Alkaline Extraction of Organomineral Potassium Humate from Coal Mining Waste

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Abstract: Organomineral potassium humate was extracted from coal mining waste from the Lenger deposit (Turkestan region, Kazakhstan) by alkaline extraction using an aqueous solution of potassium hydroxide. The time and temperature of the process were investigated for the degree of extraction and yield of the product. A comprehensive study of the physicochemical properties of the raw material and the resulting production potassium humate was carried out by chemical analysis, scanning electron microscope, energy dispersion, IR-Fourier spectrometric and X-ray diffractographic analyses. The maximum degree of extraction and yield of the product was achieved at 80 °C and 90 min. Moreover, the experimental data were subjected to kinetic processing, as a result of which it was established that the process of extraction of potassium humate occurs in the external diffusion region.

Keywords: potassium humate; organomineral; coal mining waste; activation energy; alkaline extraction

1. Introduction

Currently, the use of environmentally friendly and safe substances in agriculture is becoming relevant. One of the directions of the future is the use of humic substances. Humic substances are high-molecular compounds of natural origin, which are formed as a result of the oxidation of coal or changes in dead biomass, and are shapeless formations with a chaotic structure of dark brown color, which can dissolve or swell in water. [1]. These compounds do not have a single chemical formula, but it is known that their main structures are aromatic rings and functional groups (hydroxyl, carboxyl, carbonyl, alkyl and methoxyl) [2]. In addition to aromatic rings, the substance may contain polypeptide and polysaccharide fragments. Even simple compounds, such as fulvic acids, have a complex chemical structure.

Since the structure of the humic substances molecule cannot be quantitatively described by traditional methods, researchers have developed a classification method based on solubility in alkalis and acids. Thus, humic substances are classified into three categories: humins—substances insoluble neither in acids nor in alkalis; humic acids—substances insoluble in acids, but soluble in alkalis; fulvic acids—substances soluble in acids and alkalis [3]. Humic acids are fractions of humic substances that are soluble in an alkaline medium, semi-soluble in water, and insoluble in an acidic medium. This classification parameter may vary depending on the content of humic acids, pH and ionic bonds. Due to their amphiphilic nature, humic acids form micelle-like structures called false micelles in a neutral and acidic environment. This property is used for use in water treatment plants and to increase the solubility of hydrophobic preparations in water [4,5]. Humic substances contain various functional groups, the number of which depends on the origin, timing, climate and environmental conditions during the extraction and production of humic substances [6].
The various functions of humic substances mainly relate to the functional groups of phenols and carboxylic acid. These properties provide humic substances with many positive properties, such as improved plant growth and complex formation with heavy and variable metals, which means that they can remove heavy metals from the body and form chelated compounds. In addition, their antiviral and anti-inflammatory activity has been proven [7]. It has been proven that the presence of phenols, carboxylic acids and quinones in the structure of humic substances is associated with their antioxidant, fungicidal and bactericidal activity [8].

In the literature, a number of authors have a common opinion about the chemical composition of humic substances obtained from various sources [9,10]. Thus, substances prepared on the basis of humic substances contain 50% carbon, 35% oxygen and 5% hydrogen, and the remaining percentage is nitrogen and sulfur [11]. The largest amount of carbon is contained in hard and brown coal, and its content can reach 60–65%. The ability of humic substances to bind cationic metals and complexes makes them useful in various fields. Thus, they ensure the transfer of micronutrients from soil to plants and from feed additives to the body of farm animals [12]. In addition, humic substances reduce the content of heavy metals in soil, water and living organisms [13].

The main source of humic substances is brown coal. Its reserves in Kazakhstan amount to 34 billion tons [14]. It was found that brown coal differs in chemical composition compared to other sources of humic substances. It contains various trace elements that can be used in the production of animal feed additives [15].

The main methods of isolation of humic substances include alkaline extraction with ammonia solutions or potassium/sodium hydroxides. Such methods convert humic substances into water-soluble salts, that is, potassium or sodium humates with high biological activity. This method is practically waste-free, therefore it is widely used in many countries [16,17].

The aim of this research was to complete a comprehensive study of the process of extraction of potassium humate from coal mining wastes of the Lenger deposit, considering the kinetic processing of experimental data, and the composition and structure of the resulting potassium humate. According to known information, these wastes have a complex organomineral composition and are a valuable component for the synthesis of humic substances. In addition, the disposal of these wastes, the volume of which is more than 6 million tons, is environmentally relevant for the local population. The scientific novelty lies in the use of technogenic resources in the form of coal mining waste for the extraction of organomineral potassium humate. The scientific interest of the authors is founded in obtaining organomineral complex compounds used in the agro-industrial sector of the economy.

2. Materials and Methods

The extraction of potassium humate was carried out according to a well-known technique [18], where the sample of coal mining waste is leached with an alkaline solution of potassium pyrophosphate and stirred for 1 h. The resulting suspension was centrifuged, the solution was decanted and collected in a conical flask, and the insoluble residue was washed twice with a solution of potassium hydroxide. The suspension was centrifuged after each wash by collecting the washing solution into another flask. The washed precipitate was transferred to a flask, and a solution of potassium hydroxide was added and heated for 2 h in a boiling water bath. After cooling to room temperature, the contents of the flask were centrifuged for 15 min.

The effectiveness of the studied process was evaluated by the extraction degree indicator (α), which was determined by the following formula:

$$\alpha = \frac{(A - B) \times 100}{A}$$  \hspace{1cm} (1)

where $A$ is the initial concentration of the alkaline solution, mol/L; and $B$ is pulp concentration, mol/L.
The chemical analysis was carried out in accordance with the regulatory documents of the analysis: determination of the content of silicon dioxide according to the method based on the formation of a blue reduced silica-molybdenum complex, the optical density of which was measured by differential photometry. The method for determining the mass fraction of iron oxide was based on the formation of an orange-red complex compound of divalent iron with orthophenanthroline or its analogues that is stable for several hours. The method for determining the mass fraction of aluminum oxide was based on the formation of a complex compound of trilon B with aluminum at pH 2–3 and titration of an excess amount of trilon B with zinc acetic acid at pH 5.5 with an orange xylene indicator. The method for determining the mass fraction of oxide was based on measuring the radiation intensity of the resonant lines of elements formed in the flame of a gas–air mixture when the analyzed solutions and comparison solutions are introduced into it. The radiation intensity of the sodium line was measured at 590 nm, and potassium at 770 nm. Carbon, hydrogen and nitrogen were determined simultaneously from a single sample using a corresponding device—a CHN analyzer. When the sample was burned at a high temperature in an oxygen atmosphere, carbon, hydrogen and nitrogen were quantitatively converted into the corresponding gaseous substances (CO, HO, N₂/NOₓ). Nitrogen oxide (NOₓ) formed during combustion was reduced to N₂ before the gases entered the detector. Carbon dioxide, water vapor and elemental nitrogen in the gas stream were quantified by suitable instrumental methods.

The microstructures of the initial sample and the resulting product, as well as the element-weight composition, were determined using a scanning electron microscope JSM6490 LV, and infrared spectroscopy was performed on SHIMADZU IR PRESTIGE-21 equipment. X-ray diffraction analysis was carried out on D8 Advance (Bruker) equipment, scanning speed −0.1–100 degrees/min, shooting angle 3–180°θ. The resulting diffractograms were processed in EVA software.

Kinetic processing of experimental data was carried out in accordance with the equation:

\[ 1 - \frac{2}{3} \alpha - (1 - \alpha)^{\frac{2}{3}} = \kappa \cdot \tau \]  

To calculate the “apparent” activation energy of the potassium humate extraction process, the following formula was used:

\[ E_A = 8.314 \cdot \tan \varphi \cdot (kJ/mol) \]  

Statistical processing of the received data was carried out in the STATISTICA Visual Basic (SVB) software.

3. Results and Discussion

3.1. Characteristics of Coal Mining Waste

Brown coal is a solid fossil fuel of humus nature and a low degree of carbonification. In the series of fossil coals, brown coal occupies the lowest stage, a transitional link between peat and hard coal [19]. Brown coal deposits in the city of Lenger in the Turkestan region were exploited from the time of tsarist Russia until the 1960s. At that time, mining and open-pit methods were used for the extraction of brown coal. As a result, there are currently seven dumps accumulated in the form of landfills on the territory of the city. Samples for experimental studies were taken from landfill No. 1 (Figure 1).
As can be seen from the map, four landfills are located on the territory of the city, and the remaining three are in nearby areas. The total volume of all landfills is approximately 34 thousand tons. Wind erosion significantly affects the ecological situation in the city and nearby villages, although the impact of these types of waste on air quality in the city has not been studied. However, there are publications about the complaints of local residents about coal dust, which rises during winds and hurricanes [20,21]. The impact of coal dust on the human body is very toxic, causing chronic lung diseases [22]. In this regard, the study of physico-chemical properties and the search for methods of coal mining waste disposal is relevant.

Chemical, elemental-weight and microstructural analysis of samples taken from this dump were carried out. The surfaces of the studied samples were examined in the spectrum at 40-fold magnification. The results of the study are presented in Tables 1 and 2 and Figure 2.

**Table 1. Chemical composition of coal mining waste.**

| Compounds | Composition, % | Standard Deviation, s, \( n = 8 \) |
|-----------|----------------|---------------------------------|
| C         | 48.19          | 1.84                            |
| H         | 5.30           | 1.21                            |
| N         | 2.12           | 0.43                            |
| Al\(_2\)O\(_3\) | 5.14       | 2.20                            |
| SiO\(_2\)  | 9.86           | 2.13                            |
| K\(_2\)O   | 0.91           | 0.56                            |
| CaO        | 0.29           | 0.73                            |
| Fe\(_3\)O\(_3\) | 5.73       | 1.05                            |
Table 2. Element-weight composition of coal mining waste.

| Element | Weight, % | Oxides       | In Terms of Oxides, % |
|---------|-----------|--------------|----------------------|
| C       | 43.00     | -            | -                    |
| O       | 39.43     | -            | -                    |
| Al      | 3.79      | Al₂O₃        | 7.16                 |
| Si      | 6.42      | SiO₂         | 13.73                |
| S       | 1.03      | SO₃          | 2.57                 |
| K       | 0.40      | K₂O          | 0.48                 |
| Ca      | 0.43      | CaO          | 0.60                 |
| Fe      | 5.49      | Fe₂O₃        | 7.85                 |

Figure 2. Microstructure and energy dispersion analysis of coal mining waste.

According to the above data, the main part of coal mining waste is carbon, as well as substances such as sulfur, aluminum and silicon oxides. Potassium and calcium compounds are also present in small amounts. While in the microstructure of the obtained sample, minerals of sulfur, iron and calcium compounds are represented by whole clusters, minerals in the form of a small hexagonal crystal prove the presence of calcium aluminates. The silicon-containing compounds in the test sample are described by fine-type chain compounds [23].

The results of X-ray diffraction analysis of coal mining waste are shown in Figure 3.

Figure 3. X-ray diffraction analysis of coal mining waste.
According to the data shown in the figure, the structure of coal mining waste was characterized by minerals such as quartz, kaolinite and muscovite. It was found that a significant part of the structure was occupied by quartz-type minerals (90.4%). Moreover, compounds in the form of kaolinite and muscovite had fractions of 7.1% and 2.4%, respectively. X-ray diffraction analysis showed only the inorganic part of the original sample. To describe the organic part the method of IR spectral analysis was used, carried out on a modern IR-Fourier device Shimadzu IR Prestige-21. The results of the study are presented in Table 3 and Figure 4.

Table 3. Peaks of IR spectral analysis of coal mining waste.

| No. | Peak | Intensity | Corr. Intensity | Base (H) | Base (L) | Area | Corr. Area |
|-----|------|-----------|----------------|---------|---------|------|------------|
| 1   | 555.50 | 87.320    | 3.204          | 570.93  | 540.07  | 1.610 | 0.269      |
| 2   | 597.93 | 86.390    | 3.257          | 613.36  | 574.79  | 2.111 | 0.317      |
| 3   | 644.22 | 83.190    | 0.746          | 648.08  | 617.22  | 2.034 | 0.092      |
| 4   | 694.37 | 80.421    | 2.647          | 721.38  | 655.80  | 5.771 | 0.488      |
| 5   | 759.10 | 81.668    | 0.230          | 759.38  | 725.23  | 2.942 | 0.033      |
| 6   | 779.24 | 81.211    | 0.717          | 786.96  | 763.81  | 2.056 | 0.043      |
| 7   | 794.67 | 81.701    | 0.746          | 860.25  | 786.96  | 5.389 | −0.173     |
| 8   | 910.40 | 82.571    | 4.018          | 948.98  | 860.25  | 6.375 | 0.782      |
| 9   | 1010.70| 77.444    | 0.798          | 1014.56 | 952.84  | 5.143 | 0.099      |
| 10  | 1029.99| 76.948    | 1.394          | 1153.43 | 1018.41 | 12.500| 0.452      |
| 11  | 1238.30| 86.867    | 0.109          | 1269.16 | 1234.44 | 2.106 | 0.020      |
| 12  | 1361.74| 88.043    | 0.198          | 1489.05 | 1357.89 | 6.502 | 0.241      |
| 13  | 1504.48| 90.824    | 0.075          | 1508.33 | 1492.90 | 0.630 | 0.000      |
| 14  | 1589.34| 87.409    | 3.778          | 1674.21 | 1516.05 | 7.906 | 1.583      |
| 15  | 1697.36| 90.939    | 1.460          | 1816.94 | 1678.07 | 3.745 | 0.380      |
| 16  | 2854.65| 93.339    | 0.902          | 2881.65 | 2827.64 | 1.472 | 0.080      |
| 17  | 2924.09| 92.271    | 1.826          | 2989.66 | 2881.65 | 3.198 | 0.364      |

Figure 4. IR spectra of coal mining waste.

According to the IR spectrogram, the composition of coal mining waste contained compounds C-H, O-H, occurring at wavelengths 3700–2630 cm\(^{-1}\), whereas the wavelengths 1900–1500 cm\(^{-1}\) were characteristic of compounds with a double bond C=C. Diffraction peaks between 1230 and 850 cm\(^{-1}\) indicated the presence of organosilicon compounds such as Si-O-C, Si-O-Si. Moreover, IR peaks between 870–690 cm\(^{-1}\) and 650–520 cm\(^{-1}\) were characteristic of sulfo- and aluminate compounds [24].
According to the standard [25] applied to solid waste obtained during coal mining, this type of waste is classified as high-carbon in terms of carbon content, and also in terms of the content of other impurity elements such as S, Fe, Al and Ca, with low sulfur, low iron, low alumina and low calcium.

3.2. Kinetic Study of the Alkaline Extraction Process

This section presents the results of studies to determine the regime parameters of the process of alkaline extraction of coal mining waste with potassium hydroxide. Crushed coal mining waste was used to conduct experimental studies. Taking into account the known data on humate extraction [16], the duration of the process was selected within 60–100 min, and the concentration of potassium hydroxide was 1%. The effectiveness of the investigated process was evaluated by the degree of extraction (\(\alpha\)). Experimental studies were carried out at various temperature conditions (60–100 °C).

In the process of alkaline extraction by the recalculation of pH according to the formula \([H^+] = 10^{-pH}\), the concentration of pulp C, mol/L was observed. Using this value, the degree of extraction (\(\alpha\)) was calculated according to Formula (1). Moreover, one of the factors for evaluating the effectiveness of the process was the yield of the product actually obtained during the experiment. The results obtained on the effect of temperature and time on the process under study are presented in Figures 5 and 6 and in Table 4.

![Figure 5](image1.png)

Figure 5. Influence of temperature and time on the degree of extraction.

![Figure 6](image2.png)

Figure 6. Influence of temperature and time on product yield.
Table 4. Results of experimental studies on the extraction of potassium humate.

| Time, min | pH   | C, mol/L        | α, %  | Product Yield, gr |
|-----------|------|-----------------|-------|-------------------|
|           |      |                 |       |                   |
| 60 °C     |      |                 |       |                   |
| 60        | 9.69 | 0.0000000000204 | 37.11 | 40.76             |
| 70        | 9.61 | 0.0000000000245 | 49.73 | 45.51             |
| 80        | 9.54 | 0.0000000000288 | 56.08 | 49.18             |
| 90        | 9.46 | 0.0000000000346 | 61.12 | 53.75             |
| 100       | 9.31 | 0.0000000000489 | 64.76 | 56.57             |
| 80 °C     |      |                 |       |                   |
| 60        | 8.57 | 0.000000002691  | 48.85 | 52.19             |
| 70        | 8.49 | 0.000000003235  | 57.16 | 57.28             |
| 80        | 8.33 | 0.000000004677  | 70.70 | 65.21             |
| 90        | 8.25 | 0.000000005623  | 87.03 | 73.84             |
| 100       | 8.11 | 0.000000007762  | 85.98 | 71.66             |
| 100 °C    |      |                 |       |                   |
| 60        | 8.03 | 0.000000009332  | 62.96 | 62.71             |
| 70        | 7.96 | 0.000000010964  | 66.84 | 68.16             |
| 80        | 7.92 | 0.000000012022  | 78.09 | 66.94             |
| 90        | 7.91 | 0.000000012302  | 89.01 | 65.36             |
| 100       | 7.90 | 0.000000012589  | 88.12 | 62.23             |

From the experimental work performed, it was determined that the degree of extraction (α) rises with increasing time and temperature. The decrease in the yield of the product at high 100 °C and a time duration of 90–100 min is due to the fact that during the research there was intense evaporation of the pulp, although the degree of extraction at these values was higher. Experimental studies conducted at 80 °C and 90 min were determined as optimal regime parameters of potassium humate extraction.

Kinetic processing of experimental data of potassium humate extraction process from coal mining waste was performed according to Formula (2), and is shown in Table 5.

Table 5. Results of experimental data processing.

| α (Unit Fraction) | 1 − 2α − (1 − α)³ | τ |
|-------------------|---------------------|---|
| 60 °C             |                     |   |
| 0.3711            | 0.321241            | 60|
| 0.4973            | 0.303349            | 70|
| 0.5608            | 0.291102            | 80|
| 0.6112            | 0.279459            | 90|
| 0.6476            | 0.269809            | 100|
| 80 °C             |                     |   |
| 0.4885            | 0.304858            | 60|
| 0.5716            | 0.288761            | 70|
| 0.7070            | 0.251387            | 80|
| 0.8703            | 0.174138            | 90|
| 0.8598            | 0.180902            | 100|
| 100 °C            |                     |   |
| 0.6296            | 0.274721            | 60|
| 0.6684            | 0.263764            | 70|
| 0.7809            | 0.222527            | 80|
| 0.8901            | 0.160306            | 90|
| 0.8812            | 0.166712            | 100|

Based on the data in Table 5, a dependency plot of $1 - \frac{2}{3}a - (1 - a)^{\frac{2}{3}} = f(\tau)$ was constructed (Figure 7).
The reaction rate constants are found along the tangent of the angle of the straight line to the abscissa axis shown in Figure 7:

- at 60 °C, \( \tan \varphi_1 = k_1 = 0.0005458 \);
- at 80 °C, \( \tan \varphi_2 = k_2 = 0.0003379 \);
- at 100 °C, \( \tan \varphi_3 = k_3 = 0.0001375 \).

The “apparent” activation energy of the process of alkaline extraction of potassium humate was determined graphically. For this purpose, a plot of the dependence \( \ln k = f \left( \frac{1}{T} \right) \) was constructed (Figure 8).

According to the data in Figure 8 and Formula (3), the “apparent” activation energy of the potassium humate extraction process from coal mining waste was calculated. As a
result of calculations, it was found that \( E_A = 10.01 \text{ kJ/mol} \). This, in turn, indicates that the extraction process of potassium humate occurs in the external diffusion zone.

### 3.3. Characteristics of the Obtained Potassium Humate

The results of a comprehensive study of the composition and structure of the obtained potassium humate are given below.

Based on chemical and elemental-weight analysis, carbon and potassium oxide were found to occupy a predominant share (Tables 6 and 7, Figure 9). The content of impurity compounds such as aluminum, silicon and iron oxides decreased significantly. This was due to the fact that they passed into the washing alkaline solution during extraction. The production of potassium humate with this composition can be used in the form of fertilizers and plant growth stimulants.

#### Table 6. Chemical composition of production potassium humate.

| Compounds | Composition, % | Standard Deviation, s, \( n = 8 \) |
|-----------|----------------|-------------------------------------|
| C         | 47.29          | 1.34                                |
| H         | 5.83           | 1.15                                |
| N         | 2.28           | 0.81                                |
| CaO, %    | 0.42           | 1.29                                |
| K\(_2\)O, %| 19.21          | 2.60                                |
| Al\(_2\)O\(_3\), %| 0.63 | 1.11                                |
| SiO\(_2\), %| 0.97           | 1.56                                |
| Fe\(_2\)O\(_3\), %| 0.36 | 0.94                                |

#### Table 7. Element-weight composition of production potassium humate.

| Element | Weight, % | Oxides | In Terms of Oxides, % |
|---------|-----------|--------|-----------------------|
| C       | 42.30     | -      | -                     |
| O       | 41.88     | -      | -                     |
| Al      | 0.64      | Al\(_2\)O\(_3\) | 1.20                  |
| Si      | 0.85      | SiO\(_2\) | 1.81                  |
| S       | 0.33      | SO\(_3\) | 2.57                  |
| K       | 14.11     | K\(_2\)O | 17.01                 |
| Na      | 0.17      | Na\(_2\)O | 0.22                  |

#### Figure 9. Microstructure of potassium humate extracted from coal mining waste.

It was established that the sample under study had a complex crystalline mineral structure. The presence of aluminosilicate compounds in the microstructure of the sample under study indicated the presence of fine-grained crystals. Potassium compounds are characterized by crystals of split and hexagonal shapes, and crystals of a long structure indicate the presence of calcium and iron compounds [23].

IR spectroscopy is one of the methods that enable the study of the structural features and composition of functional groups. To determine the qualitative composition of the
organic part of the resulting product and describe its organic structure, an IR spectral analysis was performed on the Shimadzu IR-Prestige 21 device (Table 8, Figure 10).

Table 8. Peaks of the IR spectra of potassium humate.

| No. | Peak   | Intensity | Corr. Intensity | Base (H)  | Base (L)  | Area   | Corr. Area |
|-----|--------|-----------|-----------------|-----------|-----------|--------|------------|
| 1   | 601.79 | 72.808    | 0.759           | 609.51    | 597.93    | 1.576  | 0.033      |
| 2   | 648.08 | 63.858    | 1.094           | 651.94    | 613.36    | 6.041  | 0.039      |
| 3   | 667.37 | 61.698    | 0.910           | 675.09    | 675.80    | 3.933  | 0.062      |
| 4   | 682.80 | 61.226    | 1.322           | 871.82    | 675.09    | 31.869 | 1.708      |
| 5   | 883.40 | 79.655    | 0.946           | 914.26    | 871.82    | 3.960  | 0.052      |
| 6   | 937.40 | 79.228    | 4.267           | 1014.56   | 914.26    | 7.291  | 0.718      |
| 7   | 1072.42| 81.501    | 9.272           | 1103.28   | 1018.41   | 5.402  | 1.765      |
| 8   | 1153.43| 85.666    | 4.698           | 1195.87   | 1118.71   | 4.407  | 0.994      |
| 9   | 1643.35| 82.088    | 13.154          | 1739.79   | 1566.20   | 8.961  | 5.333      |
| 10  | 3240.41| 74.757    | 0.327           | 3244.27   | 2916.37   | 25.535 | 0.744      |
| 11  | 3263.56| 74.475    | 0.114           | 3271.27   | 3248.13   | 2.945  | 0.009      |
| 12  | 3332.99| 74.218    | 0.053           | 3336.85   | 3302.13   | 4.473  | 0.009      |

Figure 10. IR spectra of potassium humate.

The results of IR-Fourier spectroscopy established that the wave numbers between 3400 and 3300 cm\(^{-1}\) were characteristic of hydroxyl groups, mainly interconnected by hydrogen bonds. The same opinion was held by scientists in other works [26]. Nitrogen-containing compounds in the structure of humic acid were determined at maxima with values of 3200–3100 cm\(^{-1}\). According to other data, nitrogen-containing compounds in these absorption regions show the presence of amides and amines with hydrogen bonds [27]. Absorption peaks in the region of 1650–1531 cm\(^{-1}\) are characterized by carboxyl groups. In other studies [26,28,29], this value indicates aromatic stretching of the phenolic ring, and the presence of carboxylate anions \(\nu_{\text{C-O}}\). It is also necessary to take into account the fact that quinones are characterized in the same area [29]. Valence fluctuations of hydroxyl groups of the aliphatic series in the absorption region of 1150–1000 cm\(^{-1}\) are also noticeable. The following absorption peaks correspond to inorganic compounds and impurity elements in the composition of coal mining waste. For example, 975–900, 795–750 cm\(^{-1}\) correlate to Si-O valence vibrations, and 660–420 cm\(^{-1}\) to Si-\(\Omega\)-Al valence vibrations [30,31].
The results of the X-ray diffraction analysis carried out on the D8 Advance (Bruker) device in order to describe the inorganic structure of the extraction potassium humate are shown in Figure 11.

Figure 11. Results of X-ray diffraction analysis of potassium humate.

The diffractogram shown in the figure shows that the inorganic part of potassium humate contained minerals such as kalcinite 57.6% and buetschlite 32.5%, as well as quartz 9.9%. The presence of minerals such as kalcinite and buetschlite, which are well soluble in water, indicates the reaction between coal mining waste and an aqueous solution of potassium hydroxide.

The ecological and socio-economic advantages of using coal mining waste for the extraction of potassium humates is to improve the ecological situation of the Lenger by utilizing these technogenic resources. In addition, Lenger is located in the Turkestan region of the Republic of Kazakhstan, where agriculture is very developed. Melons and cotton crops, fruits and berries are grown there. This region accounts for about 70% of agricultural exports in the CIS and Europe. In this regard, the proposed method of obtaining organomineral potassium humate from coal mining waste would help local farmers and agrarians to improve soil fertility [32], to use this product as a plant growth stimulant, to relieve plant stress after treatment with pesticides [33], and to obtain stable yields [34]. The use of technogenic resources significantly reduces the cost of the resulting product, the results of which are very profitable for the agro-industrial complex.

4. Conclusions

In this research, which was a scientific qualification work based on the study of the interaction of brown coal mining waste with impurity elements with potassium hydroxide, the actual scientific task of improving the environmental safety of the disposal of these wastes was solved. The optimal operating parameters of the potassium humate extraction process were established: temperature 80 °C, time 90 min. The study of the kinetics of this process made it possible to determine the “apparent” activation energy of the process equal to 10.01 kJ/mol. This means that the process of the extraction of potassium humate occurs in an externally diffusive region, which is characterized by the rate of diffusion of reagents from the flow to the outer surface. As a result, it is necessary to use finely ground raw materials to intensify the process of the alkaline extraction of potassium humate from coal mining waste in the conditions of an external diffusion regime.
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