An Effective Method for Adsorption of Pb$^{2+}$, Cd$^{2+}$, and Cu$^{2+}$ from Wastewater by Using NaXzeolite-Derived from Coal Gangue

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**Abstract**

A study was conducted to investigate the behavior and mechanics of NaXzeolite on the adsorption of (Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$) from simulated wastewater. NaXzeolite was synthesized from coal gangue by an Alkali-based hydrothermal process. A number of techniques have been employed to analyze the production of adsorbents, including X-ray diffraction (XRD), scanning electron microscopy with X-ray energy analysis (SEM-EDX), Fourier transform infrared (FT-IR), X-ray fluorescent (XRF), and Brunauer-Emmett-Teller (BET). The effects of adsorbent dosage, pH, time, temperature, and initial concentration of NaXzeolite on the adsorption of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ were investigated. To investigate the mechanisms and capacities of experimental adsorption, Langmuir, Freundlich, and Temkin isotherms were employed. In certain conditions, the Langmuir isotherm showed that the adsorbent layer had an adsorption capacity of 88.3, 87.9 and 88.5 mg/g of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$, with linear regression coefficients ($R^2 > 0.979$) for all three metals. Bioavailability, Optimal doses of 0.5 g/L NaXzeolite at pH of 5 & 6 in condition 25°C in 90 minutes removed >99% for all three metals.

**Subject Areas**

Water and Wastewater Research

**Keywords**

Coal Gangue, Adsorption of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$, NaXzeolite, Langmuir,
Freundlich and Temkin Isotherms

1. Introduction

Efficient Rapid urbanization and industrialization have resulted in severe environmental damage, including contaminated water by heavy metals (HMs) [1]. Many industries discharge wastewater containing HMs, including the battery and leather industry, mining, and smelting [2]. Despite their relatively low concentration, HMs are highly toxic, carcinogenic, and bioaccumulative, making them extremely dangerous and a serious threat to human health and the environment [3]. The toxicity and environmental hazards of HMs are further exacerbated by their capacity to coexist with other ions and easily form complexes with complexing agents [4]. At present, various conventional technologies are in use, The purpose of remediation HMs is to keep the public safe and to preserve the environment [5]. In addition to chemical precipitation, [6] membrane, [7] ion exchange, [8] flotation, and phytoremediation, these methods may also include bioremediation [9]. Nevertheless, these methods are expensive and produce hazardous secondary wastes Consequently, even provided effective control of volatile organic compounds The results were good, but the costs and environmental risks were high, [10] therefore, it is imperative to find effective methods for the effective removal of heavy metals that are cost-effective and environmentally friendly. For the remediation of contaminated wastewater containing HMs, adsorbent materials are a frequent and effective solution [11]. Coal is one of the most important industrial wastes, as it is a hazardous and complex solid byproduct produced during coal mining. About 15% of the world’s coal production is produced by burning coal, and 27% of the energy used by humans is generated by burning coal, [12]. In coal gangue, there is a high concentration of Si and Al, which can be used to create zeolite, inorganic porous material with high value-added. Zeolite synthesized from coal gangue, which can be regarded as a primary industrial raw material [13]. Aim this research we, NaX zeolite was synthesized from coal gangue, foradsorption of (Pb2+, Cu2+ and Cd2+) at low cost and high efficiency and find out best environment for heavy metals adsorption.

2. Method and Meterials

2.1. Test Material

The coal gangue obtained from Shanxi Coal Mine in Jinzhong district, taking about 2 kg of coal gangue and bringing it to the laboratory. First, the samples were washed with distilled water, to remove the surface soil, dried in a drying oven at 105°C for 5 h, and then stored in a desiccator. For well-known of coal gangue chemicals materials using XRF Al2O3 (29%), SiO2 (56%) exist in the form of quartz, kaolinite, and also contain a small amount of Fe2O3, K2O, Na2O, SO3, TiO2, other (15%). Sodium hydroxide (NaOH), nitric acid (HNO3), Lead chlo-
ride (PbCl₂), Copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) and Cadmium chloride monohydrate (CdCl₂·H₂O) were all analytically pure. Use an analytical balance to weigh 1.343 g, 3.821 g and 1.79 g and of Lead Chloride, Copper(II) nitrate trihydrate and Cadmium chloride monohydrate dissolved in 1000 mL of deionized water to obtain 1000 mg/L of Pb²⁺, Cu²⁺ and Cd²⁺ solutions for use. Zeolite was synthesized using NaOH. This study was conducted using deionized water with a conductivity of 2.7 *s/cm.

2.2. Preparation of NaX<sub>zeolite</sub>
For Preparation of NaX<sub>zeolite</sub>, first Coal Gangue powder is obtained by crushing raw coal samples and passing them through a sieve with a mesh size of 120 after crushing, to obtain a homogenous mixture, 5 g of Coal Gangue powder were mixed and ground in a mortar for 15 minutes with a 1g amount of NaOH(s). In the muffle furnace, Coal Gangue powder was activated and unburnt carbon was removed by placing the homogeneous mixture in the crucible and placing it under an air atmosphere at 800°C for 2 hours. As soon as the fused samples had cooled to room temperature, they were ground into a powder, dissolved in a solution of 100 mL deionized water, stirred for 15 minutes, and crystallized under 90 degrees around 24 hours, respectively. Before characterization and adsorption experiments, the product was separated through vacuum filtration several times with deionized water until pH reached natural.

2.3. Test Equipment
This experiment was carried out in the Microbiology Laboratory, Taiyuan University of Technology, Taiyuan, Shanxi China. The main equipment used included to determine the Pores and specific surface area of the NaX<sub>zeolite</sub> is using the Brunauer-Emmett-Teller (BET) method. The chemical composition of NaX<sub>zeolite</sub> samples was examined by X-ray fluorescence analyzer spectrometer (XRF). Fourier transform infrared spectrophotometer (FTIR, PerkinElmer, L1600400 spectrum TWO FT-IR, UK), used for the functional groups on NaX<sub>zeolite</sub>. A scanning electron microscope (SEM) was used to examine the morphological structure of the NaX<sub>zeolite</sub>, in addition, total metal concentrations in the simulated wastewater were determined using the (PerkinElmer Analyst 400) atomic absorption spectrometer.

2.4. Design of Adsorption Experiments
In this research 100 mL of Pb²⁺, Cu²⁺ and Cd²⁺ solutions with a mass concentration of 200 mg/L was accurately pipetted into a conical flask as simulated wastewater. Investigation of the effect of adsorption of dosage, Simulated wastewater was first treated with different masses of NaX<sub>zeolite</sub> (0.03, 0.05, 0.1, 0.2, 0.4 and 0.5 g), put the conical flask into the constant temperature shaker, at 25°C shaking for 60 min, After the adsorption, the samples were taken after pass through a 0.45 μm filter paper and determine the Pb²⁺, Cu²⁺ and Cd²⁺ concentration. The
effects of pH on the adsorption of heavy metals examined with different pH values 3, 4, 5, 6, 7, 8 and 9 respectively. Use 0.1 mol/L of HNO₃ and 0.1 mol/L NaOH solution to adjust the pH of simulated wastewater. The effects of temperature on the adsorption heavy metals was shaken at 15˚C, 25˚C, 35˚C, and 45˚C for 180 min. After the adsorption is over, the Pb²⁺, Cu²⁺ and Cd²⁺ samples concentration was detected after filtered with 0.45 μm. for effect of time on adsorption of heavy metals increase the time from 5, 10, 20, 30, 40, 60, 75 and 90 minutes shaking at 25˚C. pH5 for Pb²⁺ and pH6 for Cu²⁺ and Cd²⁺, 0.2 g of the prepared NaXzeolite 150 rpm use for all those experimental processing. In the adsorption isotherm test, 10 mL of 50, 100, 250, 200, 250, and 300 mg/L Pb²⁺, Cu²⁺ and Cd²⁺ solutions were accurately pipetted into a conical flask as simulated wastewater, for accurately weighed using an analytical balance, 0.2 g of the prepared coal gangue-based NaXzeolite was added to the simulated wastewater, and then the conical flask was placed in a constant temperature oscillator, and the adsorption was carried out at room temperature of 25˚C for 60 min. The concentration of Pb²⁺, Cu²⁺ and Cd²⁺ were detected after filtered with 0.45 μm filter membrane, and the experiment of each adsorption condition was repeated twice. Concentration of metals ion were detected by the atomic absorption spectrophotometer The Pb²⁺, Cu²⁺ and Cd²⁺ adsorption capacity and removals was calculated by Equations (1) and (2): 

\[ R = \frac{C_0 - C_e}{C_0} \times 100 \]  

(1) 

\[ q_e = \frac{C_0 - C_e}{M} \times V \]  

(2) 

\( q_e \) (mg/g) is the Pb²⁺, Cu²⁺ and Cd²⁺ adsorption amount by adsorbent. \( C_0 \) (mg/L) and \( C_e \) (mg/L) represent the initial and after adsorption Pb²⁺, Cu²⁺ and Cd²⁺ concentration in solution, respectively. \( V \) (L) is the solution volume, and \( m \) (g) stand for the mass of adsorbent. \( R \) is removal percentage. 

3. Results and Discussion

3.1. Characterization of Adsorbent

The coal gangue and the obtained molecular sieve XRD images (Figure 1) were analyzed, and it was found that the main components of coal gangue were quartz, kaolinite and mica. However, the diffraction peaks of quartz, kaolinite and mica are no longer contained in the XRD image of the alkali melt, indicating that after alkali melting, the quartz, kaolinite and mica structures in the coal gangue have been destroyed and transformed into soluble ones. Aluminosilicate, the obtained product contains some impurity peaks, but at 2θ = 20.2°, 26.3°, 46.1°, 38.26°, 73.2°. There is an obvious FAU diffraction peak near 04°. 

It can be seen from the SEM image in Figure 2 that the surface of coal gangue is rough and has a lamellar structure. Kaolinite is a silicate with a layered structure, and mica is also an aluminosilicate with a layered structure. The SEM results
and the XRD results of coal gangue can confirm each other. In the SEM image of the synthesized product, the octahedral structure with uniform particles and complete structure can be clearly seen, and its size is about 5 μm, which is the structural shape of NaX zeolite.

In the infrared spectrum of the product, the bending vibration bands of the T-O (T Si or Al) bond appear near 490 cm$^{-1}$ - 520 cm$^{-1}$, The –OH group appears near at ranges 3380 cm$^{-1}$ - 3460 cm$^{-1}$, the C-H appears near at ranges 1020 cm$^{-1}$ - 1050 cm$^{-1}$, the C=C appears near at ranges 1900 cm$^{-1}$ - 1600 cm$^{-1}$ but it Changed a bit on their violent included, the =C-H group appears near at ranges 760 cm$^{-1}$ -
780 cm$^{-1}$ (see Figure 3). These characteristic bands are consistent with the infrared characteristic bands of typical NaX$_{zeolite}$, indicating that the prepared materials have the typical framework structure of NaX$_{zeolite}$.

By using BET, the specific surface area and porosity of the NaX$_{zeolite}$ and coal gangue analyzed. Coal gangue surface area is about 238.1 m$^2$/g, the total pore volume is 0.212 m$^3$/g, the specific surface area and NaX$_{zeolite}$ molecular sieves synthesized 380.1 m$^2$/g total pore volume is 0.211 m$^3$/g, synthesized by low-grade kaolin.

### 3.2. Effect of Parameters

#### 3.2.1. The Effect of Adsorbent Dosage

For investigation of effect of adsorbent dosage, 100 mL of simulated wastewater (Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$) single metal mass concentration of 200 mg/L was treated with NaX$_{zeolite}$ of different dosage amount (0.03, 0.05, 0.1, 0.2, 0.40 and 0.5 g). The adsorption results showed that the removal rate of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ were increased with the increasing of NaX$_{zeolite}$ dosage, while the adsorption capacity decreased with the increase of NaX$_{zeolite}$ dosage. In the range of 0.03 to 0.5 g/L, the removal rate increased rapidly (see Figure 4). This is because increasing the amount of NaX$_{zeolite}$ provides more adsorption sites and promotes the progress of adsorption. When the dosage of NaX$_{zeolite}$ reaches 0.2 g/L, the removal rate of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ is 70.6%, 60.3% and 61.5%. As the amount of NaX$_{zeolite}$ continues to increase, the removal of heavy metal ions finally reached more than 99% at 0.5 g adsorbent dosage, but the growth was slow, because most of the heavy metal ions had been adsorb, and most of the adsorbent was reached to equilibrium. From the economical point of view, the dosage of 0.2 g/L molecular sieve was selected as the optimal dosage for subsequent experiments.

![Figure 3. Infrared spectrum of the prepared product.](image)
3.2.2. Effect pH

For effect of initial pH value, 0.2 g of the prepared NaX zeolite was added to the simulated wastewater and set the pH values 3, 4, 5, 6, 7, 8, and 9, respectively. The concentration of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ was measured after filtered with 0.45 µm membrane filter. The results show that the initial pH value of simulated wastewater is an important factor in the adsorption process. It can be seen from Figure 5 that the adsorption capacity of NaX zeolite is lower at pH = 3. With the increase of pH value, the removal rate of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ also increased gradually. In general, adsorption heavy metals by NaX zeolite are weak in acidic condition. The result shows good adsorption capacity and good adaptability under pH (5, 6) conditions. But when the solution is alkaline, Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ and OH$^-$—produce precipitation. Adsorption is weak and decreases metal precipitation even though the removal rate remains the same. Heavy metal ions will ionize and form metal complexes during adsorption based on wastewater’s pH value at the beginning of the process. Heavy metal ions will ionize and form metal complexes during adsorption based on wastewater’s pH value at the beginning of the process. Therefore, pH = 6 for Pb$^{2+}$ and pH = 5 for Cu$^{2+}$ and Cd$^{2+}$ was chosen as the optimal initial pH value of the solution in the experiment.

3.2.3. The Effect of Temperature

For the effect of temperature, 0.2 g of the prepared NaX zeolite was added to 100 mL of 200 mg/l of (Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$) simulated wastewater, and the adsorption was shaken for 60 min at 15°C, 25°C, 35°C and 45°C, respectively. The concentration of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ was measured after filtered with 0.45 µm filter membrane. Analysis of Figure 6 shows that the adsorption capacity rate of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ on NaX zeolite was increase with the increasing of temperature. When the temperature increased from 10°C to 45°C, the adsorption capacity of...
NaX zeolite for Pb\textsuperscript{2+}, Cu\textsuperscript{2+} and Cd\textsuperscript{2+} increased from 63, 56.5 and 57.5 mg/g to 79.5, 66 and 66.5 mg/g. NaX zeolite is able to adsorb heavy metals at higher temperatures, although the increase in adsorption is not large, so the temperature does not necessarily affect the adsorption process.

### 3.2.4. The Effect of Time

The Effect of the contact time (0, 5, 10, 15, 30, 45, 75 and 100) minutes on adsorption of Pb\textsuperscript{2+}, Cu\textsuperscript{2+} and Cd\textsuperscript{2+} by NaX zeolite in Figure 7 at shows that in 60 minutes NaX zeolite adsorbent was almost reached equilibrium, and the absorption
was rapid in the first 20 minutes and almost 50% of the adsorption was done due to the active groups and large surface area NaX_{zeolite} gave this ability to adsorbent. After 60 minutes, attraction of the adsorption process was silenced. The highest adsorption was done after 60 minutes for Pb^{2+}, Cu^{2+} and Cd^{2+} were 71.5, 62 and 60.5 mg/g, respectively.

3.3. Isothermal Adsorption Model

Isothermal Langmuir, Freundlich and Temkin models for well-known adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} by NaX_{zeolite}. 0.2 g of the prepared NaX_{zeolite} was added to the simulated wastewater with Pb^{2+}, Cu^{2+} and Cd^{2+} mass concentrations of 25, 50, 100, 150, 200, 250 and 300 mg/L, respectively. The adsorption was carried out with shaking at 25°C for 60 min. After the adsorption is over, the concentration of Pb^{2+}, Cu^{2+} and Cd^{2+} was measured after filtered with 45 μm filter paper. It can be seen from Figure 8 and Table 1 that the adsorption effect of NaX_{zeolite} on heavy metal ions is closer to Langmuir model. The correlation coefficient of the Langmuir model (R^2 = 0.99, 0.983 and 0.978) for Pb^{2+}, Cu^{2+} and Cd^{2+}, greater than the correlation coefficient of the Freundlich model (R^2 = 0.838, 0.859 and 0.78) for Pb^{2+}, Cu^{2+} and Cd^{2+}, and the correlation coefficient of the Temkin model (R^2 = 0.935, 0.879 and 0.886) for Pb^{2+}, Cu^{2+} and Cd^{2+}. According to the fitting results in Table 1, the separation coefficient $R_L$ was calculated. For different initial concentrations, the RL of Pb^{2+}, Cu^{2+} and Cd^{2+} is between 0 and 1. It shows that the adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} NaX_{zeolite} belongs to preferential adsorption, has a strong affinity. The maximum saturated adsorption capacity of Pb^{2+}, Cu^{2+} and Cd^{2+} by coal gangue-based NaX_{zeolite} reached 87.33 mg/g, 87.95 mg/g and 88.57 mg/g. There is a strong relationship between the adsorption capacities of different metal ions and the chemical properties of the element and...
Figure 8. Langmuir’s, Freundlich’s and Temkin isotherm plots for the adsorption of Pb²⁺, Cu²⁺ and Cd²⁺.

Table 1. Fitting results of isotherm adsorption.

| isotherm’s           | parameters | Pb²⁺            | Cu²⁺            | Cd²⁺            |
|----------------------|------------|-----------------|-----------------|-----------------|
|                      | Qmax (mg/g) | 88.3392226      | 87.9507476      | 88.5739593      |
| Langmuir model       | KL (L/mg)  | 0.07740171      | 0.03441908      | 0.03744734      |
|                      | R²         | 0.99006         | 0.98383         | 0.97889         |
|                      | Kf         | 12.5504703      | 8.06956269      | 8.70422282      |
| Freundlich model     | 1/n        | 0.39361         | 0.44191         | 0.4312          |
|                      | R²         | 0.83899         | 0.85904         | 0.78061         |
|                      | BT (J·mol⁻¹) | 14.32466       | 14.02034        | 13.91482        |
| Temkin model         | KT (L·mg⁻¹) | 1.49625905      | 0.71378433      | 0.81256449      |
|                      | R²         | 0.93553         | 0.87903         | 0.86629         |
the adsorbent.

4. Conclusion

Finally, the hazardous heavy metals of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ were successfully removed from the simulated wastewater using blending and grafting procedures. FTIR, XRD, SEM, and EDX tests were used to establish the adsorbent’s production and applicability. The si-o-al and si-na bond creation was confirmed by the FTIR data. XRD tests clearly demonstrated the change in crystalline nature caused by the alteration of the NaX$_{zeolite}$ composite. SEM analysis was used to establish the material’s compatibility for the adsorption procedure due to its rough surface and porous structure. The corresponding adsorption isotherms were tested to explore their adsorption behavior. The Langmuir model was shown to be the most appropriate for describing the adsorption of Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ on NaX$_{zeolite}$ with $q_{max}$ 88.3, 87.9 and 88.5 mg/g with linear regression coefficients ($R^2 > 0.979$) for all three metals respectively. NaX$_{zeolite}$ can be used as a cost-effective adsorbent to remove heavy metal contaminants in wastewater.

Conflicts of Interest

The authors declare no conflicts of interest.

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