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Eco-friendly Zeolite Synthesis for Phenol Adsorption: Kinetic and Isotherm Studies

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ABSTRACT

The presence of phenolic compounds in aquatic systems has become a significant environmental concern due to their toxicity and persistence. This study evaluates the effectiveness of synthetic zeolites as adsorbents for removing phenol from contaminated aqueous solutions. The adsorbent was synthesized from natural clay using ZnCl₂ as an activating agent through a straightforward three-step process: (i) calcination at 90°C, (ii) aging for 24 hours, and (iii) crystallization for 8 hours. The synthesized material was then characterized by X-ray diffraction (XRD) to determine its mineralogical composition and the crystalline structure of the zeolite. The efficiency of phenol removal was assessed as a function of adsorbent dosage (0.1 g.L⁻¹ to 0.3 g.L⁻¹), contact time (20 to 60 minutes), and initial phenol concentration (500 mg.L⁻¹ to 5000 mg.L⁻¹). The adsorption kinetics were analyzed using pseudo-first-order and pseudosecond-order models, while equilibrium data were fitted to the Freundlich and Langmuir isotherm models. The results confirmed the successful synthesis of FAU-X zeolite from smectitic-kaolinitic clay. The zeolite-based adsorbent demonstrated high efficiency in phenol removal, exhibiting a sorption capacity of 125 mg.g⁻¹ after 60 minutes. The adsorption process followed pseudo-second-order kinetics, while equilibrium data were best described by the Langmuir isotherm model, indicating a monolayer adsorption pattern. The retention of pollutants was primarily governed by chemical interactions, including hydrogen bonding and electrostatic attraction between phenol molecules and the adsorbent surface. This study highlights the potential of synthesizing cost-effective zeolite-based adsorbents for wastewater treatment, contributing to the development of sustainable and environmentally friendly remediation technologies.

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1. Introduction

Water pollutants, encompassing both organic and inorganic substances, primarily originate from industrial discharges and human actions, notably the extreme application of pesticides and fertilizer [1]. Consequently, substantial volumes of industrial effluents, comprising various organic contaminants like pesticides, antibiotics, hydrocarbons, herbicides, phosphate, fluoride, dyes, phenols...etc., are released into aquatic environments [2, 3]. Phenol and its derivative compounds are discharged by numerous industrial sectors, which include pharmaceuticals, petroleum and petrochemicals, pesticides, plastics, paper production, and various other manufacturing processes [4]. Phenolic compounds have attracted considerable attention due to their essential role in various everyday applications. These compounds hold substantial economic importance across multiple industries, including food, medicine, agriculture, chemical synthesis, aviation, and cosmetics. However, despite their industrial significance, their presence in the environment, even at low concentrations, remains a serious concern. Phenol, in particular, is one of the most common pollutants in wastewater, frequently originating from industrial processing and refining plants [5-7]. Because of their toxicity and detrimental impact on the environment, phenolic compounds have been designated as priority pollutants by the United States Environmental Protection Agency (EPA); in fact, EPA determined a limit of less than 1 (ppb) for surface waters; so usually, a stringent effluent discharge limit of less than 0.5 mg.L⁻¹ is imposed [8, 9]. Hence, the elimination of phenol from industrial wastewater stands as a pressing global challenge.

Various treatment approaches, encompassing biological, chemical, and physical processes, are being employed to address the removal of phenol from industrial effluent charged before the released into the environment [10, 4]. Although these techniques are effective in eliminating phenols, some, notably secondary biological treatments, have constraints that restrict their application to wastewater with elevated concentrations of phenolic compounds [11, 12]. Adsorption technology has garnered considerable attention due to its ease, cost-effectiveness, environmentally friendly attributes, and extraordinary treatment competence [13-17]. Therefore, several researches confirmed the use of various adsorbent for removal of different pollutants such as heave metal, phenol, phosphate fluoride, dyes, pharmaceutical products...etc. [18-20]. Zeolites are characterized by their microporous nature and possess a crystalline three-dimensional structure consisting of aluminum, silicon, and oxygen [21-23]. Additionally, they carry cations and water within their structure. Several works investigated zeolite (natural and synthetic) and suggested considering this adsorbent to be employed for the sorption of phenol from wastewater [24-27]. Natural zeolites often come with impurities that restrict their adsorption and ion exchange capabilities. In contrast, synthetic zeolites can be tailored to achieve desired properties. Consequently, there is a growing demand for the production of synthetic zeolites, driven by the expanding range of applications for these materials.

As already known the primary raw materials used in zeolite production are silica and alumina. Clays have increasingly become a source of silicon and aluminum for zeolite preparation because of their widespread accessibility and cost-effectiveness in various countries [28-30]. Given the aforementioned context, this study endeavors to the preparation of zeolite from raw clay and assess its efficacy as a sorbent for phenol adsorption. A detailed examination of the influence of sorbent amount, contact duration, and initial phenol concentration is conducted. To elucidate the principal interactive mechanisms at play in the removal process, equilibrium data are fitted to adsorption isotherms, including Langmuir. In addition, kinetic parameters are computed founded on the Pseudo First Order (PFO) and Pseudo Second Order (PSO) to offer a more comprehensive description of the adsorption mechanism. Finally, potential adsorption mechanisms were proposed. Largely, these findings could contribute to the development of treatment strategies aimed at mitigating environmental and public health risks associated with the presence of phenol in various environmental compartments.

2. Materials and methods

2.1. Geological Studies: Localization of Raw Clay

In Tunisia, clay is a major mineral resource found throughout the country, including the north, center, and south. Many works have explored the utilization of these clay reserves in various fields [31]. In this work, a

smectite-rich clay, is collected from center Tunisia: clay of Chouabine formation from Djebel Jebbes El Meheri-Sidi Bouzid Fig. (1).



Figure 1: Simplified geological map of Jebel Jebbes El Meheri-Sidi Bouzid [32] and geological cross-section showing the clay units of the Choubine Formation.

2.2. Synthesis of Zeolites

In this study, zeolite synthesis was conducted following the alkaline fusion method, as per the approach outlined by Hamdi and Srasra in 2012 [33] and Amri *et al.* in 2022 [34]. In general, the use of hydroxides from numerous alkalis, including sodium, potassium, calcium, lithium, and silicates of sodium and potassium, is believed suitable for activating waste materials [35]. In this particular investigation, NaOH powder is employed as the alkali activator in the zeolite preparation process. The procedure involved initially blending 30g of clay powder with 40g of crushed soda crystals. The resulting mixture was subjected to calcination in an oven at 600°C for one hour, resulting in a color change to green. The ensuing product mixed with 24 ml of distilled water and agitated for one day at room temperature. Subsequently, crystallization occurred at 90°C for duration of 8 hours. The crystallized material was filtered, washed, and dried, yielding a beige powder. The nomenclature for the resulting zeolites is based on the temperature utilized, for instance, zeolite-90°C signifies a zeolite prepared at 90°C.

2.3. Phenol Stock Solution

The synthetic phenol solution was prepared with varying concentrations (C0) ranging from 500 to 5000 mg/L. Analytical grade phenol (AR) was employed. A daily preparation of the required stock solution was carried out.

2.4. Characterizations Methods

Mineralogical identification of both raw clay and synthetic zeolite was accomplished using X-ray diffraction analysis was performed using a PANalytical X'Pert diffractometer. The ATR/FT-IR studied of raw clay was conducted with Perkin Elmer FT-IR/FIR spectrometer (frontier) across the wavenumber series of 400–4000 cm⁻¹. The chemical analysis of raw clay was performed through X-Ray Fluorescence.

2.5. Phenol Adsorption Tests

The phenol adsorption experiments adhered to the following procedure: A 30 mL solution containing phenol at the desired concentration was brought into contact with a specified amount of adsorbent at room temperature, under natural pH conditions. After each experiment, the mixtures were filtered and subjected to analysis using UV/Vis spectroscopy. The ultimate concentration was determined through reference to a calibration curve in the UV spectrum at $\lambda = 254$ nm. These experiments were conducted to evaluate phenol removal by zeolite and to examine the influence of various factors, including sorbent quantity, contact time, and initial phenol concentration. Each experiment was repeated three times, and the mean value was used for analysis. The adsorption performance is quantified by measuring the quantity of phenol adsorbed (qe_{exp}, mg.g⁻¹) by equations (1) respectively :

$$qe_{exp} = \frac{Ci-Cf}{m} * V$$
 (1)

Where Ci: initial phenol concentration (mg.L⁻¹), Cf: final phenol concentration (mg.L⁻¹), m : dosage of adsorbent (g.L⁻¹), and V : volume of the phenol solution (mL).

2.6. Modeling Studies

Numerous models have been proposed in the literature to describe adsorption kinetics and isotherms, each providing a unique perspective on the adsorption process [36-38]. In this study, the kinetics of phenol adsorption were examined using first-order and second-order equations, while adsorption equilibrium was evaluated through Langmuir and Freundlich isotherm models. The accuracy of these kinetic and isotherm models in representing the experimental data was assessed using the coefficient of determination.

3. Results and Discussion

3.1. Characterization of Raw Clay

3.1.1. Mineralogical Composition

The XRD patterns for both the natural clay and the purified clay are displayed in Fig. (**2**). The outcomes suggest that this clay comprises a mixture of clay minerals (66.31%), including smectite (14.75 Å) and illite (10.55 Å), along with minor impurities (33.69%), such as dolomite (2.89 Å), hematite (2.67 Å), and quartz (2.89 Å). The <2µm fraction reveals the prevalence of smectite (51.02%) and illite (45.81%), with minor levels of kaolinite (3.15%).



Figure 2: X-ray diffraction pattern of raw clay.

3.1.2. Chemical Composition

The results of this analysis reveal that the primary constituents of the clay are silica (SiO₂: 39.58%) followed by alumina (Al₂O₃: 9.33%). The sample also contains notable quantities of magnesium (MgO: 8.04%), iron (Fe₂O₃: 4.071%), and calcium (CaO: 6.75%). In contrast, elements such as Na2O, SO₃, and TiO₂ are present in trace amounts. The relatively high percentages of silica (SiO₂) and alumina (Al₂O₃) are particularly favorable for the utilization of the studied clays in zeolite synthesis.

3.1.3. FTIR Analysis

The FTIR spectrum of raw clay is revealed in Fig. (**3**). The bands at 3,425 cm⁻¹ (H–O–S stretching), and 1639 cm⁻¹ (H–O–H bending) show the existence of adsorbed water. Absorption band at 1,026 cm⁻¹ was given to the stretching mode of Si–O. The bending bands are at 528 cm⁻¹ for Si–O–Al and 469 cm⁻¹ for Si–O–Si. The bands located at 795 represent the quartz and 1440 cm⁻¹ is characteristic of carbonate.



Figure 3: FTIR spectra of used clay.

3.2. Characterization of Synthesized Zeolites

Fig. (4) shows the XRD patterns of the zeolite synthesized at 90°C. The diffractogrammes of sample prepared at 90°C shows that all XRD peaks agree well with the characteristic peaks of zeolite (Na-X). The synthetic zeolite products still contained a significant amount of residual raw materials and/or other phases. The presence of non-zeolite phases in the converted products limits the cation exchange capacity of the products and greatly reduces the applicability of synthetic zeolite [33]. For this research the typical diffraction peaks corresponding to clay minerals (smectite, kaolinite, and illite) remarkably disappear during the crystallization step, to be replaced by the generation of Faujasite zeolite (Na-X). The small zigzag peaks found in the spectrum refer to the presence of amorphous material. The only crystalline form in the used clay was quartz, as the thermal treatment during calcination does not affect quartz [39]. The XRD of the crystals has a low background, strong intensities and sharp peaks, indicating the as-synthesized zeolite 4A crystals are perfect [33]. In practical terms, we can assume that the synthesized zeolites are pure, based on the data provided by the International Zeolite Association.



Figure 4: X-ray diffraction patterns of synthesized zeolite.

3.3. Adsorption Study of Phenol

3.3.1. Preliminary Study: Comparative Study

This study involves a comparison of the efficiency of phenol adsorption on raw clay and synthesized zeolite. The adsorption tests were conducted at room temperature for one hour, utilizing a 30 ml volume, a phenol concentration of 2000 mg.L⁻¹, natural pH conditions, and 0.2 g.L⁻¹ of adsorbent. The comparative results are depicted in Fig. (**5**). From this figure, it is evident that zeolites exhibit significantly greater adsorption efficiency compared to raw clay. The quantity of phenol adsorbed is approximately 44 mg.g⁻¹ for raw clay, increasing to 95.02 mg.g⁻¹ for zeolite-90°C. These results can be attributed to the advantageous properties of zeolite, such as a uniform micropore structure and a high surface area. In fact, according to Hamdi and Srasra in 2012 [33], synthetic zeolite, with its uniform micropore structure and high surface area, generally exhibits higher adsorption capacity when compared to clay minerals.

3.3.2. Impact of the Adsorbent Dosage

One of the significant parameters in the removal of phenolic compounds in the fungus preparations is the adsorbent dosage. The impact of the adsorbent dosage on the phenol adsorption onto zeolite-90°C was determined for 2000 mg.L⁻¹ initial aqueous concentration and at natural pH. The tested adsorbent doses varied from 0.1 g.L⁻¹ to 0.3 g.L⁻¹. The results of the effect adsorbent dosage in the phenol adsorption onto zeolite-90°C are represented in Fig. (**5**). As shown in this figure, phenol removal efficiency increased from 59.45 to 101.7 mg.g⁻¹ when the zeolite dose increased from 0.05 to 0.3 mg.L⁻¹. The increase of the phenol removal efficiency was the result of an increase in surface area which was actively effective in adsorption process. At equilibrium, the

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quantity adsorbed of phenol is in order to 95.23 mg.g⁻¹ for m=0.2g and 101.7 mg.g⁻¹ for m=0.3g; since the latter (m=0.2g and m=0.3g) present very close values we have chooses 0.2 g as a mass to determine the phenomenon of phenol adsorption for the rest of the work.



Figure 5: Adsorption study of Phenol.

3.3.3. Impact of Contact Time and Modeling of Sorption Kinetic

The time of pollutant adsorption is a very important parameter from an economic point of view. The effect of contact time was investigated at 20, 30, 40, 50 and 60 min in an ambient temperature and natural pH. For all experiments, the initial aqueous phenol concentration and adsorbent dosage were fixed to 2000 mg.L⁻¹ and 0.1 g.L⁻¹ respectively. The Fig. (**5**) illustrates the adsorption of phenol onto zeolite over time, revealing a three-phase adsorption process: a rapid initial phase, a subsequent slower phase, and finally, an equilibrium phase. These findings indicate that the phenol adsorption process can be divided into distinct stages. The rapid adsorption phase, lasting approximately 10 minutes, can be attributed to the initial abundance of active sites on the zeolite surface. This abundance results in a high sticking probability, facilitating a swift adsorption process. As time a progress, the number of available active sites gradually diminishes, leading to a decrease in the adsorption rate. Around 30 minutes into the process, a near equilibrium state is achieved, where the adsorption rate stabilizes. This deceleration in the adsorption process naturally slows down. After approximately <40 minutes, equilibrium is nearly reached, indicating that most of the available adsorption sites are now occupied. The time required to reach this state of equilibrium was estimated at about 60 min. This finding is in concordance with previous studies, where the phenol by zeolite attains an equilibrium state between 60 and 100 min [25, 40].

Adsorption kinetics is a key aspect that characterizes the rate at which a solute is taken up in a chemical reaction, ultimately influencing how long the adsorption process continues. In this study, two distinct kinetic models were employed to describe adsorption processes: the pseudo-first-order kinetic model and the pseudo-second-order kinetic model. Table **1** present the parameters associated with these two models, including R-squared values (R²), rate constants (k), and adsorption capacities (Qads), among others. These parameters offer valuable insights into the behavior of the adsorption process and provide a basis for understanding the kinetics of solute uptake in the studied systems. The pseudo-first-order kinetic model implies physical adsorption and

assumes homogeneous adsorbents [41]. However, the results from this study revealed a discrepancy between the calculated adsorption quantity ($qe_{exp} = 49.00 \text{ mg.g}^{-1}$), and the experimental adsorption quantity ($qe_{exp} = 49.00 \text{ mg.g}^{-1}$), despite a relatively high R-squared value of 0.919. This incongruity suggests that the pseudo-first-order model is not suitable for accurately representing the adsorption kinetics of phenol onto zeolite. In contrast, the pseudo-second-order kinetic model suggests chemical adsorption and assumes heterogeneous adsorbents [41]. The model yielded a higher correlation coefficient ($R^2 = 0.99$) and a calculated adsorption capacity ($qell_{cal} = 100.00 \text{ mg.g}^{-1}$), indicating that the pseudo-second-order model provides a more accurate description of the adsorption kinetics of phenol onto zeolite. Consequently, the rate of phenol adsorption onto zeolite appears to be dependent on the availability of adsorption sites and involves chemical adsorption or chemisorption, which entails valence forces through electron sharing or exchange between the adsorbent and adsorbate [12]. The same finding were reported by El-Kordy and his team in 2022 [11] when investigating the phenol removal from aqueous solution by adsorption onto synthesized Faujasite-type Y zeolite.

Model	Equations	Plot	Parameters	Value
Experiments	Equations		qe,exp (mg.g ⁻¹)	95.23
Pseudo-first-order $\operatorname{Ln}((q_e - q_t) = \operatorname{Ln}q_{eI} - K_1 t$ $\operatorname{Ln}((q_e - q_t) \text{ vs. } t$	qe _{l,cal} (mg.g ⁻¹)	49.00		
	$Ln ((q_e - q_t) = Lnq_{eI} - K_1 t$	Ln (($q_e - q_t$) vs. t	k1 (min ⁻¹)	0.13
			R ²	0.919
Pseudo-second-order	$\frac{\mathrm{t}}{\mathrm{q}_{\mathrm{t}}} = \frac{1}{\mathrm{K}_{2}\mathrm{q}_{\mathrm{eII}}^{2}} + \frac{1}{\mathrm{q}_{\mathrm{eII}}}\mathrm{t}$	$\frac{t}{q_t}$ vs.t	qe _{II,cal} (mg.g ⁻¹)	100
			k1 (min ⁻¹)	0.004
			R ²	0.998

Table 1:	Pseudo-first-order and	pseudo-second-order	parameters of phe	nol adsorption onto zeolite.
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3.3.4. Impact of Initial Phenol Concentrations and Modeling of Adsorption Isotherm

A series of experiments were conducted to investigate the influence of the initial phenol concentration (Fig. **5**). The initial phenol concentration was systematically varied within the range of 500 to 5000 mg.L⁻¹, while maintaining a fixed adsorbent dosage of 0.2 g.L⁻¹ and a contact time of 60 minutes. As depicted in Fig. **(5)**, it becomes evident that the amount of phenol adsorbed by the zeolite at 90°C increases in direct proportion to the concentrations in the aqueous phase. Specifically, the quantity of adsorbed phenol rises from 30.64 to 96.44 mg.g⁻¹ as the initial phenol concentration increases from 500 to 5000 mg.L⁻¹. Adsorption isotherm models were employed to establish the equilibrium relationship between the amount of adsorbed phenol and the concentration of the adsorbate at a constant temperature. The linear isotherm constants and their corresponding correlation coefficients (R²) for the two models used are presented in Table **2**. Based on the obtained data, it is evident that the Langmuir model provides the most suitable fit for the experimental results. This indicates that the adsorbent's

Table 2:	Langmuir and Freundlich	parameters of phenol	adsorption onto zeolite.
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Model	Fructions	Dist	Parameters	Value
Experiments	Equations	Plot	q _{max} cal (mg.g ⁻¹)	96.44
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max,L}} + \frac{1}{q_{max,L}} Ce$ $R_L = \frac{1}{1 + K_L Ci}$	$rac{C_e}{q_e}$ vs. C_e	$q_{\max}(L)$ (mg.g ⁻¹)	125
			K _L (L.mg ⁻¹)	0.001
			RL	0.66-0.16
			R ²	0.993
Freundlich		$Ln q_e = LnK_F + \frac{1}{n}LnCe \qquad \qquad Lnq_e vs. LnC_e \qquad \qquad \frac{k_F}{n_F} \qquad \qquad$	k⊧	3.17
	$Ln q_e = LnK_F + \frac{1}{n}LnCe$		2.33	
	11		R ²	0.856

surface is homogeneous in nature. The Langmuir model assumes monolayer adsorption onto a surface containing a finite number of specific and energetically equivalent homogeneous adsorption sites. The Freundlich model often used to describe the adsorption characteristics of surfaces with a non-uniform distribution of heat of adsorption and assuming a reversible and multilayer adsorption process, yielded correlation coefficients that deviated from unity. This divergence from unity rules out the possibility of non-uniform adsorption of phenol on a heterogeneous surface. Furthermore, the K_F and n_F values obtained from the Freundlich equation were 3.17 (mg.g⁻¹) (L.mg⁻¹)^{1/n}_F and 2.33, respectively. n_F value is range between 1–10, which suggests favorable phenol adsorption by zeolite at 90°C.

3.3.5. Comparative Studies with other Adsorbent

The performance and efficiency of adsorbents in industrial applications are highly dependent on their pore structure and surface properties [42]. To assess the efficacy of zeolite-90°C in phenol removal compared to other adsorbents reported in the literature, a comparative analysis based on Langmuir's adsorption capacity, denoted as "q_{max}," was conducted. The results indicate that zeolite-90°C exhibits a notably higher adsorption capacity when compared to several other adsorbents listed in Table 3. Specifically, the phenol adsorption capacity of zeolite-90°C is more than double that of Activated alumina. Furthermore, the adsorption capacity of our zeolite-90°C significantly surpasses that of relatively expensive adsorbents such as Garlic peel [43] and Banyan root activated carbon [44]. These findings suggest that the phenol adsorption rates of our synthesized zeolite are quite promising, especially when compared to other natural and synthetic zeolites with similar characteristics. Moreover, the cost of our zeolite-90°C remains competitive. Table **3** reveals that activated carbon derived from coconut coir boasts a higher maximum adsorption capacity than zeolite-90°C. However, activated carbon is the most commonly utilized adsorbent. Nevertheless, the challenges associated with carbon regeneration, coupled with its high cost, underscore the need for economically viable, stable, and efficient adsorbents. Therefore, zeolites synthesized from natural aluminosilicates materials emerge as an economical choice for the removal of phenol from aqueous solutions. In conclusion, it's worth highlighting that the clay used in the synthesis process holds promise as an attractive material for preparing zeolites dedicated to the removal of phenol from aqueous solutions.

Adsorbents	Adsorption Capacity (mg.g ⁻¹)	References		
	Zeolite			
Commercial sodium zeolite	13.051	[45]		
Faujasite-type Y zeolite	90	[11]		
Acid-modified Pseudomonas	5.96	[46]		
Faujasite-type Y zeolite	81	[47]		
Natural bioadsorbent neem	47.90	[48]		
Other Adsorbents				
Clarified sludge	1.052	[41]		
Na-bentonite	8.76	[49]		
Mg-Al LDH	82.6	[50]		
Natural clay	15	[51]		
Banyan root activated carbon	26.95	[44]		
Garlic peel	14.49	[43]		
Natural zeolites	34.5	[52]		

Table 3: Comparison of adsorption capacity of phenol onto zeolite-90°C with other mineral and organic adsorbents.

3.3.6. Mechanism of Adsorption

To gain a comprehensive understanding of phenol adsorption onto zeolites, it is essential to analyze the underlying mechanisms. This adsorption phenomenon is influenced by a series of interconnected factors, including the functional groups present in both phenol and zeolite, the textural and surface properties of the zeolite, the diffusional behavior of phenol towards the adsorbent surface, and the nature of the intermolecular interactions between these components. Three primary models have been proposed to explain the adsorption mechanism of phenol: (i) the electron donor-acceptor (EDA) complex, representing chemical adsorption, (ii) π – π dispersion interactions, characteristic of physical adsorption, and (iii) solvent effects [36]. The EDA complex model suggests that the surface oxygen functional groups of zeolite and the aromatic rings of phenol interact as electron donors and acceptors, respectively [52]. Meanwhile, solvent effects arise when adsorption sites intended for phenol are occupied by water molecules, which form hydrogen bonds with surface oxygen groups, partially blocking the zeolite's pores and limiting phenol adsorption.

4. Conclusions

In summary, the successful synthesis of a cost-effective and eco-friendly zeolite from natural clay demonstrates its strong potential for wastewater treatment applications. XRD analysis confirmed the transformation of clay into a well-crystallized zeolite structure. The synthesized zeolite exhibited remarkable adsorption performance, effectively removing 125 mg.g⁻¹ of phenol from a highly concentrated solution (5000 mg.L⁻¹) within 60 minutes using just 0.2 g of adsorbent. The adsorption process followed a pseudo-second-order kinetic model, indicating chemisorption as the dominant mechanism, while equilibrium data were best described by the Langmuir isotherm, suggesting a monolayer adsorption pattern. Compared to other reported adsorbents, the synthesized zeolite demonstrated superior efficiency, making it a promising candidate for large-scale wastewater treatment. Its high sorption capacity, rapid removal rate, and environmentally sustainable nature underscore its viability for practical applications in industrial effluent remediation.

5. Recommendations

In this study, a highly efficient synthetic zeolite was employed for water treatment applications. While the results obtained were promising, there remains significant potential for further optimization and refinement. Although batch experiments provided valuable insights into adsorption behavior, they have inherent limitations in replicating real-world conditions.

Batch studies, while essential for initial screening and understanding fundamental adsorption mechanisms, do not fully capture the dynamic flow conditions present in practical applications. To overcome this limitation, future research should transition from batch experiments to column studies. Column studies offer several advantages, including the ability to simulate continuous flow conditions, extended contact times between the adsorbent and the contaminated water, and a more realistic assessment of adsorption efficiency under operational conditions. By adopting this approach, the reliability of the findings can be further enhanced, paving the way for optimized process parameters and facilitating the scale-up of this technology for real-world wastewater treatment applications.

Conflict of Interest

The authors declare no competing interests.

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Data Availability

The datasets utilized in this study can be obtained from the corresponding author upon reasonable request.

References

- [1] Ewis D, Ba-Abbad MM, Benamor A, El-Naas MH, Adsorption of organic water pollutants by clays and clay minerals composites: A comprehensive review. Appl Clay Sci. 2022; 229: 106686. https://doi.org/10.1016/j.clay.2022.106686
- [2] Tran HN. Adsorption technology for water and wastewater treatments. Water. 2023;15(15): 2857. https://doi.org/10.3390/w15152857
- [3] Yahya K, Msadok I, Mlayah A, Srasra E, Hamdi N. Retention and selectivity of phosphate and fluoride from single and industrial aqueous solutions using purified and surfactant modified Tunisian clay. Desalination Water Treat. 2021; 216: 199-210. https://doi.org/10.5004/dwt.2021.26814
- [4] Park Y, Ayoko GA, Kurdi R, Horváth E, Kristóf J, *et al*. Adsorption of phenolic compounds by organoclays: Implications for the removal of organic pollutants from aqueous media. J Colloid Interface Sci. 2013; 406: 196-208. https://doi.org/10.1016/j.jcis.2013.05.027
- [5] Patel M, Patel D, Pillai P. Comparison of different treatment methods which are used for phenol removal: A mini review. Water Pract Technol. 2024; 19(7): 2761-73. https://doi.org/10.2166/wpt.2024.143
- [6] Saputera WH, Putrie AS, Esmailpour AA, Sasongko D, Suendo V, *et al*. Technology advances in phenol removals: Current progress and future perspectives. Catalysts. 2021; 11(8): 998. https://doi.org/10.3390/catal11080998
- [7] Petkovic S, Adnadjevic B, Jovanovic J. Novel kinetics model for adsorption of pollutant from wastewaters onto zeolites. Kinetics of phenol adsorption on zeolite-type silicalite. Adsorpt Sci Technol. 2019; 37(3-4): 349-64. https://doi.org/10.1177/0263617419833201
- [8] Veeresh GS, Kumar P, Mehrotra I. Treatment of phenol and cresols in upflow anaerobic sludge blanket (UASB) process: a review. Water Res. 2005; 39(1): 154-70. https://doi.org/10.1016/j.watres.2004.07.028
- [9] Mohammadi S, Kargari A, Sanaeepur H, Abbassian K, Najafi A, *et al*. Phenol removal from industrial wastewaters: a short review. Desalination Water Treat. 2015; 53(8): 2215-34. https://doi.org/10.1080/19443994.2014.883327
- [10] Dehmani Y, Alrashdi AA, Lgaz H, Lamhasni T, Abouarnadasse S, *et al.* Removal of phenol from aqueous solution by adsorption onto hematite (α-Fe₂O₃): Mechanism exploration from both experimental and theoretical studies. Arab J Chem. 2020; 13(5): 5474-86. https://doi.org/10.1016/j.arabjc.2020.03.026
- [11] El-Kordy A, Dehmani Y, Douma M, Bouazizi A, El Moustansiri H, El Abbadi S, *et al*. Experimental study of phenol removal from aqueous solution by adsorption onto synthesized Faujasite-type Y zeolite. Desalination Water Treat. 2022; 277: 144-54. https://doi.org/10.5004/dwt.2022.28958
- [12] Wang C, Shao N, Xu J, Zhang Z, Cai Z. Pollution emission characteristics, distribution of heavy metals, and particle morphologies in a hazardous waste incinerator processing phenolic waste. J Hazard Mater. 2020; 388: 121751. https://doi.org/10.1016/j.jhazmat.2019.121751
- [13] Fawcett-Hirst W, Temple TJ, Ladyman MK, Coulon F. A review of treatment methods for insensitive high explosive contaminated wastewater. Heliyon. 2021; 7(7): e07438. https://doi.org/10.1016/j.heliyon.2021.e07438
- [14] Sodha V, Shahabuddin S, Gaur R, Ahmad I, Bandyopadhyay R, *et al*. Comprehensive review on zeolite-based nanocomposites for treatment of effluents from wastewater. Nanomaterials. 2022; 12(18): 3199. https://doi.org/10.3390/nano12183199
- [15] Yousef R, Qiblawey H, El-Naas MH. Adsorption as a process for produced water treatment: A review. Processes. 2020; 8(12): 1657. https://doi.org/10.3390/pr8121657
- [16] Chakravorty S, Chatterjee R, Majumder C. A review of phenol removal from wastewater by adsorption. J Indian Chem Soc. 2020; 97(12b): 2820-3
- Bello IA, Oladipo MA, Giwa AA, Adeoye DO. Adsorptive removal of phenolics from wastewater: A review. Int J Basic Appl Sci. 2013; 2(1): 79-90.
- [18] Ho S. Low-cost adsorbents for the removal of phenol/phenolics, pesticides, and dyes from wastewater systems: A review. Water. 2022; 14(20): 3203. https://doi.org/10.3390/w14203203
- [19] Ben Amor A, Ouakouak A, Boucetta S, Mahmoudi K, Hamdi N. Synthesis and characterization of geopolymer foams from mineral wastes: Application as adsorbent for Cu(II) and Pb(II) ions from aqueous solutions. Desalination Water Treat. 2023; 284: 165-74. https://doi.org/10.5004/dwt.2023.29291
- [20] Pérez Ramírez EE, Asunción ML, Rivalcoba VS, Martínez Hernández AL, Velasco Santos C. Removal of phenolic compounds from water by adsorption and photocatalysis. In: Soto-Hernández M, Palma-Tenango M, Garcia-Mateos MDR, editors. Phenolic compounds natural sources, importance and applications. InTech; 2017. https://doi.org/10.5772/66895

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- [21] Mudaber S, Batur J. Differences in heavy metals adsorption on natural, modified, and synthetic zeolites: A review. J Turk Chem Soc Sect A. 2023; 10(3): 847-60. https://doi.org/10.18596/jotcsa.1263041
- [22] Derbe T, Temesgen S, Bitew M. A short review on synthesis, characterization, and applications of zeolites. Adv Mater Sci Eng. 2021; 2021(1): 6637898. https://doi.org/10.1155/2021/6637898
- [23] Mgbemere HE, Ekpe IC, Lawal GI. Zeolite synthesis, characterization and application areas: A review. 2017; 6: 45-59
- [24] Khalid M, Joly G, Renaud A, Magnoux P. Removal of phenol from water by adsorption using zeolites. Ind Eng Chem Res. 2004; 43(17): 5275-80. https://doi.org/10.1021/ie0400447
- [25] Asgari G, Seid Mohammadi A, Ebrahimi A, Hosseinzadeh E. Adsorption of phenol from aqueous solution by modified zeolite with FeCl3. Int J Environ Health Eng. 2013; 2(1): 6. https://doi.org/10.4103/2277-9183.107915
- [26] Koubaissy B, Toufaily J, El-Murr M, Daou TJ, Hafez H, Joly G, *et al*. Adsorption kinetics and equilibrium of phenol drifts on three zeolites. Open Eng. 2012; 2(3): 435-44. https://doi.org/10.2478/s13531-012-0006-4
- [27] de Magalhães LF, da Silva GR, Peres AEC. Zeolite application in wastewater treatment. Adsorpt Sci Technol. 2022; 2022: 4544104. https://doi.org/10.1155/2022/4544104
- [28] Kordala N, Wyszkowski M. Zeolite properties, methods of synthesis, and selected applications. Molecules. 2024; 29(5): 1069. https://doi.org/10.3390/molecules29051069
- [29] Khaleque A, Alam MM, Hoque M, Mondal S, Haider JB, Xu B, *et al.* Zeolite synthesis from low-cost materials and environmental applications: A review. Environ Adv. 2020; 2: 100019. https://doi.org/10.1016/j.envadv.2020.100019
- [30] El Ouardi Y, Achalhi N, Butylina S, Geng S, Fadeev E, Virolainen S. A review on synthesis of zeolites from natural clay resources and waste ash: Recent approaches and progress. Miner Eng. 2023; 198: 108086. https://doi.org/10.1016/j.mineng.2023.108086
- [31] Yahya K, Msadok I, Moussa KB, Ba M, Hajri AK, Mlayah A, *et al*. Optimization of fluoride removal by activated clays using response surface methodology: Box–Behnken design, kinetic and isotherm studies. Int J Environ Sci Technol. 2024; 21(12): 7923-40. https://doi.org/10.1007/s13762-024-05535-6
- [32] Lafi A, Felhi M, Jaballi F, Guermit F, Trabelsi H, Zayani K, Tlili A. Exploration et cartographie géologique des séries phosphatées du Jebel Jebes (Région de Maknassy, Tunisie Centrale). In Annales des Mines et de la Géologie. 2016; 47: 90-99.
- [33] Hamdi N, Srasra E. Removal of phosphate ions from aqueous solution using Tunisian clay minerals and synthetic zeolite, J Environ Sci. 2012; 24(4): pp. 617–623, https://doi.org/10.1016/S1001-0742(11)60791-2.
- [34] Amri I, Assadi AA, Mellah B, Hamdi N. Optimized removal of chloroform and DMDS using synthetic zeolite (Na-P1) and activated carbon composite. Model Earth Syst Environ. 2024; 10: 2309-28. https://doi.org/10.1007/s40808-023-01911-2
- [35] Ben Amor A, Ouakouak A, Boucetta S, Mahmoudi K, Hamdi N. Synthesis and characterization of geopolymer foams from mineral wastes: application as adsorbent for Cu(II) and Pb(II) ions from aqueous solutions. Desalination Water Treat. 2023; 284: 165-74. https://doi.org/10.5004/dwt.2023.29291
- [36] Tran HN, Nguyen DT, Le GT, Tomul F, Lima EC, Woo SH, et al. Adsorption mechanism of hexavalent chromium onto layered double hydroxides-based adsorbents: A systematic in-depth review. J Hazard Mater. 2019; 373: 258-70. https://doi.org/10.1016/j.jhazmat.2019.03.018
- [37] A.O D. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk. IOSR J Appl Chem. 2012; 3(1): 38-45. https://doi.org/10.9790/5736-0313845
- [38] Singh NB, Nagpal G, Agrawal S, Rachna. Water purification by using adsorbents: A review. Environ Technol Innov. 2018; 11: 187-240. https://doi.org/10.1016/j.eti.2018.05.006
- [39] Bahgaat AK, Hassan HE, Melegy AA, Abdel Karim A, Mohamed MH. Synthesis and characterization of Zeolite-Y from natural clay of Wadi Hagul, Egypt J Chem. 2020; 63(10): 3791-800. https://doi.org/10.21608/ejchem.2020.23195.2378
- [40] Dalang S, Tuah PM. Removal of phenol by zeolite. Trans Sci Technol. 2016; 3(1-2): 107-13
- [41] Mandal A, Das SK. Phenol adsorption from wastewater using clarified sludge from basic oxygen furnace. J Environ Chem Eng. 2019; 7(4): 103259. https://doi.org/10.1016/j.jece.2019.103259
- [42] Cheng WP, Gao W, Cui X, Ma JH, Li RF. Phenol adsorption equilibrium and kinetics on zeolite X/activated carbon composite. J Taiwan Inst Chem Eng. 2016; 62: 192-8. https://doi.org/10.1016/j.jtice.2016.02.004
- [43] Muthamilselvi P, Karthikeyan R, Kumar BSM. Adsorption of phenol onto garlic peel: optimization, kinetics, isotherm, and thermodynamic studies. Desalination Water Treat. 2016;57(5):2089-103. https://doi.org/10.1080/19443994.2014.979237
- [44] Nirmala G, Murugesan T, Rambabu K, Sathiyanarayanan K, Show PL. Adsorptive removal of phenol using banyan root activated carbon. Chem Eng Commun. 2021; 208(6): 831-42. https://doi.org/10.1080/00986445.2019.1674839
- [45] Saravanakumar K, Kumar A. Removal of phenol from aqueous solution by adsorption using zeolite. Afr J Agric Res. 2013; 8(23): 2965-9. https://doi.org/10.5897/AJAR11.194
- [46] Dong R, Chen D, Li N, Xu Q, Li H, He J, *et al*. Removal of phenol from aqueous solution using acid-modified Pseudomonas putidasepiolite/ZIF-8 bio-nanocomposites. Chemosphere. 2020; 239:124708. https://doi.org/10.1016/j.chemosphere.2019.124708
- [47] Ba Mohammed B, Yamni K, Tijani N, Alrashdi AA, Zouihri H, Dehmani Y, *et al*. Adsorptive removal of phenol using faujasite-type Y zeolite: adsorption isotherms, kinetics and grand canonical Monte Carlo simulation studies. J Mol Liq. 2019; 296: 111997. https://doi.org/10.1016/j.molliq.2019.111997

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- [48] Mandal A, Bar N, Das SK. Phenol removal from wastewater using low-cost natural bioadsorbent neem (Azadirachta indica) leaves: adsorption study and MLR modeling. Sustain Chem Pharm. 2020; 17: 100308. https://doi.org/10.1016/j.scp.2020.100308
- [49] Asnaoui H, Dehmani Y, Khalis M, Hachem EK. Adsorption of phenol from aqueous solutions by Na-bentonite: kinetic, equilibrium and thermodynamic studies. Int J Environ Anal Chem. 2022; 102(13): 3043-57. https://doi.org/10.1080/03067319.2020.1763328
- [50] He X, Wang B, Zhang Q. Phenols removal from water by precursor preparation for Mg Al layered double hydroxide: isotherm, kinetic and mechanism. Mater Chem Phys. 2019; 221: 108-17. https://doi.org/10.1016/j.matchemphys.2018.09.046
- [51] Djebbar M, Djafri F, Bouchekara M, Djafri A. Adsorption of phenol on natural clay. Appl Water Sci. 2012; 2(2): 77-86. https://doi.org/10.1007/s13201-012-0031-8
- [52] Yousef RI, El-Eswed B, Al-Muhtaseb AH. Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: kinetics, mechanism, and thermodynamics studies. Chem Eng J. 2011; 171(3): 1143-9. https://doi.org/10.1016/j.cej.2011.05.012