

Article

Y-Type Zeolite Synthesized from an Illite Applied for Removal of Pb(II) and Cu(II) Ions from Aqueous Solution: Box-Behnken Design and Kinetics

Kinjal J. Shah , Jiacheng Yu, Ting Zhang and Zhaoyang You 

College of Urban Construction, Nanjing Tech University, Nanjing 211800, China; kjshah@njtech.edu.cn (K.J.S.)

* Correspondence: youzhaoyang@njtech.edu.cn; Tel.: +86-1333-7829-930; Fax: +86-2-2366-1642

Abstract: A Y-type zeolite was prepared from illite clay, which was activated and synthesized by a solid-phase alkali fusion technique with reduced reaction conditions and crystal methods. The optimal synthesis conditions were investigated using the Box-Behnken design for a NaOH/illite (mass ratio) of 1:2, an activation temperature of 185 °C, and an activation time of 2.7 h. The synthesized Y-type zeolites were characterized by various analytical techniques such as FT-IR, XRD, and SEM, and the results obtained show that small amounts of quartz and P-type zeolites are present in the synthesized products. The mixture was classified as a zeolitic mineral admixture (ZMA). The adsorption performance of ZMA on Pb(II) and Cu(II) in solution was evaluated by batch adsorption experiments. The results showed that ZMA had good adsorption performance for Pb(II) and Cu(II), with maximum adsorption amounts of 372.16 and 53.46 mg/g, respectively. From the investigation, it was concluded that the adsorption process is chemisorption occurring in monomolecular layers and relying on electrostatic adsorption, ion exchange and complexation of hydroxyl groups on the ZMA surface for heavy metal cations. The ZMA reusability result shows that sodium chloride has the ability to regenerate the active site by restoring the ion exchange capacity without significant loss of Pb(II) and Cu(II) adsorption.

Keywords: zeolite-Y; heavy metals; bio-retention system; illite; kinetics

Citation: Shah, K.J.; Yu, J.; Zhang, T.; You, Z. Y-Type Zeolite Synthesized from an Illite Applied for Removal of Pb(II) and Cu(II) Ions from Aqueous Solution: Box-Behnken Design and Kinetics. *Water* **2023**, *15*, 1171. <https://doi.org/10.3390/w15061171>

Academic Editor: Laura Bulgariu

Received: 8 February 2023

Revised: 14 March 2023

Accepted: 15 March 2023

Published: 17 March 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The amount of heavy metal ions in wastewater is increasing rapidly due to the rapid development of the current industrial economy, which threatens the ecological balance and human health [1]. Lead ions (Pb(II)) are toxic and can damage the kidneys, liver, brain function, cellular processes, and the human reproductive system if ingested improperly [2]. Similarly, improper intake of copper ions (Cu(II)) can lead to severe capillary damage, liver and kidney damage, stomach, and intestinal irritation, anemia, etc. [3]. Hence, the removal of metal ions from the aqueous environment has been a popular research area for scientists.

Adsorption [2], membrane filtration [4], ion exchange [5], and electrochemical treatment [6] are currently used for heavy metal removal. Among these, adsorption is widely used due to its high efficiency, easy operation and recoverability [7]. Materials such as biochar [8], nanofibers [9], clay [1], metal organic frameworks [10], powdered marble [11], and activated charcoal [12] can be extensively used as adsorbents. However, adsorbents are expensive, and regeneration of adsorbents, recovery of heavy metals and secondary contamination are also a problem. In this context, zeolites are widely used as adsorbents for heavy metal removal because of their unique properties: low cost, high specific surface area, ion exchange capacity, affinity for heavy metal cations, and excellent heat resistance [13].

Y-type zeolite as a synthetic zeolite has a typical microporous structure (50% pore volume, 7.4 Å pore size, high acidity, etc.) and a three-dimensional channel system. It has a high cation exchange capacity, hydrothermal stability, and adsorption properties,

and has a large specific surface area due to its well-developed pore structure [14]. Y-type zeolite has been shown to be an excellent heavy metal adsorbent [15–17] and can effectively adsorb heavy metal pollutants present in urban stormwater runoff such as lead, copper, cadmium, and chromium. Khalilet et al. [18] used a 3D-printed Y-shaped zeolite adsorption device for the removal of Pb(II) and Cu(II) with an efficiency of more than 90%. Yusof and Malek showed that the adsorption capacity of common Y-type zeolite for Cr(VI) and Cs(II) is low [19], and for the treatment of wastewater containing Cr(VI) and Cs(II) organic modification is needed to enhance the treatment capacity. Y-type zeolite is not limited to heavy metals and has recently been used to remove lanthanides as well [20]. However, the available reported raw materials for the synthesis of Y-zeolites are expensive and the synthesis process is energy-intensive. There is an urgent requirement for a low-energy synthetic method and inexpensive chemical materials for the synthesis of Y-type zeolites. Recently, Kankara clay [21] and Attapuligite clay [22] have been used to synthesize Y-type zeolites.

As a natural clay mineral with abundant reserves, illite contains a large amount of silica and aluminum elements and can be used as a cheap synthetic raw material for Y-type zeolite. Studies have been conducted on the use of illite as a raw material for the synthesis of zeolites [23]. However, such methods require extremely high temperatures for calcination, and the extremely high energy consumption does not correspond to the concept of a green environment. Rayalu et al. [14] used an alkali fusion hydrothermal synthesis method to synthesize zeolite molecular sieves with good crystallinity, which reduced both the reaction time of the overall synthesis and the amount of waste water.

Diatomaceous earth, which contains a large amount of undefined silica, was chosen as an additional source of silica and can be further activated using high temperature calcination to make it easier to precipitate in alkaline environments [24], thus crystallizing with activated illite to form Y-type zeolites.

Currently, illite is only used as an additive in cosmetic, rubber, ceramic and other industries, with no depth of processing, resulting in low value-added products and few applications. The synthesis of Y-type zeolite as a raw material for use in the field of environmental protection can broaden the direction of its development and use, as well as reduce the cost of heavy metal adsorption management.

Therefore, in this study, illite clay was used as a raw material to activate illite and synthesize Y-type zeolite by a solid-phase alkaline fusion method with reduced reaction conditions and a crystal method. The synthesis conditions were systematically optimized using response-surface modeling. The structures of the synthesized Y-type zeolites were characterized by SEM, XRD, and FTIR. Additionally, adsorption kinetics and adsorption isotherm models were used to analyze the adsorption mechanism in adsorption experiments.

2. Materials and Methods

2.1. Materials

The raw material illite was purchased from HebeiYanxi Mineral Products Processing Plant, and diatomite was purchased from Xilong Chemical. The general chemicals HNO_3 , $\text{NaSiO}_3 \cdot 9\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were purchased from Sinopharm Chemical Reagent. 1000 $\mu\text{g}/\text{mL}$ standard solution of Pb(II), Cu(II) is the national standard sample produced by Steel Research Nachem NCS. All chemicals used in the experiments were of analytical grade and used without further purification. All aqueous solutions used for adsorption studies were prepared with deionized water.

2.2. Preparation of Synthetic Y-Type Zeolite from Illite

2.2.1. Pretreatment of Illite Minerals

The illite activation process adopts the process of solid-phase alkali melt pretreatment. In this process, the illite, NaOH and pure water were ground until fully mixed to destroy the original layered silica-alumina molecular structure of illite. The mass ratio of raw materials is R:1:0.3. The homogeneous solid mixture was heated at the temperature T (50–250 °C) by

maintaining air circulation for a certain time t and then crushed into powdery samples to obtain activated illite powder, which was named AAP-T-R-t (alkali activation product).

2.2.2. Synthesis of ZMA-T-R-t from AAP-T-R-t

The Y-type zeolite crystal seed solution was configured according to the method of LotfiSellaoui [25]. In this method, 4.1 g of NaOH, 2.1 g of NaAlO_2 and 20 g of pure water were fully mixed, then 22.7 g of sodium silicate was added and stirred for 10 min and aged at room temperature for 1 day to obtain a Y-type zeolite crystal seed solution. Diatomaceous earth was activated in a muffle furnace at 400 °C for 4 h to obtain heat-treated diatomaceous earth to adjust the elemental silicon content of the intermediate product [24,25].

Figure 1 shows the flow chart of Y-type zeolite synthesis. In this process, 34 g of pure water, 5 g of illite activation product AAP-T-R-t, a certain amount of heat-treated diatomaceous earth and 8 g of crystal seed solution are aged thoroughly at room temperature for 24 h. The homogeneous mixture of solids was then placed in a stainless steel autoclave lined with PTFE and heated to 100 °C for 6 h. The sample was fully crystallized and the mixture was classified as ZMA. Next, the synthesized ZMA pellets were collected, cleaned with pure water and dried at 80 °C for 12 h. The pellets are named as ZMA-T-R-t according to the different activation conditions.

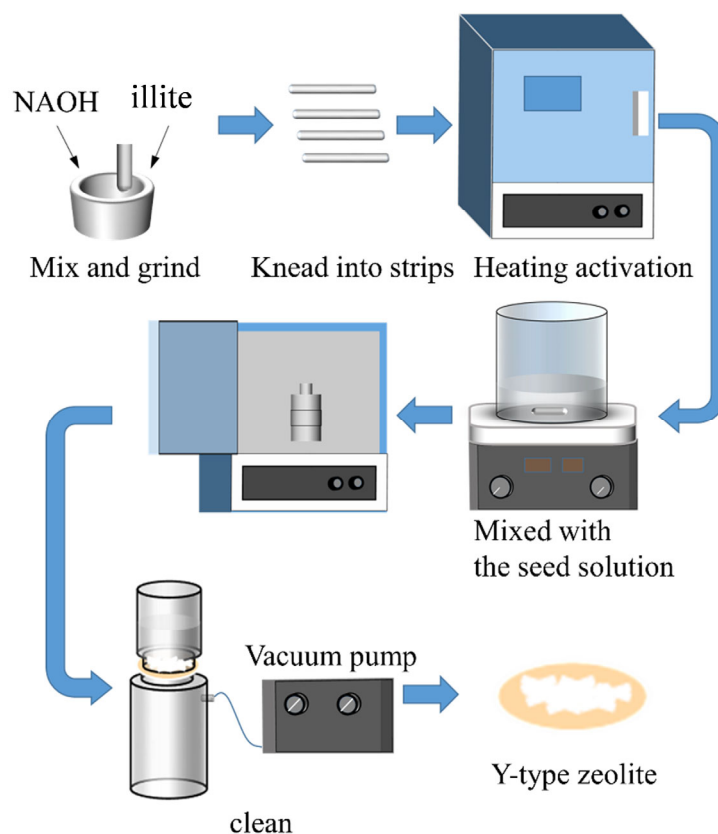


Figure 1. Diagram of synthesis of Y-type zeolite.

2.3. Instrumentation and Techniques

X-ray diffraction (XRD) measurements were performed on a diffractometer (Smart-lab 9kw, Rigaku, Tokyo, Japan), operating at 40 kV and 40 mA with Cu K α radiation ($\lambda = 1.5406$ nm). The surface topography of Zeolite-Y was observed by SEM (Quanta 250 FEG, FEI, Thermo Fisher Scientific, Waltham, MA, USA). The powder sample was placed on the base and Fourier transform infrared spectroscopy (Nicolet iS20, Thermo Scientific) was used to detect the functional surface groups of the sample in the 400–4000 cm. The Pb and Cu content in the solution was determined with a SavantAA atomic absorption spectrometer (SAVANTAAZ, GBC).

2.4. BBD Optimizes the Synthesis Conditions of Y-Type Zeolite

The Box-Behnken design (BBD) is a mathematical statistical method for evaluating the effect of independent variables on response variables, as well as for modeling and process optimization. The method is widely used to optimize the conditions for zeolite synthesis [26,27]. Based on the results of the univariate analysis test, alkaline soil ratio, activation temperature, and activation time were selected as the independent variable factors for analysis of the BBD test with Pb(II) removal rate as response value, and 17 sets of experiments were designed according to the Box-Behnken Design response surface method in Design-Expert 10.0 software.

The calculated input variables of the BBD model and their ranges are summarized in Table 1. According to Table 2, the parameters were alkaline to soil ratio, activation temperature, and activation time, and the rest of the adsorption test conditions were the same. The experimental design matrix with original and coded variables are presented in Table 2. Among them, 12 center point repetitions of the analytical test were conducted five times. A quadratic polynomial was used to describe the relationship between the selected variable factors and the Pb(II) removal rate, and the quadratic polynomial equation is shown in Equation (1).

$$Y(\%) = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i < j} \beta_{ij} X_i X_j \quad (1)$$

Table 1. Coded levels of input variables.

Original Variable	Encoding Variable	Coded Level of Variables		
		−1	0	1
NaOH/illite	A	0.8	1.0	1.2
Temperature (°C)	B	1.0	2.0	3.0
Time (h)	C	1.2	1.4	1.6

Table 2. Box-Behnken experimental design matrix with original and coded variables.

Standard	Coding Variables			Original Variables		
	x ₁	x ₂	x ₃	NaOH/Illite	Temperature (°C)	Time (h)
1	−1	−1	0	0.8	100	2
2	1	−1	0	1.2	100	2
3	−1	1	0	0.8	200	2
4	1	1	0	1.2	200	2
5	−1	0	−1	0.8	150	1
6	1	0	−1	1.2	150	1
7	−1	0	1	0.8	150	3
8	1	0	1	1.2	150	3
9	0	−1	−1	1	100	1
10	0	1	−1	1	200	1
11	0	−1	1	1	100	3
12	0	0	1	1	200	3
13	0	0	0	1	150	2
14	0	0	0	1	150	2
15	0	0	0	1	150	2
16	0	0	0	1	150	2
17	0	0	0	1	150	2

Y is the predicted answer, β_0 is a constant coefficient, β_1 , β_2 , β_3 are linear effects, β_{11} , β_{22} , β_{33} are square effects, β_{12} , β_{13} , β_{23} are interacting effects and ε is the error of prediction equation. The Design-Expert10.0 software was used for data analysis and plotting the diagrams in the BBD method.

The batch experiments designed according to the BBD method were performed in 50 mL conical flasks containing 50 mL Pb(II) (300 mg/L) and 0.05 g adsorbent, then shaken at 25 °C for 180 min. After adsorption, the upper solution was filtered through a 0.45 µm membrane and the Pb(II) concentration in the solution was measured. The removal percentage (R%) of Pb(II) and the equilibrium adsorption capacity (q_e) were determined using the following equations [28], respectively:

$$R\% = \frac{100(C_0 - C_e)}{C_0} \quad (2)$$

where R, C_0 , C_e represent the removal rate of heavy metal ions, the concentration of heavy metal ions in the initial solution (mg/L), and the equilibrium concentration of heavy metal ions (mg/L).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

The equations q_e , m and V represent the mass of heavy metal ions adsorbed per unit mass of adsorbent (mg/g), the amount of adsorbent dosed (g) and the volume of solution (L).

2.5. Adsorption Kinetics and Isotherms

Adsorption experiments were performed in 250 mL conical flasks. Before performing batch experiments, all conical flasks used were soaked in 5% HNO₃ for 24 h to eliminate metal contamination from the glass walls, then washed with ultrapure water and dried in an oven at 60 °C for 12 h. 50 mL of adsorbent containing different metal concentrations and 0.25 g were placed in the bottle. Next, the bottles were shaken at 25 °C and 150 rpm. Simultaneous blank experiments (without adsorbent) was performed.

Kinetics experiments were performed with initial concentrations of the metal ions Pb(II) and Cu(II) of 300 mg/L and 100 mg/L, respectively. Adsorbent concentration of 1g/L; Solution pH is 5. The solutions were collected at the given time intervals (2, 5, 10, 30, 60, 90, 120, 180 min) and filtered through 0.45 µm filter paper for analytical determination. Residual concentrations of liquid phase metals were determined using flame atomic absorption spectrometry.

Metal adsorption isotherms were performed at 15, 25 and 35 °C; Pb(II) initial concentrations of 300, 400, 500, 600, 700 mg/L; The initial concentrations of Cu(II) were 50, 100, 150, 200, 250, 300 mg/L; The adsorption time was 120 min. All other conditions were the same as those used in kinetic experiments.

2.6. Desorption and Reusability of ZMA

In order to study the reusability of ZMA adsorption material, three different eluents, namely pure water, sodium acetate and sodium chloride system, were used to perform an adsorption-desorption cycle. This cycle was performed with Pb(II) adsorption, and the adsorption capacity of each cycle was measured. In each experiment, adsorption experiments were performed as mentioned before with 300 mg/L Pb(II) solution for 120 min and the residual aqueous solution concentration was measured by atomic absorption spectrometry. Then, for the reusability test, the adsorbent was rinsed with pure water and 0.2 M sodium acetate and sodium chloride system. The adsorbent was dried at 80 °C before the next adsorption, and the process was repeated three times.

3. Results and Discussions

3.1. Characterization of the Synthesized Y-Type Zeolite

ZMA has octahedral particles with diameters of 1~4 µm and smooth surfaces, and there is particle aggregation in Figure 2a. These particles have the characteristics of Y-type zeolites [29]. In addition, there is a larger spherical particle composed of nanospheres, which may be a FAU zeolite [30] or a P-type zeolite [31]; a heterocrystal produced during the crystallization process. After solid-phase alkali fusion activation, the illite contains a

large amount of undetermined material and the original lamellar structure of illite is not observed in the activation products (See Figure 2b) [32]. This suggests that low-temperature alkali melt activation can effectively break down the structure of the and convert it into silicates and aluminates, which can be dissolved, causing them to polymerize in solution to form amorphous silica-aluminate gels that crystallize in hydrothermal reactions to form Y-type zeolites [33].

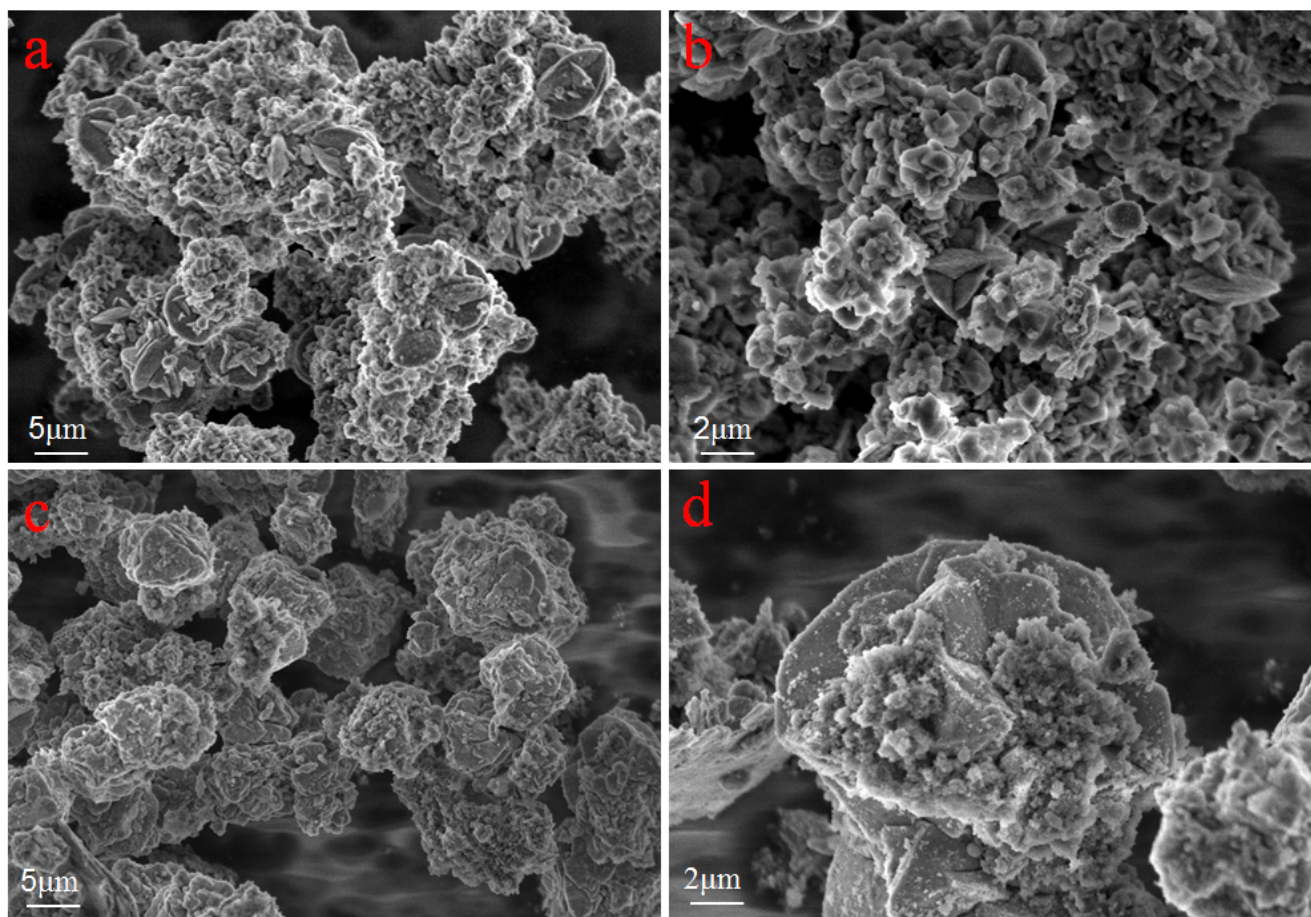


Figure 2. SEM images of (a,b) ZMA and (c,d) alkali activation product.

FTIR analysis of illite and synthesized Y-type zeolite were performed separately as shown in Figure 3. The FTIR spectrum of ZMA with the peak located at 454 cm^{-1} indicates the T-O-T bending vibration (T = Si/Al). The peak at 690 cm^{-1} (743 cm^{-1}) indicates the internal (external) T-O-T (T = Si/Al) symmetric vibration of the synthetic zeolite [34], and the peak at 990 cm^{-1} (1467 cm^{-1}) is the internal (external) T-O-T (T = Si/Al) asymmetric vibration [35–38]. The two peaks located at 672 and 610 cm^{-1} are double-ring vibrations, indicating the presence of zeolites with double-ring structures [39]. The peaks at 1648 and 3475 cm^{-1} are bending and stretching vibrations of the O-H group [40], with the strong and broad peak at 3475 cm^{-1} , while the peak at 1648 cm^{-1} is associated with water molecules adsorbed in the cavity of the molecular sieve [41]. It can be noted that these two peaks, located at 539 and 467 cm^{-1} in the characteristic mapping of illite, do not appear in the mapping of ZMA, which represent the Si-O-Al groups in the clay structure [42]. There was no peak of $781\sim 800\text{ cm}^{-1}$ in ZMA which represents Si-O-Si of quartz [43]. The absence of characteristic peaks of quartz and clay in the final product confirms that illite can be effectively activated by low-temperature solid-phase alkali fusion, and its activator can then be hydrothermally synthesized to produce Y-type zeolite. However, the intensity of the characteristic peak of the synthesized product was not high, indicating the low purity

of the sample. This can be caused by the high adsorption properties of the sample, which easily binds to water in air, or by the limitation of the crystallization time, resulting in incomplete crystallization.

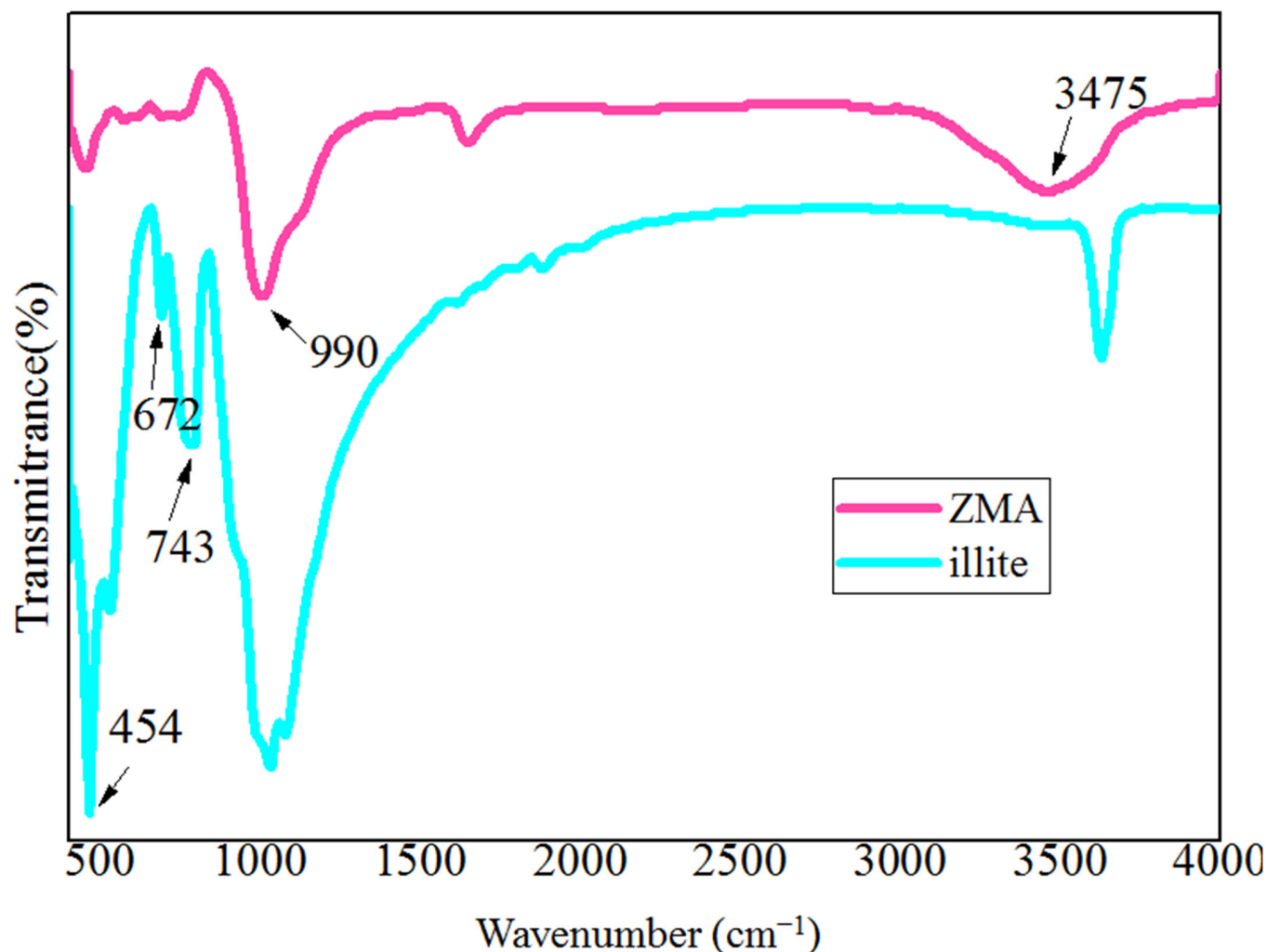


Figure 3. FTIR spectra of the illite and ZMA.

As shown in Figure 4a, the characteristic peaks of illite at $2\theta = 8.84^\circ$, 17.73° , 27.84° , and 39.46° disappear, but the characteristic peaks of quartz at $2\theta = 20.84^\circ$, 26.62° , 36.52° , 50.12° and 59.92° are preserved. This is because the alkali fusion process before the low-temperature solid phase can only destroy part of the molecular structure of illite, but not the quartz contained therein. It indicates that high temperature calcination of illite cannot effectively change the structure of illite, and only high temperature fusion with alkali at 700°C can effectively activate it, but quartz is still present in the activation products, which is consistent with the conclusion of Khalifa et al. [44]. The presence of Y-type zeolite, P-type zeolite and quartz in ZMA is indicated in Figure 4b. The generation of P-type zeolites in ZMA may be related to the hydrothermal crystallization reaction time or temperature, as a reaction time that is too long or not long enough may cause the generation of heterocrystals. A too high temperature may also cause this phenomenon; further research on the crystallization conditions is needed. However, the generation of small amounts of P-type zeolite does not affect the synthesis of Y-type zeolite molecular sieve ZMA, because P-type zeolite is also a molecular sieve which possesses a high ion exchange capacity and can adsorb heavy metals efficiently [45]. From XRD data it can be said that Y-type zeolite is successfully synthesized without the use of additional Al and Si sources other than illite clay.

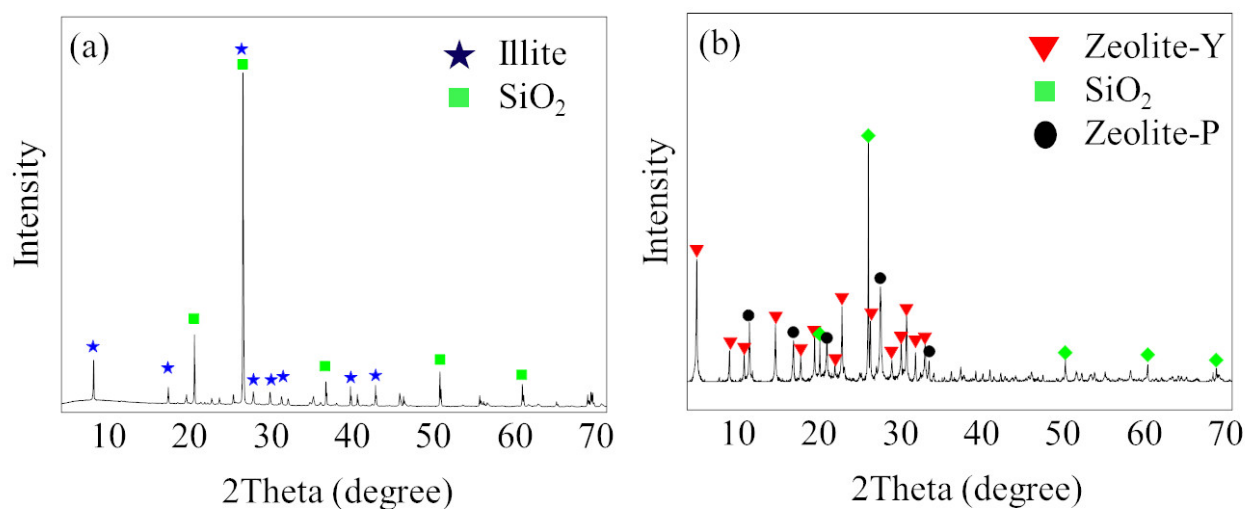


Figure 4. XRD patterns of (a) illite and (b) ZMA including zeolite-Y, Zeolite-P material.

3.2. BBD Experimental Analysis

The results of the statistical analysis obtained by the Box-Behnken design are shown in Table 3. The normal probability plot and the actual vs. predicted control plot are shown in Figure 5, where the experimental values match well with the predicted values and show no significant deviations. The results of the analysis of variance (ANOVA) based on the selected impact factors are shown in Table 4. The results showed that factors A, B, C, A², B² and C² had a significant effect ($p < 0.05$) on the Pb²⁺ adsorption capacity R (%) of the synthesized products. Based on the experimental results, the second-order polynomial obtained by fitting the response values to the regression with the variable factors having significant effects is shown in Equation (4).

$$R(\%) = 85 + 4.75 \times A + 11.38 \times B + 5.38 \times C + 1.25 \times AB^2 + 0.5 \times BC - 3.5A^2 - 5.75B^2 - 2.75C^2 \quad (4)$$

Table 3. Box-Behnken experimental design matrix with original and coded variables and experimental results.

Standard	A	B	C	%R	Standard	A	B	C	%R
1	0.8	100	2	61	10	1	100	1	82
2	1.2	100	2	66	11	1	200	3	70
3	0.8	200	2	83	12	1	150	3	92
4	1.2	200	2	93	13	1	150	2	85
5	0.8	150	1	67	14	1	150	2	85
6	1.2	150	1	78	15	1	150	2	85
7	0.8	150	3	79	16	1	150	2	85
8	1.2	150	3	91	17	1	150	2	85
9	1	100	1	62					

According to Table S1, the correlation coefficient of the model, $R^2 < 0.0001$, indicates that the model is very accurate and the adjusted R^2 values are very close to the predicted R^2 values ($\text{Adj } R^2 - \text{Pred } R^2 < 0.2$), further confirming the applicability of the polynomial model.

Three-dimensional response surfaces plotted as a function of two input parameters are often used to understand the interactions between the independent variables and to determine the best conditions for achieving the highest response values [46]. The 3D response surface plot of this test is shown in Figure 6. As shown in Figure 6a, the removal rate of Pb²⁺ increased with the increase of activation temperature. The highest removal rate was 95.15% at high activation temperature and high NaOH/illite ratio. The Pb²⁺ removal rate decreased significantly with decreasing NaOH/illite ratio and activation

time, but the enhancement of both had only a slight effect on the increased removal rate in Figure 6b. Figure 6c shows that the removal rate of Pb increases with the increase of activation temperature and activation time. The main objective of this statistical study was to maximize the adsorption capacity of the material by optimizing three key variable factors.

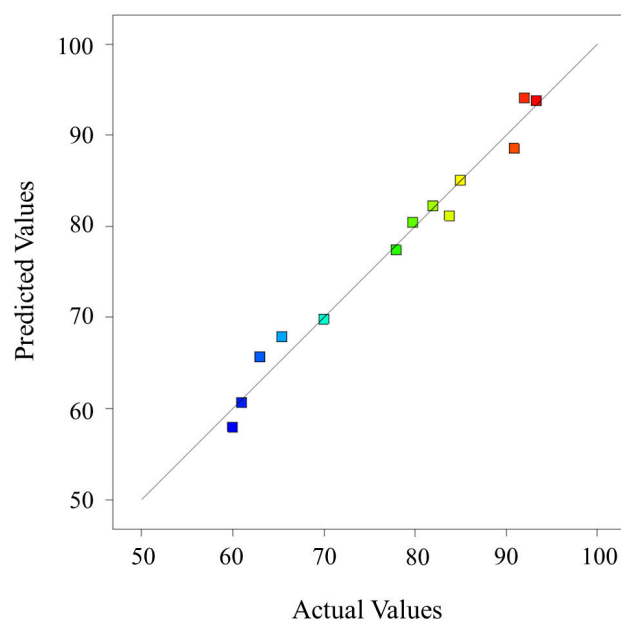


Figure 5. Predicted vs. observed values for adsorption efficiency.

Table 4. Analysis of variance parameter for Pb²⁺ separation.

Source	DF	SS	MS	F-Value	p-Value	Remark
Model	8	1699.38	212.42	82.90	<0.0001	Significant
A-NaOH/illite ratio	1	180.50	180.50	70.44	<0.0001	Significant
B-Activation temperature (°C)	1	1035.13	1035.13	403.95	<0.0001	Significant
C-Activation time (h)	1	231.13	231.13	90.20	<0.0001	Significant
AB	1	6.25	6.25	2.44	0.1570	
BC	1	1.00	1.00	0.39	0.5496	
A ²	1	51.58	51.58	20.13	0.0020	Significant
B ²	1	139.21	139.21	54.33	<0.0001	Significant
C ²	1	31.84	31.84	12.43	0.0078	Significant
Residual	8	20.50	2.56			
Lack of Fit	4	20.50	5.12			
Pure Error	4	0.000	0.000			
Cor Total	16	1719.88				

Note: SS sum of squares, DF degrees of freedom, MS mean sum of squares.

The validation tests were performed under the optimized conditions of response surface. Considering the convenience of the synthesis process, the optimal synthesis conditions were modified, and the modified conditions and experimental results are shown in Table S2. The modified illite activation condition is NaOH/illite (mass ratio) 1.2, the activation temperature is 185 °C, and the activation time is 2.7 h. The zeolite material synthesized from activated illite under these conditions showed a removal rate of 94.5% for Pb, which was very close to the model prediction of 95.15%. It was proved that the illite activation conditions optimized by the response surface model were feasible, and subsequent experiments were conducted using the zeolite material synthesized by activating illite under the adjusted conditions, which was named ZMA.

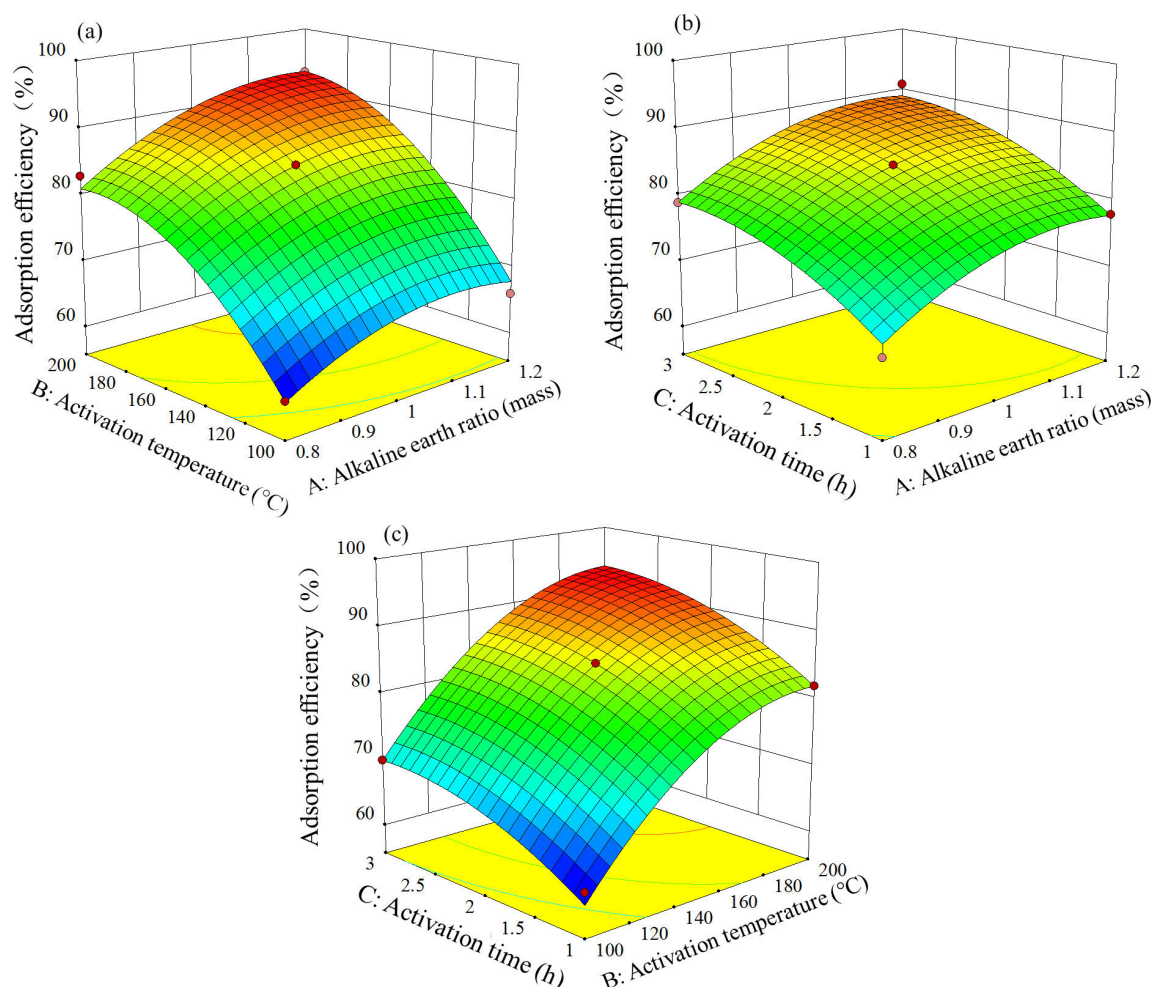


Figure 6. Response surface plots for adsorption efficiency as a function of activation temperature and NaOH/illite ratio (a); activation time and NaOH/illite ratio (b); activation time and activation temperature (c).

3.3. Adsorption Isotherm

To further elucidate the adsorption behavior of ZMA for Pb(II) and Cu(II), experiments according to the isothermal adsorption equations of Langmuir and Freundlich [36] were performed at three different temperatures (15, 25, 35 °C). Isothermal adsorption equations from Langmuir and Freundlich are given in Equations (5) and (6).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (6)$$

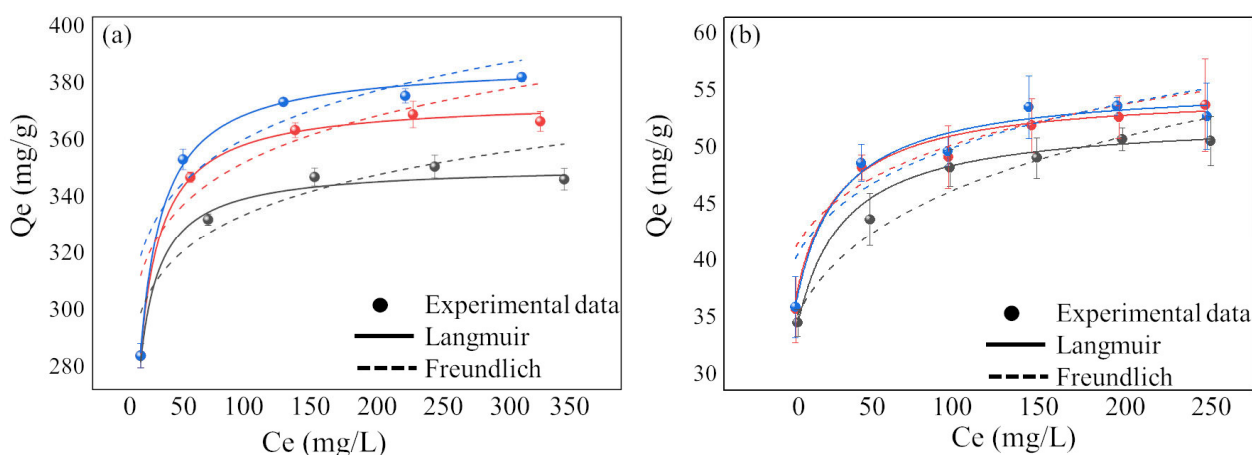
q_m is the maximum adsorption in (mg/g); q_e is the adsorption capacity of the adsorbent at a given moment; C_e is the metal ion concentration at equilibrium (mg/g); and K_L is the Langmuir adsorption equilibrium constant (L/mg). The Freundlich empirical constant (K_F) reflects the adsorption potential, and Freundlich empirical constant ($1/n$) responds to the adsorption strength. These parameters can be obtained from the plot of $\ln(q_e)$ versus $\ln(C_e)$, as shown in Figure 6. Table 5 shows that the Freundlich intensity constant of ZMA is $n > 1$, pointing to good adsorption of Pb^{2+} and Cu^{2+} by ZMA.

Table 5. Isothermal adsorption fitting data of Pb(II) and Cu(II).

T	$q_{e,exp}(mg/g)$	Langmuir			Freundlich				
		$q_{e,cal}(mg/g)$	K_L	R^2	χ^2	K_F	n	R^2	χ^2
Pb(II)									
15 °C	345.69	350.15	0.32	0.9672	0.2388	261.59	18.79	0.7724	1.1985
25 °C	334.95	372.16	0.25	0.9959	0.0299	268.66	17.06	0.6666	2.9341
35 °C	379.83	384.75	0.21	0.9930	0.0446	273.73	16.84	0.6694	3.9399
Cu(II)									
15 °C	49.25	51.17	0.11	0.9907	0.0868	22.27	6.62	0.9674	0.2361
25 °C	52.37	53.47	0.12	0.9698	0.0449	29.90	9.45	0.7947	0.8478
35 °C	52.27	54.14	0.12	0.9387	0.1049	28.40	8.63	0.8438	0.7354

Note: χ^2 is the Chi-Square value.

As shown in Figure 7 and Table 5, the adsorption amounts of Pb(II) and Cu(II) increased almost linearly at low equilibrium concentrations, but leveled off at high equilibrium concentrations. When the initial concentration of Pb(II)(Cu(II)) is higher than about 400 mg/L (100 mg/L), the adsorption amount of the metal increases slowly and approaches the adsorption maximum.

**Figure 7.** Isothermal adsorption fitting curve of Pb(II) (a) and Cu(II) (b) at different temperatures (Blue 35 °C, red 25 °C, gray 15 °C).

The adsorption amount of Pb(II) and Cu(II) by ZMA increased with the increase of temperature and initial concentration, indicating that the adsorption was endothermic. High temperature can improve the adsorption capacity, because as the temperature of the adsorption system increases, the kinetic energy of the cation increases [47]. Comparing the correlation coefficients and Chi-squared (χ^2) of the two models, the Langmuir model correlation coefficients R^2 for Pb(II) and Cu(II) are greater than 0.967 and 0.938, respectively, higher than the Freundlich model, and at the same time χ^2 values are lower than Freundlich model. As the value shown in Table 5 suggests, the lower χ^2 values and the higher R^2 values are best fit for the models. The Langmuir model agrees better with the data from the adsorption tests than the Freundlich model, which implies that the Pb(II) and Cu(II) at ZMA adsorption is mainly monolayer adsorption [48].

The maximum adsorption capacities for Pb(II) and Cu(II) at 15 °C, 25 °C, and 35 °C were calculated by the Langmuir model to be 352.46 mg/g, 371.51 mg/g, and 383.39 mg/g and 48.78 mg/g, 51.91 mg/g, and 53.56 mg/g, respectively, which were consistent with the actual adsorption data, while the Freundlich model could not predict the saturation. The value of Freundlich's empirical constant $1/n < 1$ usually indicates that the adsorption capacity is only slightly suppressed at lower equilibrium concentrations [49], and ZMA is preferable for both Pb(II) and Cu(II) adsorption. Meanwhile, the adsorption amount of

ZMA on Pb(II) was much larger than that on Cu(II), which indicated that the affinity of ZMA for Pb(II) was stronger than that of Cu(II), that is, it was more selective for Pb(II) adsorption.

3.4. The Adsorption Kinetics

The ideal adsorption material should have higher Pb(II) and Cu(II) adsorption capacity. The adsorption capacity was carried out at pH 5 and a concentration of Pb(II) and Cu(II) of 300 mg/L and 100 mg/L, respectively. In both cases, the adsorption of Pb(II) and Cu(II) started rapidly and then saturated at any given time. The adsorption of Pb(II) and Cu(II) is shown in Figure 8, where Pb(II) is more strongly adsorbed compared to Cu(II). This is due to the higher concentration of the solution and the affinity of metal ions to interact with ZMA. The results obtained are in line with previous studies using synthetic mineral to removal of Cd(II) and Pb(II), with lower pH and higher concentration improving the adsorption by enhancing the ion-exchange and followed by precipitation and adsorption [2].

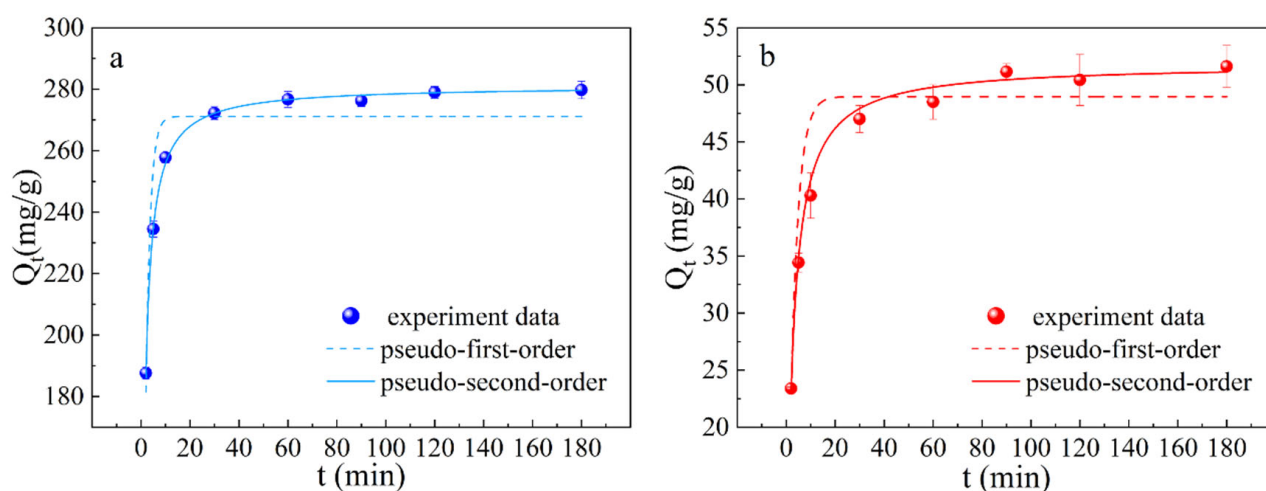


Figure 8. Non-linear fitting of pseudo-1st-order and pseudo-2nd-order for (a) Pb(II) and (b) Cu(II) adsorption by ZMA.

Kinetic analysis is important for understanding the adsorption process and it can demonstrate the adsorption rate as well as the residence time of ions in the adsorption system. In order to be able to elucidate the adsorption behavior of ZMA for Pb(II) and Cu(II), quasi-primary and quasi-secondary kinetic models were used to fit the adsorption data in Figure 7. The quasi-level dynamics and model equations are shown in the Equations (7) and (8).

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

In the above equation, q_t and q_e refer to the mass of Pb(II) or Cu(II) adsorbed per unit mass of adsorbent (mg/g) at a given time and equilibrium state, respectively. k_1 (min^{-1}), k_2 ($\text{g}/\text{mg} \cdot \text{min}$) are the rate constants for the quasi- and quasi-secondary kinetic models, respectively.

As in Figure 8, the maximum time required for equilibrium is 180 min. The adsorption process of ZMA on Pb(II) and Cu(II) is very fast: the removal of lead and copper ions by the ZMA material reached the highest rates of 93.2% and 51.6%, respectively, at 30 min; the adsorption of Pb(II) and Cu(II) by ZMA reached an equilibrium adsorption capacity of 91.43% and 84.00% within the first 10 min. This behavior is related to the well-developed porous structure of synthetic zeolites and the abundance of active sites on the structure which are easily accessible to lead and copper ions to form complexes.

Considering the assumption of the kinetic models, the pseudo first-order is used for reversible reactions in which equilibrium is attained between liquid and solid phases. In the pseudo second-order model, the chemisorption mechanism (electron sharing or

electron transfer between the adsorbent and the adsorbate) controls the adsorption rate. Combining the model parameters in Table 3 with the fit of the kinetic model in Figure 7, the pseudo second-order model with $R^2 > 0.999$ and lower χ^2 values (less than 0.5) is the best model for describing the kinetics of lead and copper ion adsorption. Furthermore, the pseudo-first-order model shows higher χ^2 values, indicating that the experimental values are far from the simulated values, and that the saturation of Pb(II) and Cu(II) does not follow the pseudo-first-order model (see Figure 8). The adsorption process may be controlled by a chemisorption mechanism involving ion exchange or -OH complexation. The adsorption rate of ZMA on heavy metal cations decreases as the adsorption process proceeds, due to the decrease in the number of active sites that can be bound on the ZMA surface as the adsorption proceeds [50].

3.5. Desorption and Reusability of ZMA

Considering the need to economize the adsorption process, it is essential to reuse the adsorbent through a process called desorption and carry out harmless treatment. This experiment attempts to use three eluents to regenerate Pb(II)-loaded ZMA. Sodium chloride and sodium acetate were chosen as the eluents, pure water was used as the blank control group, and the removal amount after the initial adsorption was used as the basis for comparison (100% regeneration efficiency). As shown in Figure 9, sodium acetate has the best regeneration effect after three adsorption-desorption cycles. Compared with sodium chloride, sodium acetate has a better regenerative effect, which is 67.8~89.9% and 66.6~89.9%, respectively. On the other hand, the ineffective regeneration of ZMA by H₂O shows that physical adsorption is not the dominant factor in the process of metal cation adsorption by ZMA. In practical application scenarios, heavy metals adsorbed by ZMA are stable and not easily desorbed. Effective regeneration of ZMA by sodium salt confirmed the presence of ion exchange in the Pb(II) adsorption process.

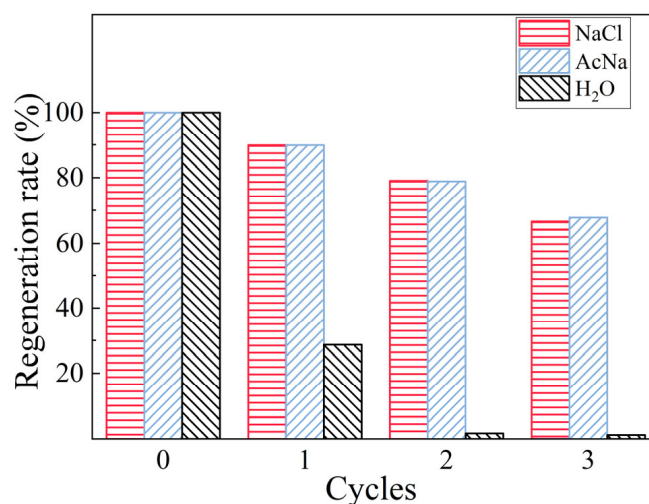
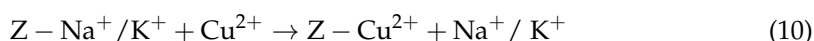
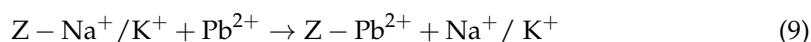


Figure 9. Comparison of three kinds of eluent in three adsorption–desorption cycles of ZMA with Pb(II).

Both eluents caused the regeneration rate of ZMA to decrease with increasing regeneration time, but the regeneration rate was still at least 66.6% after three regeneration times. This is in line with relevant studies on sodium ion-modified zeolite [16], since the adsorption of heavy metal cations by zeolite is mainly due to ion exchange, and the use of high-concentration sodium ion solution can regenerate the active site on the surface of zeolite and restore ion exchange capacity. From this it can be concluded that both sodium acetate and sodium chloride can regenerate ZMA. Since the regeneration efficiency of sodium chloride is slightly lower than that of sodium acetate with increasing regeneration time, sodium acetate is a more suitable eluent for ZMA regeneration.

3.6. Mechanism Analysis

FT-IR characterization results proved that the surface of ZMA is rich in -OH functional groups, as they are prepared from illite. Ion exchange is one of the important properties of illite clay, and hence the ion exchange property is likely to be observed in ZMA surfaces. Basically, heavy metal cations hydrate with water molecules, and the hydration radius is inversely proportional to the cation radius, so Na^+ and K^+ have a small hydration radius to exchange easily with heavy metal ions [51], and the exchange mechanism between ZMA-rich Na^+ and K^+ and heavy metal ions in the adsorption system is shown in Equations (9) and (10).



In addition to ion exchange, the surface reactive groups of ZMA, such as hydroxyl radicals, react with heavy metal cations (Pb(II) and Cu(II)) to form complexes or precipitates, making heavy metals more stable after being adsorbed. These chemical reactions and the ion exchange that takes place within the pore channels within the zeolite are irreversible adsorptions, stronger than electrostatic adsorption, which is a weaker bond. This is one of the main reasons why the ZMA enhances the fixation effect of heavy metals and reduces the risk of migration. This phenomenon is also justified by a reusability study of Pb(II) -adsorbed ZMA, where water shows less regeneration compared to sodium acetate and sodium chloride eluent. This ZMA has potential application in a bio-retention system.

3.7. Comparison of Synthesised ZMA with Other Adsorbents for Pb(II) and Cu(II) Adsorption

Many studies on the applicability of zeolite for removing heavy metals have been published in the last 3 years. The adsorption capacity of various zeolites and zeolite-modified adsorbents is shown in Table 6. The results show that the natural zeolites, Y-type zeolite, P-type zeolite, Mg zeolite, and FAU-type zeolite, have all been used for Cu(II) and Pb(II) removal in the past three years. These data show the importance of this type of study. It can be seen that studies on Y-type zeolite for removing heavy metals are dominant compared to others because of its good adsorption capacity under weak acidic conditions, and also can improve adsorption capacity with organic modifications. At the same time, Y-type zeolite has a higher cation exchange capacity, resulting in enhanced ion exchange to accelerate strong metal removal with higher cationic pollutants. The results show that the adsorbent made from illite in this study has a very high Cu(II) and Pb(II) removal capacity, which is higher than other adsorbents. Being inexpensive and non-toxic, this new adsorbent is not only a potential adsorbent, but also an environmentally friendly material that can be reused and regenerated for multiple uses. Not only can this adsorbent be used in industrial heavy water treatment, but it can also work at a low pH, which is suitable for use as an adsorbent in heavy metal treatment of storm water runoff.

Table 6. Comparison of adsorption capacity of zeolite adsorbent for Cu(II) and Pb(II) adsorption.

Zeolite Type	Modifier	Synthetic Method	Type and Capacity of Heavy Metal Adsorption	Reference
Y-type zeolite	glutamic acid or L-arginine	Hydrothermal method	Cu 105.82 mg/g Pb 83.26 mg/g	[52]
Y-type zeolite	prepared seed gel of sodium aluminate and sodium silicate	Hydrothermal synthesis	Ag 320.91 mg/g Cu 86.32 mg/g Co 124.82 mg/g	[25]
Y-type zeolite	Class C fly ash	Fusion-hydrothermal method	Cu 235 mg/g Ni 170 mg/g	[53]

Table 6. Cont.

Zeolite Type	Modifier	Synthetic Method	Type and Capacity of Heavy Metal Adsorption	Reference
P-type zeolite	Aluminum nitrate nonahydrate and Sodium metasilicate nonahydrate	Facial hydrothermal method	Pb 649 mg/g Cd 210 mg/g Cu 90 mg/g Zn 88 mg/g	[45]
Na-X zeolite	H ₃ PO ₄ modified hydrochar	Hydrothermal carbonization method	Cd 67.01% Cu 57.01% Pb 78.72%	[54]
Mg-Zeolite	Magnesium chloride	Ion-exchange	Pb 99.03 mg/L 99.86% removal	[55]
Chifeng zeolite (Natural-China)	-	Calcination	Pb 75 mg/L (75%) Cu 40 mg/L (40%)	[56]
Natural zeolite	-	-	Pb 6.5 mg/g Cu 2.2 mg/g	[57]
Zeolite	JIS Type-II fly ash	Alkaly hydrothermal treatment	Cd 1.4 mg/g Pb 18.1 mg/g Hg 5.6 mg/g	[58]
Natural zeolite (Indonetian)	HCl acid activation		Pb 71 mg/g Cu 61.56 mg/g	[59]
Natural zeolite	3-Aminopropyltriethoxysilane		Cu 20.66 mg/g Pb 100 mg/g	[60]
FAU-type zeolite	Vermiculite-kaolinite clay	Hydrothermal crystalization	Cu 46.7 mg/g Cd 41.9 mg/g	[61]
FAU-type zeolite	Lithium silica fumes	Hydrothermal treatment	Cu 94.46 mg/g	[62]
Y-type zeolite (present study)	Illite clay	Hydrothermal treatment	Pb 372.1 mg/g Cu 53.46 mg/g	Present study

4. Conclusions

In this study, a Y-type zeolite molecular sieve was successfully synthesized by hydrothermal crystallization using illite as the raw material and low-temperature alkali melt activation. The mathematical model and response surface fitted by the Box-Behnken design test results analysis were able to determine the optimal activation conditions for illite. The optimal activation conditions were sodium hydroxide/illite (mass ratio) of 1.2, activation temperature T of 185 °C, and activation time t of 2.7 h.

The simulation of the adsorption isotherm and the isothermal equation were studied. The adsorption of ZMA was very fast for Pb(II) and Cu(II), and the adsorption equilibrium was reached at about 60 min with the maximum adsorption amounts of 372.16 and 53.46 mg/g for Pb(II) and Cu(II), respectively. In isothermal adsorption experiments, two adsorption isotherm models, Langmuir and Freundlich, were used to fit at three different temperatures. The Langmuir isotherm model and the quasi-secondary kinetic model can describe the adsorption process more precisely. The adsorption process is considered to be mainly chemisorption occurring in monomolecular layers, relying on electrostatic adsorption, ion exchange, and complexation of hydroxyl groups on the ZMA surface for heavy metal cations.

In a future study, this material will be used in a bioretention system to remove effluent heavy metals in further studies to specifically identify the binding sites for zeolite and the structural property relationships.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15061171/s1>, Table S1: Summary of quadratic model; Table S2: The experimental results are verified under optimized conditions; Table S3: Parameters of kinetic models predicting the experimental data for Pb(II) and Cu(II).

Author Contributions: First author K.J.S. participated in the research as principal investigator (PI), organized the data and wrote the manuscript, J.Y. experiments carried out, data maintenance, analyzes carried out and participation in technical discussions and the design methodology; T.Z. designed the experiments and wrote the first draft; Z.Y. Performed visualization, supervised the project and review the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available in article and supportive materials.

Acknowledgments: K.J.S. would like to thank NJTech University for providing startup funding for this research.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Chen, G.; Shah, K.J.; Shi, L.; Chiang, P.-C.; You, Z. Red Soil Amelioration and Heavy Metal Immobilization by a Multi-Element Mineral Amendment: Performance and Mechanisms. *Environ. Pollut.* **2019**, *254*, 112964. [\[CrossRef\]](#) [\[PubMed\]](#)
- Chen, G.; Shah, K.J.; Shi, L.; Chiang, P.-C. Removal of Cd (II) and Pb (II) Ions from Aqueous Solutions by Synthetic Mineral Adsorbent: Performance and Mechanisms. *Appl. Surf. Sci.* **2017**, *409*, 296–305. [\[CrossRef\]](#)
- Pawar, R.R.; Lalhmunsiam; Bajaj, H.C.; Lee, S.M. Activated Bentonite as a Low-Cost Adsorbent for the Removal of Cu(II) and Pb(II) from Aqueous Solutions: Batch and Column Studies. *J. Ind. Eng. Chem.* **2016**, *34*, 213–223. [\[CrossRef\]](#)
- Ates, N.; Uzal, N. Removal of Heavy Metals from Aluminum Anodic Oxidation Wastewaters by Membrane Filtration. *Environ. Sci. Pollut. Res.* **2018**, *25*, 22259–22272. [\[CrossRef\]](#) [\[PubMed\]](#)
- Hussain, S.T.; Khaleefa Ali, S.A. Removal of Heavy Metal by Ion Exchange Using Bentonite Clay. *J. Ecol. Eng.* **2020**, *22*, 104–111. [\[CrossRef\]](#)
- Wang, Z.; Tan, Z.; Li, H.; Yuan, S.; Zhang, Y.; Dong, Y. Direct Current Electrochemical Method for Removal and Recovery of Heavy Metals from Water Using Straw Biochar Electrode. *J. Clean. Prod.* **2022**, *339*, 130746. [\[CrossRef\]](#)
- Zhang, L.; Li, W.; Cao, H.; Hu, D.; Chen, X.; Guan, Y.; Tang, J.; Gao, H. Ultra-Efficient Sorption of Cu²⁺ and Pb²⁺ Ions by Light Biochar Derived from Medulla Tetrapanacis. *Bioresour. Technol.* **2019**, *291*, 121818. [\[CrossRef\]](#)
- Gholami, L.; Rahimi, G. The Efficiency of Potato Peel Biochar for the Adsorption and Immobilization of Heavy Metals in Contaminated Soil. *Int. J. Phytoremed.* **2023**, *25*, 263–273. [\[CrossRef\]](#)
- Xiong, W.; Tong, J.; Yang, Z.; Zeng, G.; Zhou, Y.; Wang, D.; Song, P.; Xu, R.; Zhang, C.; Cheng, M. Adsorption of Phosphate from Aqueous Solution Using Iron-Zirconium Modified Activated Carbon Nanofiber: Performance and Mechanism. *J. Colloid Interface Sci.* **2017**, *493*, 17–23. [\[CrossRef\]](#)
- Gul Zaman, H.; Baloo, L.; Kutty, S.R.; Aziz, K.; Altaf, M.; Ashraf, A.; Aziz, F. Insight into Microwave-Assisted Synthesis of the Chitosan-MOF Composite: Pb(II) Adsorption. *Environ. Sci. Pollut. Res.* **2023**, *30*, 6216–6233. [\[CrossRef\]](#)
- Boujelben, R.; Ellouze, M.; Aziz, F.; Ouazzani, N.; Sayadi, S. Box-Behnken Approach for Optimization of Cr(III) Removal from a Real Tanning Effluent Using Powdered Marble. *Int. J. Environ. Sci. Technol.* **2022**, *19*, 4305–4320. [\[CrossRef\]](#)
- Zhang, Y.; Yan, X.; Yan, Y.; Chen, D.; Huang, L.; Zhang, J.; Ke, Y.; Tan, S. The Utilization of a Three-Dimensional Reduced Graphene Oxide and Montmorillonite Composite Aerogel as a Multifunctional Agent for Wastewater Treatment. *RSC Adv.* **2018**, *8*, 4239–4248. [\[CrossRef\]](#)
- Lehman, S.E.; Larsen, S.C. Zeolite and Mesoporous Silica Nanomaterials: Greener Syntheses, Environmental Applications and Biological Toxicity. *Environ. Sci. Nano* **2014**, *1*, 200–213. [\[CrossRef\]](#)
- Rayalu, S.; Meshram, S.U.; Hasan, M.Z. Highly Crystalline Faujasitic Zeolites from Flyash. *J. Hazard. Mater.* **2000**, *77*, 123–131. [\[CrossRef\]](#)
- Keane, M.A. The Removal of Copper and Nickel from Aqueous Solution Using Y Zeolite Ion Exchangers. *Colloids Surfaces A Physicochem. Eng. Asp.* **1998**, *138*, 11–20. [\[CrossRef\]](#)
- Ahmed, S.; Chughtai, S.; Keane, M.A. The Removal of Cadmium and Lead from Aqueous Solution by Ion Exchange with Na-Y Zeolite. *Sep. Purif. Technol.* **1998**, *13*, 57–64. [\[CrossRef\]](#)
- Kim, J.S.; Keane, M.A. Ion Exchange of Divalent Cobalt and Iron with Na-Y Zeolite: Binary and Ternary Exchange Equilibria. *J. Colloid Interface Sci.* **2000**, *232*, 126–132. [\[CrossRef\]](#)
- Khalil, A.; Hashaikh, R.; Hilal, N. 3D Printed Zeolite-Y for Removing Heavy Metals from Water. *J. Water Process Eng.* **2021**, *42*, 102187. [\[CrossRef\]](#)
- Yusof, A.M.; Malek, N.A.N.N. Removal of Cr(VI) and As(V) from Aqueous Solutions by HDTMA-Modified Zeolite Y. *J. Hazard. Mater.* **2009**, *162*, 1019–1024. [\[CrossRef\]](#)
- Pikus, S.; Zienkiewicz-Strzałka, M.; Skibińska, M. Synthesis of New Mesostructured Cellular Foams (MCFs) with NaY Zeolite and Their Application to Sorption of Thorium Ions. *Mater. Sci. Pol.* **2019**, *37*, 488–495. [\[CrossRef\]](#)
- Agbendeh, Z.M.; Gimba, C.E.; Ande, S.; Ekanem, S.F. Synthesis and Characterization of Zeolite Y From Kankara Clay Using Alkaline Fusion Method. *J. Chem. Soc. Niger.* **2021**, *46*, 1016–1031. [\[CrossRef\]](#)

22. Li, X.Y.; Jiang, Y.; Liu, X.Q.; Shi, L.Y.; Zhang, D.Y.; Sun, L.B. Direct Synthesis of Zeolites from a Natural Clay, Attapulgitic. *ACS Sustain. Chem. Eng.* **2017**, *5*, 6124–6130. [\[CrossRef\]](#)
23. Li, X.; Han, S.; Guan, D.; Jiang, N.; Xu, J.; Park, S.E. Rapid Direct Synthesis of Nano-H-ZSM-5 from Leached Illite via Solid-like-State Conversion-Based Crystallization. *Appl. Clay Sci.* **2021**, *203*, 106028. [\[CrossRef\]](#)
24. Yue, Y.; Kang, Y.; Bai, Y.; Gu, L.; Liu, H.; Bao, J.; Wang, T.; Yuan, P.; Zhu, H.; Bai, Z.; et al. Seed-Assisted, Template-Free Synthesis of ZSM-5 Zeolite from Natural Aluminosilicate Minerals. *Appl. Clay Sci.* **2018**, *158*, 177–185. [\[CrossRef\]](#)
25. Sellaoui, L.; Hessou, E.P.; Badawi, M.; Netto, M.S.; Dotto, G.L.; Silva, L.F.O.; Tielens, F.; Ifthikar, J.; Bonilla-Petriciolet, A.; Chen, Z. Trapping of Ag⁺, Cu²⁺, and Co²⁺ by Faujasite Zeolite Y: New Interpretations of the Adsorption Mechanism via DFT and Statistical Modeling Investigation. *Chem. Eng. J.* **2021**, *420*, 127712. [\[CrossRef\]](#)
26. Pinheiro, D.R.; Neves, R.d.F.; Paz, S.P.A. A Sequential Box-Behnken Design (BBD) and Response Surface Methodology (RSM) to Optimize SAPO-34 Synthesis from Kaolin Waste. *Microporous Mesoporous Mater.* **2021**, *323*, 111250. [\[CrossRef\]](#)
27. Sivalingam, S.; Sen, S. Optimization of Synthesis Parameters and Characterization of Coal Fly Ash Derived Microporous Zeolite X. *Appl. Surf. Sci.* **2018**, *455*, 903–910. [\[CrossRef\]](#)
28. Chang, Y.C.; Chen, D.H. Preparation and Adsorption Properties of Monodisperse Chitosan-Bound Fe₃O₄ Magnetic Nanoparticles for Removal of Cu(II) Ions. *J. Colloid Interface Sci.* **2005**, *283*, 446–451. [\[CrossRef\]](#)
29. Sun, Z.; Song, H.; Xing, Y.; Li, J.; Lu, Y.; Wang, J. Simulation of rainwater infiltration and heavy metal pollutant migration in permeable brick pavement system in sponge City. *Environ. Eng.* **2020**, *38*, 46–52+100.
30. Wang, H. Migration and Transformation of Dissolved Organic Matter and Heavy Metals in Runoff Rainwater in LID Facilities. Master's Thesis, Beijing University of Architecture, Beijing, China, 2019; p. 78.
31. Yang, K.; Li, Y.; Guo, H.; Liu, X.; Chen, X.; Cao, J. Rapid Synthesis of Zeolite P from Potassic Rocks by Gel-like-Solid Phase Method. *Asia-Pacific J. Chem. Eng.* **2021**, *16*, e2641. [\[CrossRef\]](#)
32. Belviso, C.; Cavalcante, F.; Niceforo, G.; Lettino, A. Sodalite, Faujasite and A-Type Zeolite from 2:1 dioctahedral and 2:1:1 Trioctahedral Clay Minerals. A Singular Review of Synthesis Methods through Laboratory Trials at a Low Incubation Temperature. *Powder Technol.* **2017**, *320*, 483–497. [\[CrossRef\]](#)
33. Belviso, C.; Giannossa, L.C.; Huertas, F.J.; Lettino, A.; Mangone, A.; Fiore, S. Synthesis of Zeolites at Low Temperatures in Fly Ash-Kaolinite Mixtures. *MicroporMesopor Mat.* **2015**, *212*, 35–47. [\[CrossRef\]](#)
34. Cai, X.; Yu, X.; Yu, X.; Wu, Z.; Li, S.; Yu, C. Synthesis of Illite/Iron Nanoparticles and Their Application as an Adsorbent of Lead Ions. *Environ. Sci. Pollut. Res.* **2019**, *26*, 29449–29459. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Nezamzadeh-Ejhi, A.; Kabiri-Samani, M. Effective Removal of Ni(II) from Aqueous Solutions by Modification of Nano Particles of Clinoptilolite with Dimethylglyoxime. *J. Hazard. Mater.* **2013**, *260*, 339–349. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Caballero, I.; Colina, F.G.; Costa, J. Synthesis of X-Type Zeolite from Dealuminated Kaolin by Reaction with Sulfuric Acid at High Temperature. *Ind. Eng. Chem. Res.* **2007**, *46*, 1029–1038. [\[CrossRef\]](#)
37. Aly, H.M.; Moustafa, M.E.; Abdelrahman, E.A. Synthesis of Mordenite Zeolite in Absence of Organic Template. *Adv. Powder Technol.* **2012**, *23*, 757–760. [\[CrossRef\]](#)
38. Abdelrahman, E.A.; Tolan, D.A.; Nassar, M.Y. A Tunable Template-Assisted Hydrothermal Synthesis of Hydroxysodalite Zeolite Nanoparticles Using Various Aliphatic Organic Acids for the Removal of Zinc(II) Ions from Aqueous Media. *J. Inorg. Organomet. Polym. Mater.* **2019**, *29*, 229–247. [\[CrossRef\]](#)
39. Dos Santos, M.B.; Vianna, K.C.; Pastore, H.O.; Andrade, H.M.C.; Mascarenhas, A.J.S. Studies on the Synthesis of ZSM-5 by Interzeolite Transformation from Zeolite Y without Using Organic Structure Directing Agents. *Microporous Mesoporous Mater.* **2020**, *306*, 110413. [\[CrossRef\]](#)
40. Shariatnia, Z.; Bagherpour, A. Synthesis of Zeolite NaY and Its Nanocomposites with Chitosan as Adsorbents for Lead(II) Removal from Aqueous Solution. *Powder Technol.* **2018**, *338*, 744–763. [\[CrossRef\]](#)
41. Doan, T.; Nguyen, K.; Dam, P.; Vuong, T.H.; Le, M.T.; Thanh, H.P. Synthesis of SAPO-34 Using Different Combinations of Organic Structure-Directing Agents. *J. Chem.* **2019**, *2019*, 6197527. [\[CrossRef\]](#)
42. Shah, K.J.; Mishra, M.K.; Shukla, A.D.; Imae, T.; Shah, D.O. Controlling Wettability and Hydrophobicity of Organoclays Modified with Quaternary Ammonium Surfactants. *J. Colloid Interface Sci.* **2013**, *407*, 493–499. [\[CrossRef\]](#)
43. Mezni, M.; Hamzaoui, A.; Hamdi, N.; Srasra, E. Synthesis of Zeolites from the Low-Grade Tunisian Natural Illite by Two Different Methods. *Appl. Clay Sci.* **2011**, *52*, 209–218. [\[CrossRef\]](#)
44. Khalifa, A.Z.; Pontikes, Y.; Elsen, J.; Cizer, Ö. Comparing the Reactivity of Different Natural Clays under Thermal and Alkali Activation. *RILEM Tech. Lett.* **2019**, *4*, 74–80. [\[CrossRef\]](#)
45. Chen, M.; Nong, S.; Zhao, Y.; Riaz, M.S.; Xiao, Y.; Molokeev, M.S.; Huang, F. Renewable P-Type Zeolite for Superior Absorption of Heavy Metals: Isotherms, Kinetics, and Mechanism. *Sci. Total Environ.* **2020**, *726*, 138535. [\[CrossRef\]](#)
46. Gupta, V.K.; Fakhri, A.; Rashidi, S.; Ibrahim, A.A.; Asif, M.; Agarwal, S. Optimization of Toxic Biological Compound Adsorption from Aqueous Solution onto Silicon and Silicon Carbide Nanoparticles through Response Surface Methodology. *Mater. Sci. Eng. C* **2017**, *77*, 1128–1134. [\[CrossRef\]](#)
47. Li, Y.; Bai, P.; Yan, Y.; Yan, W.; Shi, W.; Xu, R. Removal of Zn²⁺, Pb²⁺, Cd²⁺, and Cu²⁺ from Aqueous Solution by Synthetic Clinoptilolite. *Microporous Mesoporous Mater.* **2019**, *273*, 203–211. [\[CrossRef\]](#)
48. El-Mekkawi, D.M.; Selim, M.M. Removal of Pb²⁺ from Water by Using Na-Y Zeolites Prepared from Egyptian Kaolins Collected from Different Sources. *J. Environ. Chem. Eng.* **2014**, *2*, 723–730. [\[CrossRef\]](#)

49. Nibou, D.; Mekatel, H.; Amokrane, S.; Barkat, M.; Trari, M. Adsorption of Zn^{2+} Ions onto NaA and NaX Zeolites: Kinetic, Equilibrium and Thermodynamic Studies. *J. Hazard. Mater.* **2010**, *173*, 637–646. [\[CrossRef\]](#)
50. Apiratikul, R.; Pavasant, P. Sorption of Cu^{2+} , Cd^{2+} , and Pb^{2+} Using Modified Zeolite from Coal Fly Ash. *Chem. Eng. J.* **2008**, *144*, 245–258. [\[CrossRef\]](#)
51. Han, S.; Liu, Y.; Yin, C.; Jiang, N. Fast Synthesis of Submicron ZSM-5 Zeolite from Leached Illite Clay Using a Seed-Assisted Method. *Microporous Mesoporous Mater.* **2019**, *275*, 223–228. [\[CrossRef\]](#)
52. Abdelrahman, E.A.; Alharbi, A.; Subaihi, A.; Hameed, A.M.; Almutairi, M.A.; Algethami, F.K.; Youssef, H.M. Facile Fabrication of Novel Analcime/Sodium Aluminum Silicate Hydrate and Zeolite Y/Faujasite Mesoporous Nanocomposites for Efficient Removal of $Cu(II)$ and $Pb(II)$ Ions from Aqueous Media. *J. Mater. Res. Technol.* **2020**, *9*, 7900–7914. [\[CrossRef\]](#)
53. Liu, Y.; Wang, G.; Luo, Q.; Li, X.; Wang, Z. The Thermodynamics and Kinetics for the Removal of Copper and Nickel Ions by the Zeolite y Synthesized from Fly Ash. *Mater. Res. Express* **2019**, *6*, 025001. [\[CrossRef\]](#)
54. Ge, Q.; Tian, Q.; Hou, R.; Wang, S. Combing Phosphorus-Modified Hydrochar and Zeolite Prepared from Coal Gangue for Highly Effective Immobilization of Heavy Metals in Coal-Mining Contaminated Soil. *Chemosphere* **2022**, *291*, 132835. [\[CrossRef\]](#) [\[PubMed\]](#)
55. Wang, J.-P.; Kim, G.-C.; Go, M.-S. A Study on the Removal of Heavy Metal with Mg-Modified Zeolite. *J. Korean Powder Metall. Inst.* **2020**, *27*, 287–292. [\[CrossRef\]](#)
56. Chen, X.; Tao, J.; Sun, P.; Yu, F.; Li, B.; Dun, L. Effect of Calcination on the Adsorption of Chifeng Zeolite on Pb^{2+} and Cu^{2+} . *Int. J. Low-Carbon Technol.* **2022**, *17*, 462–468. [\[CrossRef\]](#)
57. Elboughdiri, N. The Use of Natural Zeolite to Remove Heavy Metals $Cu(II)$, $Pb(II)$ and $Cd(II)$, from Industrial Wastewater. *Cogent Eng.* **2020**, *7*, 1782623. [\[CrossRef\]](#)
58. Kobayashi, Y.; Ogata, F.; Nakamura, T.; Kawasaki, N. Synthesis of Novel Zeolites Produced from Fly Ash by Hydrothermal Treatment in Alkaline Solution and Its Evaluation as an Adsorbent for Heavy Metal Removal. *J. Environ. Chem. Eng.* **2020**, *8*, 103687. [\[CrossRef\]](#)
59. Yulianti, E.; Abdullah; Yusniyyah, S.I.; Aini, N.; Khalifah, S.N.; Istighfarini, V.N. Removal of Cu and Pb from Wastewater Using Modified Natural Zeolite. *Proc. Int. Conf. Eng. Technol. Soc. Sci.* **2021**, *529*, 363–369. [\[CrossRef\]](#)
60. Shirendev, N.; Bat-Amgalan, M.; Kano, N.; Kim, H.J.; Gunchin, B.; Ganbat, B.; Yunden, G. A Natural Zeolite Developed with 3-Aminopropyltriethoxysilane and Adsorption of $Cu(II)$ from Aqueous Media. *Appl. Sci.* **2022**, *12*, 11344. [\[CrossRef\]](#)
61. Joseph, I.V.; Tosheva, L.; Miller, G.; Doyle, A.M. Fau—Type Zeolite Synthesis from Clays and Its Use for the Simultaneous Adsorption of Five Divalent Metals from Aqueous Solutions. *Materials* **2021**, *14*, 3738. [\[CrossRef\]](#)
62. Chen, Y.; Armutlulu, A.; Sun, W.; Jiang, W.; Jiang, X.; Lai, B.; Xie, R. Ultrafast Removal of $Cu(II)$ by a Novel Hierarchically Structured Faujasite-Type Zeolite Fabricated from Lithium Silica Fume. *Sci. Total Environ.* **2020**, *714*, 136724. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.