

Preparation of Zeolites from Coal Fly Ash and Their Application in Remediation Heavy Metals Contaminated Soils

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ABSTRACT

This study presents experimental results transacting with the potential of transforming coal fly ash to zeolitic materials to be applied as a cheap immobilizer for heavy metals in contaminated soils. Coal fly ash (CFA) was used to prepare synthetic zeolites by alkaline fusion prior the hydrothermal treatment as a function of the ratio of CFA to NaOH (1:1.4, 1:1.8) and (activation and crystallization) temperature 60 °C and 95 °C, four samples of synthesized zeolites were formed and characterized using various techniques such as X-ray diffraction XRD, scanning electron microscopy-energy dispersive X-ray SEM-EDX and BET method. The results showed increase the crystallinity of the obtained zeolites with increasing mass ratio of CFA/NaOH and increasing the crystallization temperature from 60 °C to 95 °C. The formed zeolites contained different crystalline phases of sodalite (SOD), Zeolite-A (LTA), cancrinite (CAN), and analcime (ANA), sodalite was the predominant crystalline phase in all samples where its highest content was in sample IV (84%) which synthesize with a CFA/NaOH mass ratio of 1:1.8 and a crystallization temperature of 95 °C. The results showed that the sample I was synthesized at 1:1.4 ratio of CFA/NaOH and a temperature of crystallization 60 °C has the highest value of specific surface area (S_{BET}). The surface areas of the mesopores form the major part of the total specific surface area in samples III and IV. The synthesized zeolite samples were used to study their immobilization efficiency for Cu and Pb in the soil. It was noticed that increase the application rate of the synthesized zeolite in soil, improved their effectiveness to immobilize Cu and Pb. Applying 1% synthetic sample IV treatment was significantly the most effective in lowering the DTPA extracted Cu and Pb with maximal immobilization efficiencies (E %) 39.55% and 78.37 % respectively.

Keywords: Alkaline fusion, coal fly ash, contaminated soils, heavy metals, synthetic zeolites.

INTRODUCTION

Zeolites are group of microporous, three-dimensional aluminosilicates framework minerals having SiO_4 with AlO_4^- tetrahedrons, joined simultaneously with close tetrahedrons which take part oxygen to consistence characteristic crystalline frameworks, having large void cavities and channels that have the ability to retent cations (Belviso 2018). Each substitution of SiO_4 by AlO_4^- , generates more

negative charges on the framework which is stabilized by ions that bearing positive charges such as K^+ , Na^+ , Mg^{2+} and Ca^{2+} , so that zeolites had a high cation exchange capacity (Grismer & Collison, 2017 and Wasielewski *et al.*, 2018). Recently it is found an imperious and outstanding necessity to promote the generation of new and eco-materials from byproducts, to reduce environmental threats (Koshlak, 2023). From these waste materials, coal fly ash which is a cheap and plentiful byproduct, rich in minerals having silicon and aluminum, keeping it suitable as a raw material for the preparation of zeolites. Therefore, intense overworks have been done to enhance the transformation of fly ash to zeolite materials (Zhang *et al.*, 2022). Coal ash has a main role on account of its large quantities and the sequels due to rising cumulation, about 750 million tons of fly ash are globally generated every year (Choudhary *et al.*, 2022).

Several techniques are used for the preparation of zeolites from coal flying ash: the traditional direct hydrothermal treatment (Längauer *et al.*, 2021), the hydrothermal treatment by microwave waves (Nasser *et al.*, 2019), the fusion hydrothermal procedure (Park *et al.*, 2020), and ultrasonic irradiation (Aldahri, 2019). A lot of researchers announce that the preparation of zeolites through alkaline fusion has a high effectiveness, since this method has characteristic reaction rate (Jha and Singh, 2016), and high pure prepared product (Visa and Chelaru, 2014). That is assured by the verity that in alkaline melting, the solubility of the crystalline structures rises significantly and most phases that having Si and Al are transformed to Na-silicate and Na-aluminate (Zhang *et al.*, 2022).

The synthesized zeolites by alkaline fusion of fly ash are aluminum-silicates and the method conditions like, hydroxide concentration, ratio of SiO_2/Al_2O_3 , curing time, activation and crystallization temperature, pH and the solid/liquid ratio greatly affect the composition and characteristic of formed products. divergence limits in these parameters are just expansive: the ratio of SiO_2/Al_2O_3 range from 2 to 6, (Na or K) concentration hydroxide from 1 M to 5 M, reaction time of 4–48 hours, hydrothermal temperature ranged from 80 to 150 °C, and solid/liquid ratio which are 1/1-1/4 (Izquierdo & Querol, 2001 and Criado *et al.*, 2007).

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Soil contamination with heavy metals has been increased in recent years, as a result of industrial developments and enlarged application of resources containing heavy metals. In-situ immobilization technique is the most superfine in-situ remediation access for treatment of heavy metals polluted soils by using soil treatments such as zeolite, carbonates, limes, cements, and phosphates, as it is an inexpensive, simple in application, as well as eco-friendly technique for lowering the bioavailability of metals and their mobility by different mechanisms as cation exchange, sorption, co-precipitation, and/or complexation (Palansooriya *et al.*, 2020). There has been great interest in the immobilization of heavy metals applying synthesized zeolite since they have high simplicity, selectivity, economy and reusability (Koshlak, 2023).

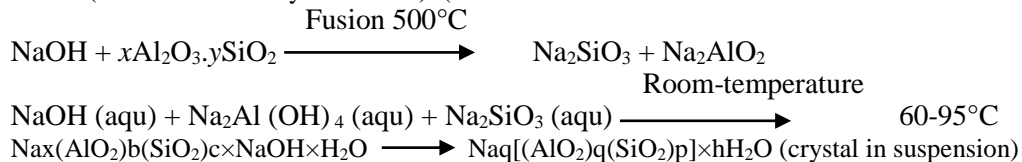
The presented work aims to investigate the potential synthesis of zeolites by using coal fly ash (CFA) as raw material through a method does not demand application under hard conditions with minimum time and less financial costs, and investigate the effect of the synthesis parameters on the type of products as well as investigate their efficiency to immobilize copper and lead in the contaminated soils.

MATERIAL AND METHODS

Coal fly ash (CFA), the raw material used in this work was collected from ovens where CFA is a result of hard coal burning, the obtained CFA was sieved down to less than 70 μm in diameter and was submitted to analyses (powder X-ray diffraction (XRD), X-ray fluorescence (XRF), by using Bruker, D2 Phaser 2nd gen. SEM- EDX, energy dispersive X-ray on a FEI Quanta FEG 250 and BET method for N_2 adsorption, using BELSORP-mini X instrument to measure the specific surface area, by with these analyses, the basic information about the raw material was obtained. The chemical composition of CFA as results of XRF analysis is illustrated in Table (1). The fly ash sample used was of 'Class F' type according to ASTM (2019) with three main components silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) and the molar ratio Si/Al was approximately 2.48.

Zeolites preparation

Zeolites were prepared from CFA and NaOH, through alkaline fusion method prior hydrothermal treatment (activation and crystallization) (Javadian *et al.*



al., 2015), synthesis of zeolites were investigated as function of the ratio CFA to NaOH, and hydrothermal temperature. Zeolites preparation was carried out according to Koshlak (2023). Where CFA and NaOH were mixed with at different ratios of CFA/NaOH at 1:1.4 and 1:1.8 and melted for 1 h at 500°C in themal muffle furnace, after completing alkaline fusion, the resulted mixture was grinded then suitable quantities of deionized water was added to maintain NaOH concentration to 3 M then stirred and shake in water bath under 60 and 95°C for 12 hours and then keep stable for crystallization for 6 h at the same temperatures of activation (60 and 95°C).

Table 1. The chemical composition of CFA as results of XRF analysis

Main constituents	Coal fly ash (wt. %)
SiO_2	37.93
Al_2O_3	15.31
Fe_2O_3	8.64
CaO	2.03
MgO	3.06
Na_2O	0.88
K_2O	0.19
TiO_2	0.08
P_2O_3	0.04
MnO	0.16
SO_3	8.23
Cl	0.01
LOI	0.69
Free CaO	0.75
Si/Al ratio	2.48
pH (1:20) t = 20	12.96
Surface area (m^2/g)	3.079

LOI = loss on ignition

After the reaction complete, the products were washed several times with deionized water to keep the pH reaches 9. The residues were dried in an oven at a temperature of 105°C for 24 h. then the samples were characterized. Table (2) illustrate the experimental conditions applied for the preparation, where the reaction takes place as the following.

Table 2. Experimental conditions applied for the preparation of synthetic zeolites under fixed fusion temperature 500 °C and NaOH (3M)

Samples	CFA/NaOH ratio	Hydrothermal treatment (°C)	
		Activation time 12 h	Crystallization time 6 h
I	1:1.4	60	60
II	1:1.4	95	95
III	1 :1.8	60	60
IV	1:1.8	95	95

Table 3. Some physical and chemical properties of the experimental soil

Soil separates %				Texture class	Chemical properties				Cu (mgkg ⁻¹)		Pb (mgkg ⁻¹)		
C. sand %	F. sand %	Silt %	Clay %	Sandy loam	pH 1:1	EC (dS/m) 1:1	OM (gkg ⁻¹)	CaCO ₃ (gkg ⁻¹)	CEC Cmolc/kg ⁻¹	Total	DTPA-extra.	Total	DTPA-extra.
19.93	48.62	17.48	13.97		7.86	4.12	19.8	22.55	9.67	164.47	24.55	103.95	15.72

C. sand=coarse sand F. sand= fine sand DTPA means DTPA-extractable

The synthesized zeolites characterization

Three techniques were employed to conceive a better assessment of characterization. The mineralogical composition of the synthesized zeolites was assessed by powder X-ray diffraction (XRD) Bruker, D₂ Phaser 2nd gen. Using CuK α radiation at 30KV and 10 mA. The morphology of the prepared samples was examined with high resolution Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), analysis experiments were carried out on a FEI Quanta FEG 250. Where, EDX is an X-ray technique used to define the elemental composition of materials. To study the textural structure of the formed products, the specific surface areas (SSA) were evaluated using the standard BET method for N₂ adsorption, data. N₂ adsorption-desorption measurements were performed at 77.35 K using BELSORP-mini X instrument.

Soil sampling and characterization

0-30 cm surface soil sample was taken from Al-Gabal Al-Asfar area, Qalyubia Egypt, which was contaminated since 1950 with many heavy metals due to effluent or sewage sludge applications. Collected sample was characterized after air-dried, ground, and sieved. through a 0.2 mm sieve. Mechanical analysis of soil texture was performed using international pipette method (Syvitski, 2007). Soil reaction (pH) and electrical conductivity (EC) were determined in soil suspension (1:1 w/v) (Black, 1965). Cation exchange capacity (CEC) was determined by ammonium acetate procedure (Rhoades, 1982). Soil organic matter (SOM) was measured by Walkley-Black Method Black (1965). Total carbonate content was estimated using Collin's calcimeter. Chemically extractable of heavy metals in soil was measured using an ammonium bicarbonate-DTPA according to Barbarick and Workman (1987) and measured by ICP (Inductively coupled plasma-mass

spectrometry). Total content of Cu and Pb was measured using method described by Ure (1995) and determined by ICP and Table (3) represented some physical and chemical properties

Batch Immobilization Experiment

To assess the effectiveness of the formed zeolites to immobilize Cu²⁺ and Pb²⁺, a pot experiment was performed in the greenhouse of the Soil Chemistry and Physics Department Desert Research Center Cairo-Egypt. The experiment was designed in a completely block randomized with four replicates. 100 g of the soil were mixed with four synthetic zeolite materials (I, II, III and IV) and incubated with 0.5 g and 1.0 g of each treatment for 30 days at 21±2 °C. Each treatment was. Soil mixtures were watered at field capacity of 70%. After the incubation period, soil pH and chemically extractable fractions of copper and lead in soils were measured. The difference between final and initial contents, used to calculate the exact immobilized amount of heavy metals. The efficiency (E %) of various applied zeolites for Cu²⁺ and Pb²⁺, immobilization can be evaluated using the equation:

$$E (\%) = [(Co - Ce)/Co] \times 100$$

Where E represents efficiency of immobilization; Ce = the extractable heavy metal concentration at the of incubation period (mgkg⁻¹) and Co= the extractable concentration (mg kg⁻¹) of untreated sample.

Statistical Analysis

The significance test was performed by ANOVA test, (L.S.D) test at level of probability = 0.05 according to Steel *et al.* (1997), were used to compare treatment means for a better perception of the relation among the measured results of the soils and effect of the treatments using IBM SPSS Statistics 20.

RESULTS AND DISCUSSION

Characterization of raw material (CFA)

The XRD pattern of the raw material (CFA) acquired from the X-ray diffraction analysis in Figure (1), showed that the CFA sample used has two substantial crystalline phases: quartz (SiO_2) and mullite ($3\text{Al}_2\text{O}_3\text{SiO}_2$), X-ray pattern has shown the predominant phases were quartz (SiO_2), with a main peak at $27.60\ 2\theta$, mullite ($3\text{Al}_2\text{O}_3\text{SiO}_2$), containing a main peak at around $26.7\ 2\theta$ (as a buttress on the peak of quartz), hematite and magnetite (ASTM, 2019). As shown in Figure (1), the slightly raised background indicates the presence of an amorphous phase; this is probably aluminosilicate glass which constitutes 40.63%, whereas quartz was 23.66% and mullite forms 33.75%, the coal fly ash also contains magnetite (3.7%) and hematite (1.35%). The relative content of mineral phases in the used fly ash takes the following order: Amorphous > Mullite > Quartz > Magnetite > Hematite. The obtained results in agreement of those found by Franus (2012) and Längauer *et al.* (2021).

SEM image of CFA is seen in Figure (2) coal fly ash particles morphology was found to be generally spherical and smooth confirmed substantial contents of aluminium and silicon which is characteristic of fly ash (Längauer *et al.*, 2021). Elemental analysis of CFA sample obtained via EDX analysis was showed that CFA particles are mainly consisted of C, O₂, Na, Si, Al, Mg, K, Ca, Fe, and P.

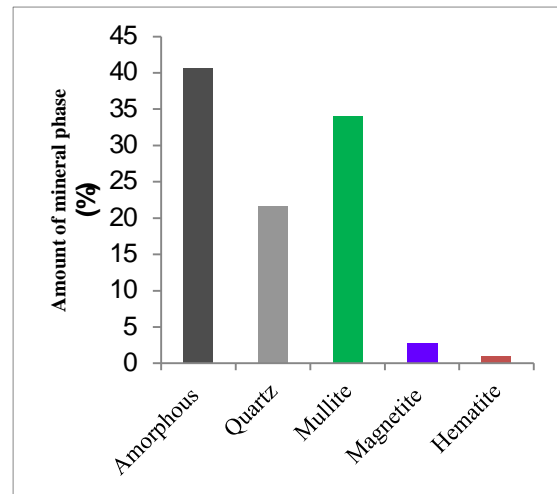
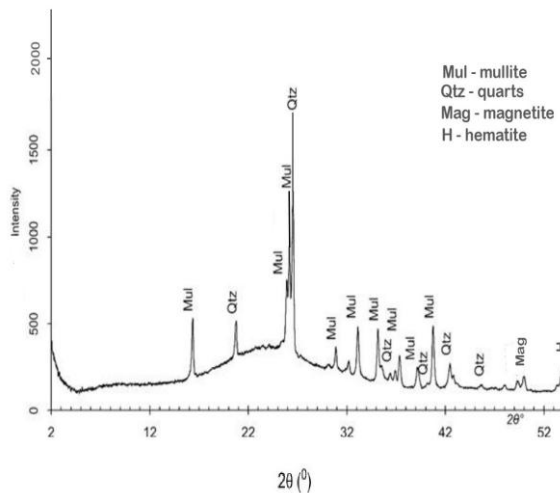


Fig. 1. XRD pattern of raw material CFA

Characterization of the synthesized zeolite

The XRD Study

The XRD patterns of the prepared materials acquired from analysis of the X-ray diffraction are found in Figures (3a, b, c and d), the synthesized materials had different phase compositions. The formed samples consisted of crystalline phases of sodalite (SOD), zeolite-A (Linde Type A), analcime (ANA) and cancrinite (CAN). In all samples, however, sodalite (SOD) was the main dominant crystalline phase. The qualitative and quantitative composition of the synthetic zeolites depended on the crystallization conditions. Figure (3a) shows the sample 1 which was prepared in 1:1.4 CFA/NaOH ratio and a hydrothermal temperature of $60\ ^\circ\text{C}$ was composed of two phases of zeolite materials. Sodalite (SOD) and Na-A zeolite (Linde Type A (LTA)), As shown in Table (4), sodalite was dominate crystalline phase in this sample, which constitutes 67%. The crystalline phase of zeolite A constitutes 31%. These results have great similarity with to samples obtained by Fechtelkord (1999) and Koshlak (2023).

Figure (3b) clarify the diffraction patterns for the synthesized sample II, which was prepared at 1:1.4 ratio of CFA/NaOH and was formed at high crystallization temperatures $95\ ^\circ\text{C}$, as shown the crystalline phase of SOD zeolite is also dominated. However, as increasing crystallization temperatures, causing appear of new crystalline phases analcim (ANA) and cancrinite (CAN), with reflexions of the zeolites Na-A, these findings correspond to the obtained samples with the results of Gatta *et al.* (2008). Data in Table (4), showed that in this sample, the content of SOD zeolite is 81%, the percentages of new framework phases analcim (ANA) and cancrinite (CAN) are 8% and 11%, respectively.

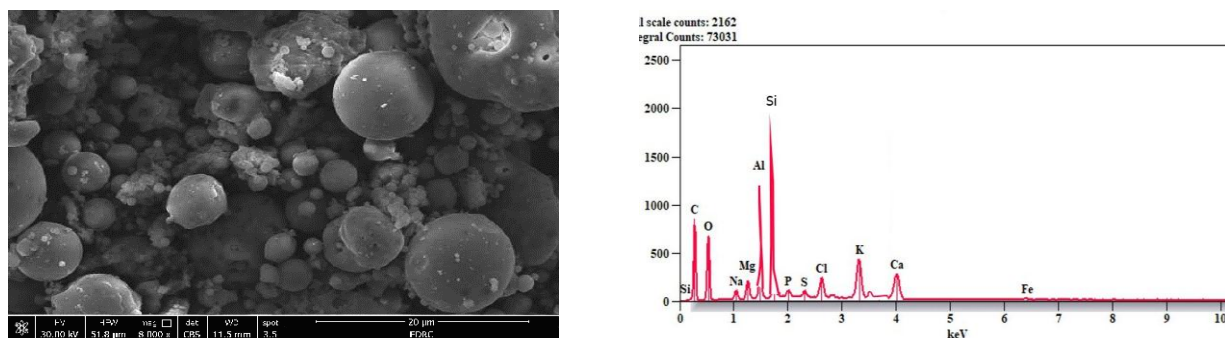


Fig. 2. The SEM image, the elemental composition and EDX spectra of CFA

	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe
Weight %	17.0	40.9	1.5	2.1	12.0	27.0	0.6	0.6	1.7	4.1	7.8	0.7
Atom %	27.6	49.8	1.3	1.7	9.0	16.7	0.4	0.3	1.0	2.0	3.64	0.2

As we can be seen that an increment in the crystallization temperature from 60 to 95 °C at the same mass ratio of fly ash to NaOH set the framework structures of analcime, sodalite, and cancrinite and the

increment in temperature led to increase the formation of sodalite crystal where was 67% at a temperature of crystallization 60°C and 81% at a.

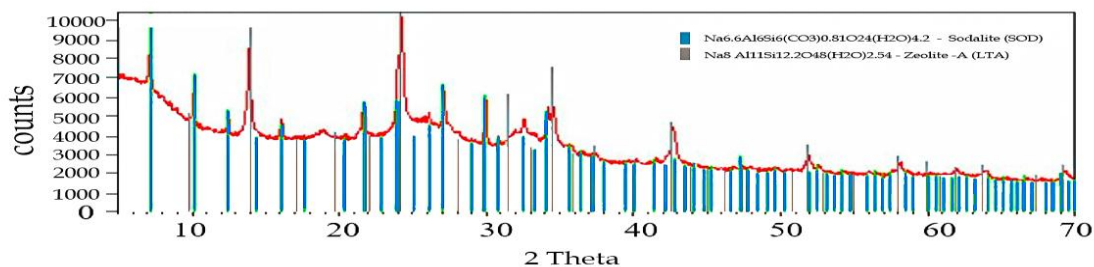


Fig. 3a. XRD pattern of synthetic zeolite sample I

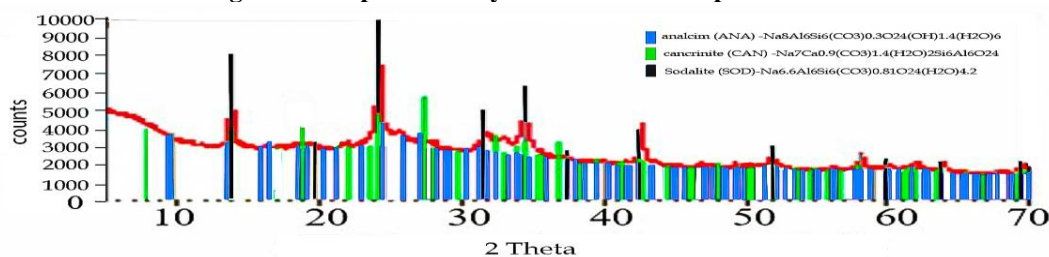


Fig. 3b. XRD pattern of synthetic zeolite sample II

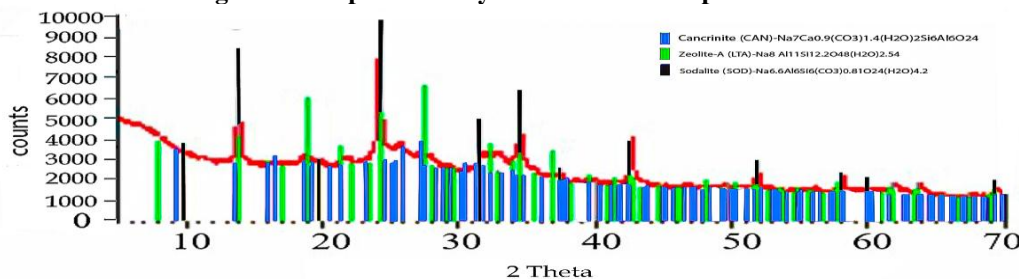


Fig. 3c. XRD pattern of synthetic zeolite sample III

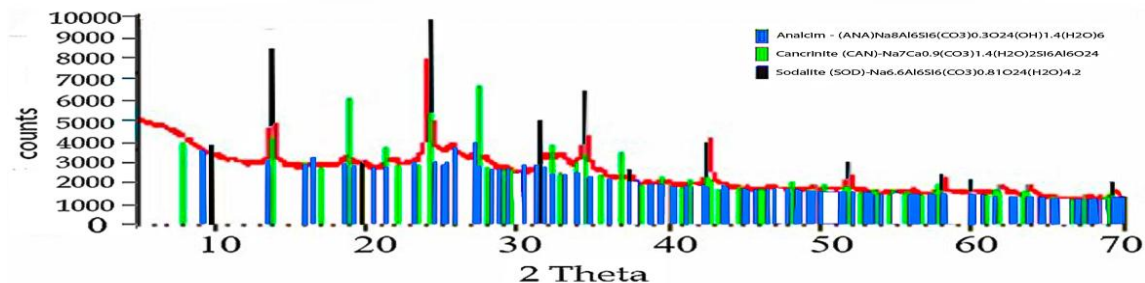
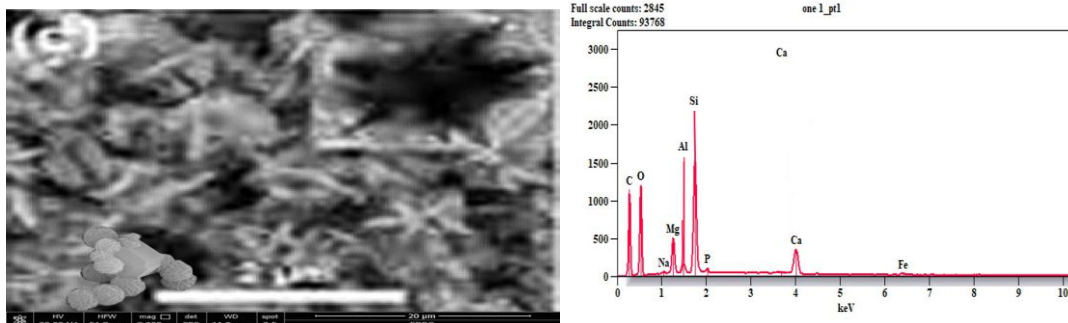


Fig. 3d. XRD pattern of synthetic zeolite sample IV

Table 4. The mineralogy composition of the synthesized samples

The synthesized samples	Zeolite materials	Chemical Formula	Semi Quant (%)
Sample I	Sodalite (SOD)	$\text{Na}_{6.6}\text{Al}_6\text{Si}_6(\text{CO}_3)_{0.81}\text{O}_{24}(\text{H}_2\text{O})_{4.2}$	67
	Zeolite -A (LTA)	$\text{Na}_8\text{Al}_{11}\text{Si}_{12.2}\text{O}_{48}(\text{H}_2\text{O})_{2.54}$	33
Sample II	Sodalite (SOD)	$\text{Na}_{6.6}\text{Al}_6\text{Si}_6(\text{CO}_3)_{0.81}\text{O}_{24}(\text{H}_2\text{O})_{4.2}$	81
	Analcim (ANA)	$\text{Na}_8\text{Al}_6\text{Si}_6(\text{CO}_3)_{0.3}\text{O}_{24}(\text{OH})_{1.4}(\text{H}_2\text{O})_6$	8
	Cancrinite (CAN)	$\text{Na}_7\text{Ca}_{0.9}(\text{CO}_3)_{1.4}(\text{H}_2\text{O})_2\text{Si}_6\text{Al}_6\text{O}_{24}$	11
Sample III	Sodalite (SOD)	$\text{Na}_{6.6}\text{Al}_6\text{Si}_6(\text{CO}_3)_{0.81}\text{O}_{24}(\text{H}_2\text{O})_{4.2}$	70
	Zeolite-A (LTA)	$\text{Na}_8\text{Al}_{11}\text{Si}_{12.2}\text{O}_{48}(\text{H}_2\text{O})_{2.54}$	13
	Cancrinite (CAN)	$\text{Na}_7\text{Ca}_{0.9}(\text{CO}_3)_{1.4}(\text{H}_2\text{O})_2\text{Si}_6\text{Al}_6\text{O}_{24}$	17
Sample IV	Sodalite (SOD)	$\text{Na}_{6.6}\text{Al}_6\text{Si}_6(\text{CO}_3)_{0.81}\text{O}_{24}(\text{H}_2\text{O})_{4.2}$	84
	Analcim (ANA)	$\text{Na}_8\text{Al}_6\text{Si}_6(\text{CO}_3)_{0.3}\text{O}_{24}(\text{OH})_{1.4}(\text{H}_2\text{O})_6$	10
	Cancrinite (CAN)	$\text{Na}_7\text{Ca}_{0.9}(\text{CO}_3)_{1.4}(\text{H}_2\text{O})_2\text{Si}_6\text{Al}_6\text{O}_{24}$	6



	C	O	F	Na	Mg	Al	Si	P	Ca	Fe
Weight %	8.2	52.8	0.0	0.5	3.6	16.6	21.3	1.5	5.9	0.7
Atom %	13.4	64.7	0.0	0.4	2.9	12.4	15.5	0.9	4.8	0.2

Fig. 4a. The SEM images, the elemental composition and EDX spectra of sample I

temperature of crystallization 95 °C, this result assured the similarity of the synthetic samples with the results of studies of Gatta *et al.* (2008) and Koshlak (2023).

Figure (3c) shows the diffraction patterns for a sample III which prepared with a CFA/NaOH ratio of 1:1.8 and temperature of crystallization 60 C. Sample III has three framework phases of zeolite materials. (SOD zeolite, Na-A zeolite and CAN zeolite, where SOD zeolite was the highest content (70%). The framework phases percentage of Na-A and CAN zeolites is much less than sodalite zeolite where they constitute 13% and

17%, respectively. The obtained results in harmony with the findings of Luhrs *et al.* (2012) and Koshlak (2023).

The morphologic analysis

The SEM-EDX is an efficient analysis to describe the morphology and the elemental composition in micro-scale of studied samples (Li *et al.*, 2019). The morphologic analysis of four samples of synthesized zeolites by SEM-EDX is shown in Figure (4a, b, c and d). SEM image of the sample 1 formed from 1:1.4 ratio of CFA/NaOH and temperature of crystallization at 60C in Figure (4a) showed SOD zeolite, which is characterized by a globular shape with fibres

encirclement by a ring and cubic framework with amputated border and peaks assisted to the zeolite a formation.

SEM micrograph of sample II, which was synthesized from 1:1.4 ratio of CFA/ NaOH and temperature of crystallization at 95 °C is shown in Figure (4b) with increasing the temperature of crystallization to 95 °C led to increase the diffraction peaks of sodalite and appear additional crystalline phases, this sample contain three crystalline phases of zeolites (SOD, CAN and ANA zeolites). In Figure (4b), shows a compact cubic shape which attributed to analcim crystal (ANA), solid, acicular and spherical crystallites of SOD zeolite and thin disks is attributed to the CAN zeolite structure that grew due to SOD, which is agreement with results obtained by Ríos et al. (2009). The EDX spectra area showed that the obtained zeolite

was composed mainly of O, Na, K, Si, Al, Mg, Fe, F, Ti, and Ca.

SEM image of sample III, which was prepared from 1:1.8 ratio of CFA/NaOH and temperature of crystallization at 60 °C, Figure (4c), illustrated the presence of cubic framework with amputated border and peaks. attributed of the zeolite A, also shows zeolite SOD, which is characterized by a globular structure.

The SEM image of sample IV, synthesized from 1:1.8 ratio of CFA/NaOH and temperature of crystallization at 95 °C, Figure (4d) showed the presence of a large number of polyhedral structures. The prepared sample consisted of sodalite globular particles and defined hexagonal crystals attributed to cancrinite, in addition analcim in the crystalline form, which is consistent with findings of Koshlak (2023).

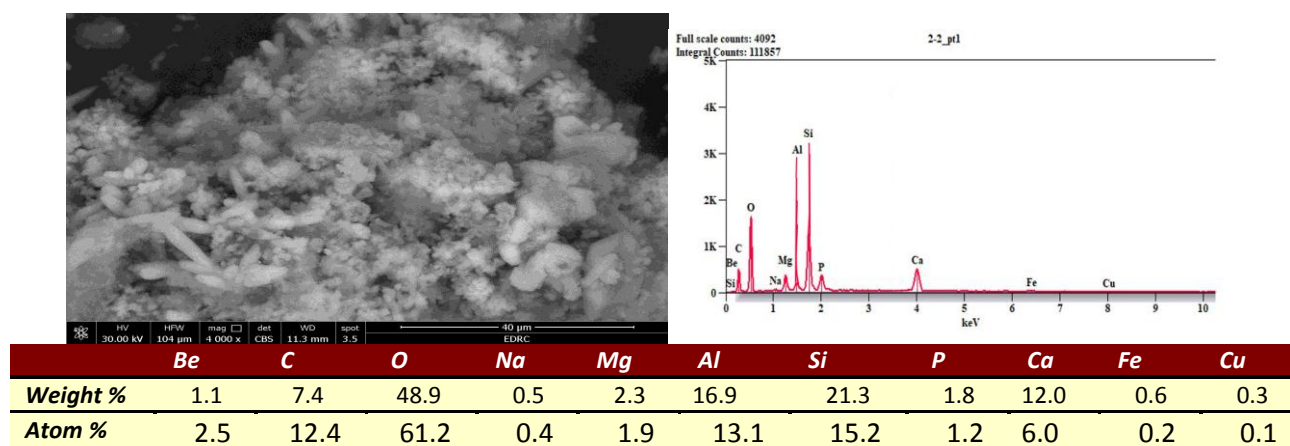


Fig. 4b. The SEM images, elemental composition and EDX spectra of sample II

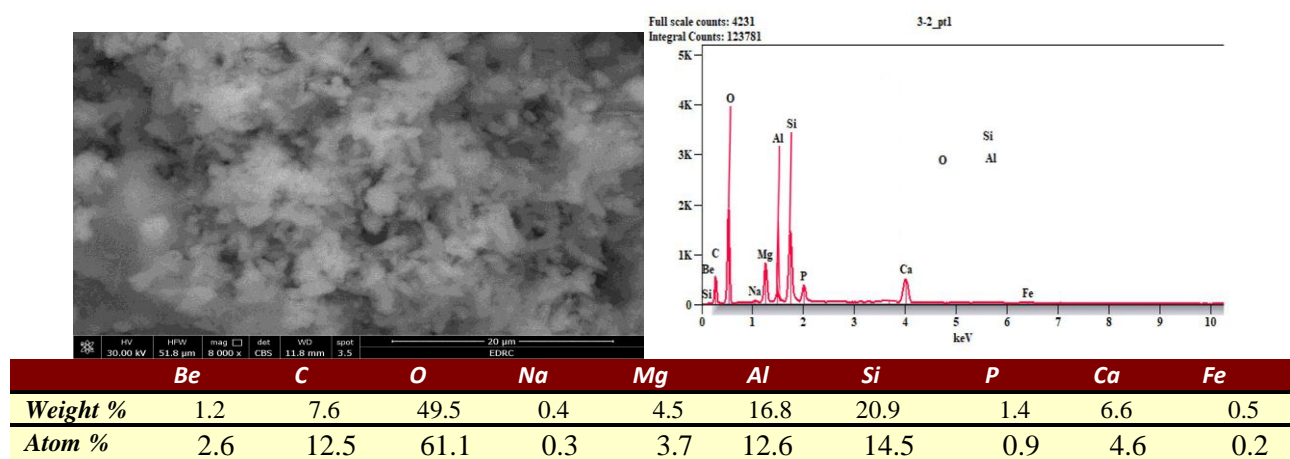


Fig. 4c. The SEM images, elemental composition and EDX spectra of sample III

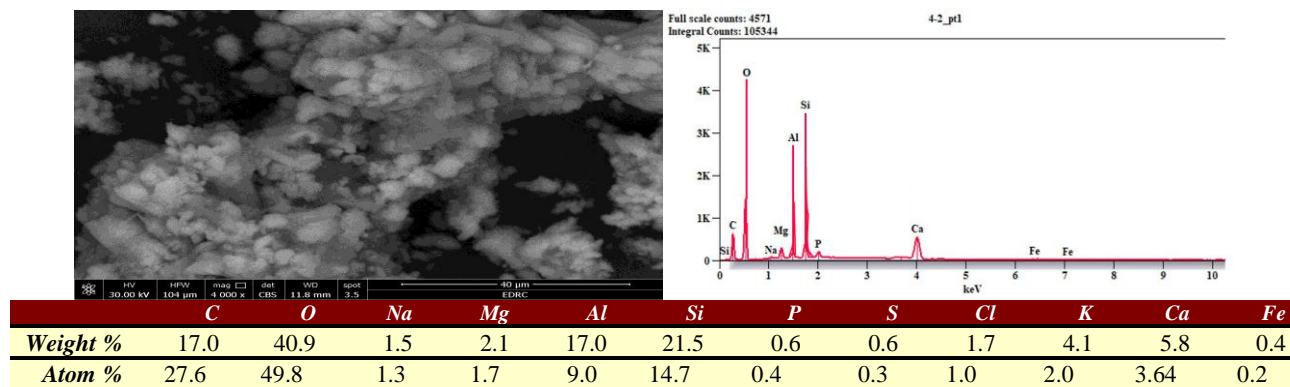


Fig. 4d. The SEM image, the elemental composition and EDX spectra of sample IV

At the same CFA/NaOH ratio, the crystallization temperature influences the quantitative content of the crystalline phases where the prepared samples had framework phases of sodalite (SOD), Analcime (ANA), Na-A zeolites (Linde Type A), and cancrinite (CAN), however, in all formed samples; sodalite was the most dominant phase depending on the crystallization conditions, it was observed there were two different types of sodalite morphology, where, large sodalite particles present in synthetic samples II and IV (95 °C) apparently formed as a result of conversion of LTA zeolite particles. The results of EDX analysis of the prepared samples had shown reduction in the concentrations of Si in favour of Al. This illustrated the transformation of the chemical composition of the original CFA to the final prepared products. It is observed that the content of elements, such as Fe and Ca significantly decreased in the synthetic zeolites compared to the initial CFA.

Textural characterization

In all experiments, sodalite crystalline phase was the predominant phase in the obtained samples Sodalite is a tectosilicate mineral with the general formula $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{X})$ with $\text{X} = \text{Cl}^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{OH}^-$ (Günther *et al.*, 2015). As a result of alkali fusion-hydrothermal procedure, different amounts and types of zeolite phases were obtained. textural characterizations This determined the different (S_{BET} , S_{micro} , and V_p) of synthesized products. The larger pore volume and higher specific surface area were due to the existence of highly mesoporous structures in the prepared products. As shown in Table (5), sample I had the largest specific

surface area ($S_{\text{BET}} = 76.39 \text{ m}^2/\text{g}$), and also had the largest micropore surface ($10.17 \text{ m}^2/\text{g}$). The highest values of the mesopore surface was for sample III and IV where $d_p = 10.99 \text{ nm}$ and 10.72 nm , respectively. In synthesized samples III and IV, mesopores started to command over micropores, which demonstrated that mesopores form the great part of the total specific surface area. At the same time, with an increase in surface and bulk parameters, it was observed reduction in the average pore volume (V_p) in the samples, which happened under the effect of crystallization conditions. The S_{BET} values are favorable to the results acquired by Ulfa *et al.* (2022) and Koshlak (2023). The high surface area of all samples are important for the adsorption of large quantities of organic and inorganic pollutants (Elsawy *et al.*, 2022).

Immobilization of Copper and Lead

The total content of Cu and Pb in the soil was 164.47 and 106.95 mgkg^{-1} , respectively. These concentrations are much higher than the limits of maximum permissible levels of total metals (mgkg^{-1}) of Kabate-Pendias and Pendias (2001) (Cu (100 mg kg^{-1}) and Pb (100 mg kg^{-1}). The chemically-extractable metal fraction was applied as an indicator for metal bioavailability in soils. DTPA-Cu and -Pb contents were 24.55 and 15.72 mgkg^{-1} , respectively, lead (Pb) showed lower availability than Cu in the investigated soil which may due to its high affinity to adsorb to the active surfaces of soil constituents and form inner-sphere complexes (Abdel-Kader *et al.*, 2013).

Table 5. The porous structure parameters of the synthesized samples

Samples	S_{BET} (m^2/g)	S_{micro} (m^2/g)	$d_p = 4V_p/S_{\text{BET}}$ (nm)	$d_p, \text{BJH (Ads)}$ (nm)	$d_p, \text{BJH(Des)}$ (nm)	$V_p, (\text{cm}^3/\text{g})$
Sample I	76.39	10.17	9.22	10.01	9.96	0.1761
Sample II	73.15	9.29	7.53	8.51	7.55	0.1377
Sample III	56.42	7.57	10.99	10.45	10.45	0.1550
Sample IV	62.08	9.75	10.72	10.83	9.65	0.1664

Data in Table (6) demonstrated that pH slightly significant increased after synthetic zeolite addition compared to control, pH value was affected by amount of zeolite, this rise in pH owing to the alkalinity of the zeolitic material added (Querol *et al.*, 2006). With increasing zeolite application rate, the availability of lead and copper decreased as shown in Table (6). The highest percentage of decrease was in the treatment of synthetic sample IV, where the DTPA-Cu significantly reduced (at $P < 0.05$) from approximately 24.55 to 16.14 mg kg^{-1} (39.42% decrease) and the DTPA-Pb significantly reduced from 15.72 to 3.40 mgkg^{-1} (78.37% decrease). Data show also that prepared sample IV treatment has the highest effectiveness in reducing DTPA-Cu and Pb relative to control after incubation period in the soil, respectively. This result could be attributed to its high sodalite crystal content (84%) which has high adsorption properties and its highest mesopore surface where mesopores form the great part of the total specific surface area.

Extractable DTPA-Cu and Pb in Table (6) showed significant decrements to nearly 31.67 & 32.52 % and 57.13 & 63.15 % of untreated soil due to the effect of the adding 1.0% synthetic samples I and II after 30 days of incubation, respectively. While in the 1.0% synthetic zeolite sample III treated soil as shown in Table (6). The concentration of DTPA-Pb had a significant decrease from 15.72 mgkg^{-1} in the control soil to 4.47 mgkg^{-1} at $P < 0.05$ after incubation period, as decreased by 71.55 % while the extractable DTPA-Cu was reduced from 24.55 mg kg^{-1} to 15.78 mgkg^{-1} compared to untreated

soil where decreased by 35.72%. These results could be a consequence of the rise in pH of the zeolitic material added (Querol *et al.*, 2006). The synthetic zeolite sample IV was significantly more effective in reducing the DTPA extracted Cu and Pb, as showed by the LSD test, in the two studied metals and applied treatments, adding sample IV at a rate of 1% resulted in the fixation of about 39.42 and 78.37% of cadmium and lead, respectively, according to the statistical analysis (Table 6). Increasing the sample IV application rate showed significant differences, indicating that 1% sample IV was adequate to achieve the least DTPA extracted Cu and Pb in the studied soil.

Table (6) shows the immobilized concentrations of Cu and Pb as a result of the prepared zeolite treatments. They were calculated by difference between the concentration after the incubation experiment, i.e., 30 days (C_{30}) and the initial concentration in the contaminated soil (C_0). The results in Table (6) illustrated that the immobilized concentrations by the applied zeolite treatments may be higher for lead than for copper in all the treatments studied. Also, the synthetic zeolite sample IV had the highest effectiveness as an immobilizer of Cu and Pb in contaminated soil. Copper (Cu) had less restraint to zeolitic materials as its immobilized concentration increased from 7.23 to 9.68 mgkg^{-1} , compared to immobilized concentration of Pb which ranged from 8.25 to 12.32 mg kg^{-1} .

Table 6. LSD analyses of the mean DTPA- and immobilized concentrations of Cu and Pb in the soil as a result of the zeolite treatments

Treatments	pH	DTPA-concentration(mgkg^{-1})		Immobilized concentration ($C_0 - C_{30}$) (mgkg^{-1})		Immobilization efficiency E (%)	
		DTPA-extra. Cu	DTPA-extra. Pb	DTPA-extra. Cu	DTPA-extra. Pb	Cu	Pb
		Control	7.86e	24.55a	15.72a		
0.5 % sample I	7.91d	17.32b	7.47b	7.23f	8.25g	29.45	52.51
1.0% sample I	7.97c	16.78c	6.74c	7.77e	8.98f	31.67	57.13
0.5 % sample II	7.92cd	16.71c	6.41d	7.84d	9.31e	31.95	59.22
1.0% sample II	8.09b	16.57cd	5.79e	7.98d	9.93d	32.52	63.15
0.5 % sample III	7.96c	16.14de	5.31ef	8.41cd	10.41c	34.25	66.25
1.0 % sample III	8.13a	15.78e	4.47f	8.77c	11.25b	35.72	71.55
0.5 % sample IV	7.95c	15.55e	4.53f	9.00b	11.19b	36.65	71.18
1.0% sample IV	8.16a	14.87f	3.40g	9.68a	12.32a	39.42	78.37
Mean	7.99	17.14	6.64	8.34	10.21		
LSD 0.05	0.011	0.032	0.051	0.013	0.022		

E (%) = immobilization efficiency in percent, the same letters in the column refers to that there is no any significant difference at 0.05 level.

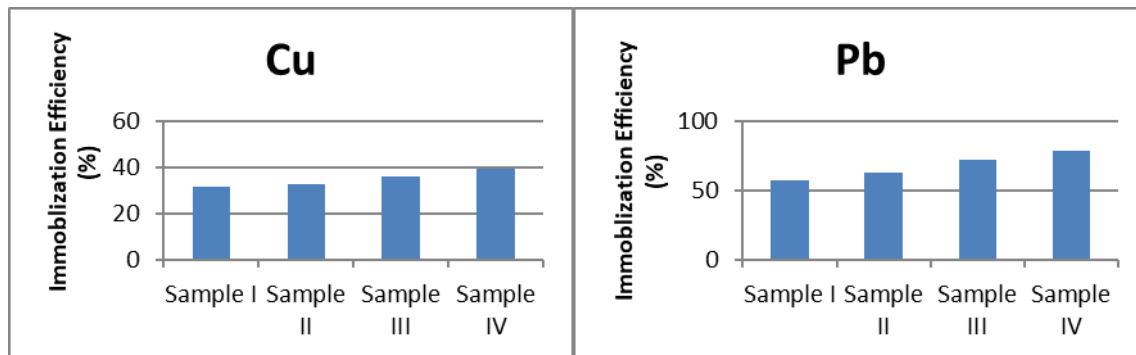


Fig. 5. The immobilization efficiency (E %) of Cu and Pb for different applied treatments at rate 1%

Figure (5) shows that the immobilization efficiencies for the synthetic zeolite samples, the maximal immobilization efficiency (E %) values were for the synthetic zeolite III and IV where was 35.72 and 39.42 % for Cu while 71.55 and 78.37 % for Pb in the studied soil, respectively, our work showed that 1% synthetic zeolite sample IV was the best treatment to immobilize Cu and Pb from the contaminated soils.

CONCLUSION

The work offered in this study points to the prospect CFA usage as a raw material for the preparation of zeolitic materials and the possibility to apply it as a cheap treatment for the immobilization of heavy metals in the contaminated soil. To improve the process of synthesis, alkaline fusion prior to hydrothermal treatment was applied as a function of ratio CFA to NaOH (1:1.4, 1:1.8) and (activation and crystallization) temperature 60 and 95 °C. Experimental results have demonstrated that the ratio of coal fly ash to Sod hydroxide had great effect on the crystals formation and crystalline phases quantity in the prepared zeolites where the crystallinity of the formed products increases as the mass ratio of coal fly ash to Sod hydroxide increase. At the same CFA / NaOH ratio the crystallization temperature influences the content of the crystalline phases where the prepared zeolites contained framework phases of sodalite (SOD). Na-A zeolites (Linde Type A), cancrinite (CAN), and analcime (ANA), however, in all products; sodalite was the most dominant framework phase relying on the temperature of crystallization, two classes of sodalite different in morphology structure were noticed. Sodalite large particles in synthetic samples II and IV (95 °C) obviously formed as a result of conversion of zeolite-A particles. In sample II and IV, the mesopore surface has the highest value indicating to the mesopores dominated

over micropores and represented the greatest part of the total specific surface area. Crystalline products have been used to immobilize Cu and Pb in the soil. It was noticed that increase the application rate of the synthesized zeolite, their ability to immobilize Cu and Pb increase, the synthetic sample IV treatment had significantly the most effectiveness in reducing the DTPA extracted metals with maximal immobilization efficiencies (E %) as indicated from LSD test.

RECOMMENDATION

Coal fly ash has great ability for usage as a cheap and alternative raw material source in the zeolites synthesis and heavy metal immobilization. The fusion method was more effective for the preparation of zeolites from coal fly ash, which does not demand application under hard conditions with minimum time and less financial costs.

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المخلص العربي

تحضير الزيوليت من الرماد المتطاير للفحم وتطبيقه في معالجة التربة الملوثة بالمعادن الثقيلة

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تقدم هذه الدراسة نتائج تجريبية تتناول إمكانية تحويل الرماد المتطاير للفحم إلى مواد زيوليتية لاستخدامها كمادة غير مكلفة لتثبيت المعادن الثقيلة في التربة الملوثة. تم استخدام رماد الفحم المتطاير (CFA) لتحضير الزيوليت المصنع عن طريق الانصهار القلوي تليها المعالجة الحرارية المائية بنسبة الرماد المتطاير للفحم إلى هيدروكسيد الصوديوم (1:1.4, 1:1.8) ودرجة الحرارة (التنشيط والتبلور) 60 و 95 درجة مئوية، تم تحضير أربع عينات من الزيوليت وتوصيفها باستخدام تقنيات مختلفة مثل حيود الأشعة السينية، المجهر الإلكتروني الماسح، الأشعة السينية المشتتة للطاقة SEM-EDX لدراسة التركيب المعدني. واستخدام طريقة BET لتقدير مساحة السطح. أظهرت النتائج أن تبلور الزيوليت المحضر يزداد مع زيادة نسب CFA/NaOH كما أن درجة حرارة التبلور تؤثر على محتوى المراحل البلورية في جميع العينات واحتوت العينات المحضرة على أطوار بلورية من السوداليت (SOD). زيوليت (Na-A (Linde Type A)، والكانكرينييت (CAN)، والأنالسايم (ANA)، في جميع العينات؛ كان السوداليت هو المرحلة البلورية السائدة وأظهرت نتائج الدراسة البنائية أن أعلى قيم مساحة السطح (SBET) وجدت في العينة الأولى التي تم تحضيرها عند نسبة

تبلغ 1:1,4 ودرجة حرارة تبلور تبلغ 60 درجة مئوية. تشكل المساحات السطحية للمسامية المتوسطة الجزء الرئيسي من إجمالي مساحة السطح المحددة في العينات الثالثة والرابعة. تم استخدام مواد الزيوليت البلورية لدراسة كفاءتهم في تثبيت النحاس والرصاص في التربة. وقد لوحظ أنه مع زيادة معدل استخدام الزيوليت المحضر في التربة تحسنت فعالية هذه المعاملات في تثبيت النحاس والرصاص. وكان استخدام الزيوليت المحضر IV هو الأكثر فعالية بشكل ملحوظ في خفض المعادن المستخلصة كيميائياً بـ DTPA مع أقصى قدر من كفاءة التثبيت (% E) كما هو موضح من اختبار LSD. ويرجع هذه الكفاءة التثبية لاحتواءها على أطوار بلورية من السوداليت (SOD) بنسبة عالية (84%) والمعروفة بقدرتها الإدمصاصية العالية وقد وجد أنه تم تثبيت ما يصل إلى 39,55% و 78,37% من النحاس والرصاص، على التوالي، بواسطة 1% من الزيوليت المحضر IV. وأظهرت الدراسة الحالية أنه من وجهة النظر الاقتصادية والعملية، فإن 1% من من الزيوليت المحضر IV كانت أفضل معالجة لتثبيت النحاس والرصاص في التربة الملوثة.

تقدم هذه الدراسة نتائج تجريبية تتناول إمكانية تحويل الرماد المتطاير للفحم إلى مواد زيوليتية لاستخدامها كمادة غير مكلفة لتثبيت المعادن الثقيلة في التربة الملوثة. تم استخدام رماد الفحم المتطاير (CFA) لتحضير الزيوليت المصنع عن طريق الانصهار القلوي تليها المعالجة الحرارية المائية بنسبة الرماد المتطاير للفحم إلى هيدروكسيد الصوديوم (1:1.4, 1:1.8) ودرجة الحرارة (التنشيط والتبلور) 60 و 95 درجة مئوية، تم تحضير أربع عينات من الزيوليت وتوصيفها باستخدام تقنيات مختلفة مثل حيود الأشعة السينية، المجهر الإلكتروني الماسح، الأشعة السينية المشتتة للطاقة SEM-EDX لدراسة التركيب المعدني. واستخدام طريقة BET لتقدير مساحة السطح. أظهرت النتائج أن تبلور الزيوليت المحضر يزداد مع زيادة نسب CFA/NaOH كما أن درجة حرارة التبلور تؤثر على محتوى المراحل البلورية في جميع العينات واحتوت العينات المحضرة على أطوار بلورية من السوداليت (SOD). زيوليت (Na-A (Linde Type A)، والكانكرينييت (CAN)، والأنالسايم (ANA)، في جميع العينات؛ كان السوداليت هو المرحلة البلورية السائدة وأظهرت نتائج الدراسة البنائية أن أعلى قيم مساحة السطح (SBET) وجدت في العينة الأولى التي تم تحضيرها عند نسبة