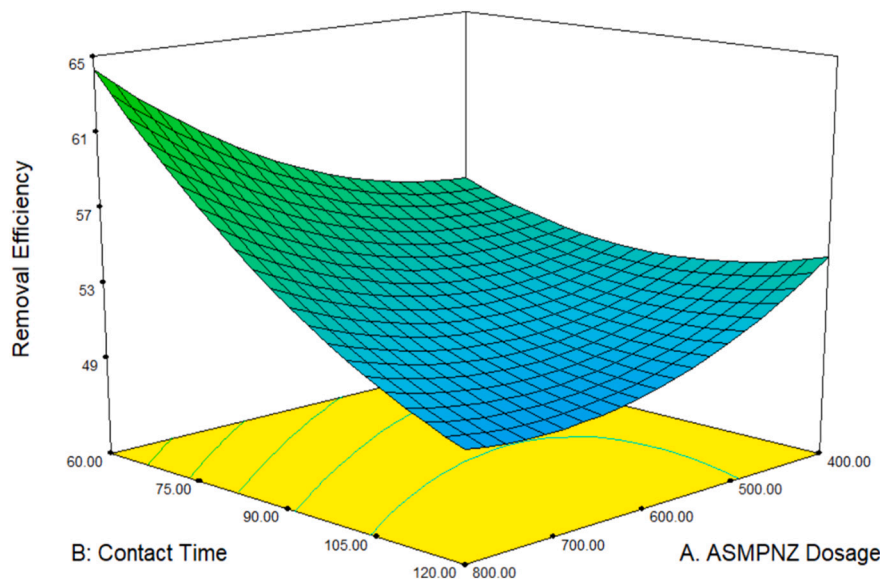


Fig. 3. 3D response surface of the interaction of ASMPNZ loading and contact time for the removal of ACT.

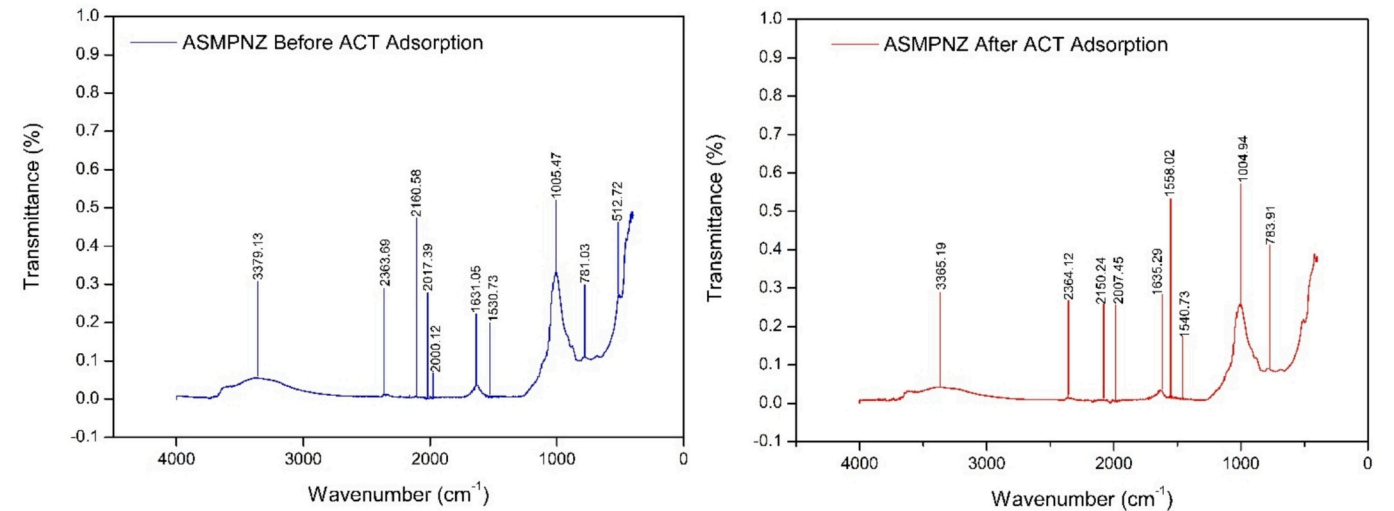


Fig. 4. FTIR spectra of ASMPNZ before and after the adsorption process.

Table 4
Summary of FTOR functional group changes before and after ACT adsorption on ASMPNZ.

Functional group	Assignment	Before adsorption (cm ⁻¹)	After adsorption (cm ⁻¹)	Observation
O-H stretching	Surface hydroxyls, H-bonded groups	3379	3365	Slight shift, reduce intensity → H-bonding with ACT -OH
C=O/ N-H	Amide, carbonyl vibrations (ACT)	–	1635, 1558, 1541	New peaks → interaction with ACT functional groups
C-O stretching	Alcohols, esters, ethers	1005	1005	Retained → surface functionality preserved
Aromatic C-H	Aromatic ring vibration (ACT)	–	784	New band → confirms ACT adsorption
N=C=S stretch	Isothiocyanate	≈2000	–	Disappeared → masked/alterd by ACT adsorption

237.47 mg/g with a Langmuir constant (K_L) of 0.0006, suggesting a weak binding affinity. This does not contradict the high model fit, as R^2 reflects the quality of the regression while K_L quantifies the strength of ACT and ASMPNZ interaction. The modest K_L value may be related to the surface chemistry resulting from acid-salt modification, which could limit strong binding of ACT molecules. Nevertheless, the high q_{max} demonstrates the practical adsorption capacity of ASMPNZ [16] [16].

On the other hand, the Freundlich isotherm describes the adsorption process of ACT onto ASMPNZ as a heterogeneous surface with the potential for multilayer adsorption dynamics, showing an $R^2 = 0.965$, with an adsorption intensity (n) of 0.756 and a Freundlich constant (K_F) of 0.026. The $n < 1$ means the exponent $1/n$ is >1 [17] [17], which indicates a stronger affinity of the ASMPNZ for the ACT. Thus, although

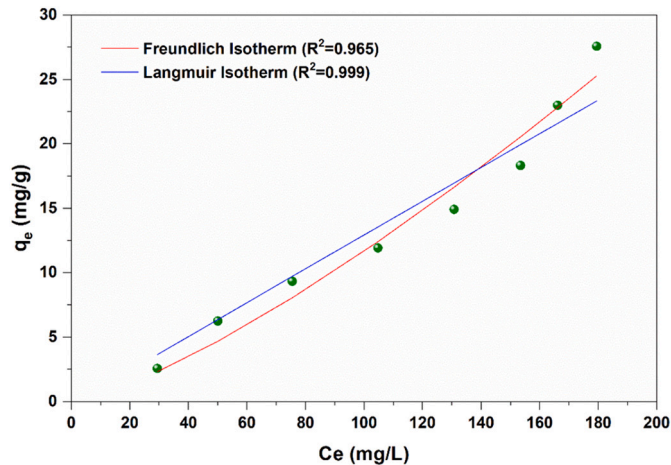


Fig. 5. Adsorption isotherm plots of ACT by ASMPNZ (dot points) compared with Langmuir and Freundlich isotherm models.

the Freundlich model provides a reasonable description of the adsorption process, the superior R^2 of the Langmuir isotherm model suggests that ACT adsorption predominantly follows monolayer coverage on a uniform surface rather than multilayer adsorption on heterogeneous sites. The insignificant difference between the two models further suggests that while some heterogeneity may be present, the overall adsorption mechanism is better captured by Langmuir [11]. This result of adsorption mechanisms of ACT onto ASMPNZ was also documented by the study [48].

3.7. Adsorption kinetics study

Fig. 6 shows the adsorption kinetic plots of ACT by ASMPNZ, and the parameters obtained from pseudo-first and pseudo-second kinetic models are reported in Table 6. The pseudo-first order model yielded an equilibrium adsorption capacity (q_e) of 14.67 mg/g and a rate constant (K_1) of 0.0073 min^{-1} , with a coefficient (R^2) of 0.992. Although the high R^2 value suggests that the model fits the experimental data reasonably well, the calculated q_e is significantly lower than the experimental equilibrium capacity, indicating a possible limitation of this model in accurately describing the adsorption kinetics.

On the other hand, the pseudo-second order model produced a higher q_e value of 21.64 mg/g and a rate constant (K_2) of 0.0003 min^{-1} , with an even stronger correlation ($R^2 = 0.994$). The superior R^2 value

Table 5
Equilibrium parameters of ACT adsorption onto ASMPNZ.

Isotherm Models	Parameters	Values
Langmuir Isotherm	q_{max} (mg/g)	237.47
	K_L (L/mg)	0.0006
	R^2	0.999
	n	0.756
Freundlich Isotherm	K_F [(mg/g)/(L/mg) ⁿ]	0.026
	R^2	0.967

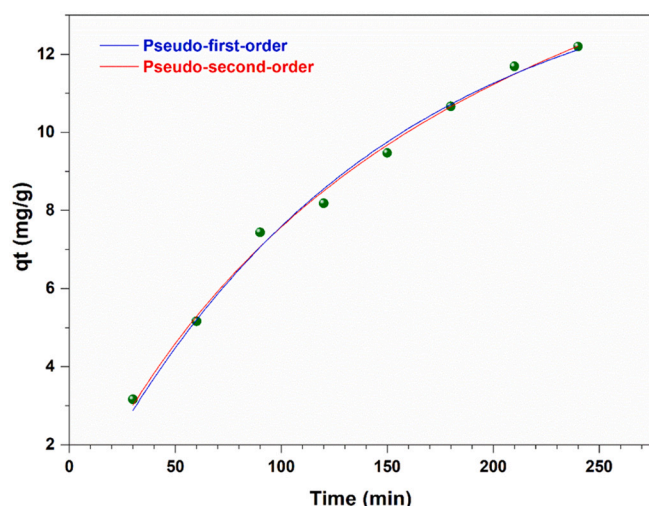


Fig. 6. Adsorption kinetic plots of ACT removal by ASPPNZ: pseudo-first-order and pseudo-second-order.

Table 6
Parameters of pseudo-first and pseudo-second kinetic models.

Model	Parameters	Values
Pseudo-first order	q_e (mg/g)	14.67
	K_1 (minute)	0.0073
	R^2	0.992
Pseudo-second order	q_e (mg/g)	21.64
	K_2 (minute)	0.0003
	R^2	0.994

and the closer agreement between the calculated and experimental q_e values imply that the adsorption process is better represented by the pseudo-second order kinetic model. This finding, which suggests that the rate-limiting step is controlled by chemisorption, is further supported by FTIR results. As observed in Fig. 4 and Table 4, the observed shift in the O—H stretching band from 3379 cm^{-1} and the appearance of new peaks corresponding to ACT functional groups provide direct evidence of chemical interactions [18].

In conjunction with the Langmuir isotherm model, this evidence suggests that the adsorption mechanism is dominated by specific chemical interactions rather than multilayer physical adsorption. Further, it indicates that the ACT molecules form a single, tightly bound monolayer on the ASPPNZ surface, which is strongly suggested a chemisorption mechanism [19]. This result is supported by the previous studies of Dávila-Estrada et al. [40], where the pseudo-second order kinetic model on paracetamol elimination using modified zeolite best matches their experimental results, further corroborated the assumption.

4. Conclusions

This study demonstrated the adsorption potential of ASPPNZ for the removal of ACT from aqueous solutions under controlled condition. Surface characterization using SEM and FTIR confirmed morphological and functional group changes indicative of successful modification. Process optimization using response surface methodology (RSM) identified conditions that maximize ACT removal efficiency, which were further validated through experimental trials. The adsorption behavior followed the Langmuir isotherm, suggesting monolayer coverage. Kinetics were best described by the pseudo-second order model, which indicates chemisorption as the likely rate-limiting step. Although these findings highlight the potential of ASPPNZ, the study was limited to controlled conditions and characterization techniques. Future research

is encouraged to use actual wastewater, incorporate advanced analyses such as XRF, SEM-EDS, and seta potential, and assess economic implications and process residuals to establish large-scale applicability.

CRediT authorship contribution statement

Alberto E. Lastimado: Writing – review & editing, Methodology, Investigation, Data curation. **Rekich R. Pahunang:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Data curation, Conceptualization. **Anamie Rabongue:** Writing – review & editing, Methodology, Investigation, Data curation. **Antonio Buonerba:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Funding acquisition, Data curation.

Submission declaration

The work has not been previously published, is not under consideration elsewhere, has approval from all authors and relevant authorities, and, if accepted, it won't be published the same way elsewhere without copyright-holder consent.

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Declaration of competing interest

The authors have declared no conflict of interest.

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Data availability

This work includes all the data gathered or analyzed in this study.

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