

Article

Processing of Phosphoric Solid Waste by Humic Acid Leaching Method

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Abstract: This article presents the results of research on the leaching of solid phosphorus-containing waste with humic acid. Such waste includes the by-products of the electrothermal processing of phosphate raw materials—phosphorus sludge and cottrel dust. Chemical and X-ray diffraction analyses have been used to study their composition and phase structure, according to which these substances have an amorphous structure. The leaching of phosphoric sludge and cottrel dust was investigated by varying the main parameters. The obtained data were processed using the method of formal kinetics to study the features of the process. The reaction rate constants and the apparent activation energy were calculated, and the values found made it possible to determine that the process under study is limited by diffusion. The scientific novelty of the article is the use of humic acid for leaching phosphoric solid waste as opposed to traditional methods. This new method may offer improved efficiency, reduced environmental impact, and a potential alternative solution for the processing of phosphoric waste.

Keywords: phosphoric sludge; cottrel dust; humic acid; phosphoric acid; amorphous structure



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1. Introduction

The production of phosphorus-containing products is one of the important branches of the chemical industry. This production is caused by the formation of various types of technogenic waste that harm the surrounding environment. To date, the production of yellow phosphorus and wet-process phosphoric acid (WPA) is carried out according to known traditional methods [1,2]. Improvements or measures to reduce various emissions and waste have not led to the expected results. Phosphorus production has generated massive amounts of solid and liquid waste since the 1920s and continues to do so today [3,4]. For example, in Kazakhstan, when processing phosphate raw materials for yellow phosphorus (electrothermal method), so-called cottrel dust and phosphorus sludge are formed. Cottrel dust is formed in electrofilters during furnace gas purification [5]. Phosphoric sludge is a by-product of a colloidal system, and it is formed during the condensation of yellow phosphorus [6]. The chemical composition of both wastes is different. For example, there is a lot of carbon in the composition of cottrel dust due to the use of coke for reduction in ore-thermal furnaces. Furthermore, the useful component phosphorus is dumped when impurity compounds are captured in electrofilters. In view of this, there is more phosphorus in its composition. Compared with cottrel dust, phosphorus sludge contains less phosphorus and carbon. It should be noted, however, that both wastes contain elemental phosphorus and mineral impurities.

Due to the excessive accumulation of these types of waste, industrialists and researchers are still searching for effective methods of disposal. This problem's scientific research can be divided into several areas: construction, heat treatment and production of especially pure substances, and mineral fertilizer production. In the USA, phosphoric

sludge was used as a filler for road construction, along with Portland cement and concrete (however, a ban was introduced in 1977) [7]. With the help of heat treatment, elementary phosphorus can be reduced [8,9]. To carry out such a process, phosphoric sludge is burned in special installations in the form of rotating drums [10]. In practice, these methods have proved impractical and uneconomical due to low productivity, high frequency, and high cost. Batkaev et al. [11] tested a method for obtaining red phosphorus from phosphorus sludge by polymerizing it and calcining it at 340 °C for 72 h. A method is known for producing phosphoric acid by burning sludge, subsequent cooling of gases, and hydration of the resulting phosphoric anhydride [12]. Incineration and heat treatment have not found full application. By capturing gases released during the combustion of sludge, phosphoric acid can be obtained. However, the burnt residue again turns into waste, for the disposal of which other studies are required.

From the above, it can be said that in all the proposed methods, only phosphoric sludge is disposed of. For cottrel dust, these methods are not suitable, since carbon is present in its composition in copious amounts. Therefore, the processing of cottrel dust is aimed at extracting phosphorus by removing carbon from its composition. For this purpose, scientists used various collectors and fatty acids, often used for flotation enrichment of phosphate raw materials [5,13]. However, the effectiveness of the proposed solutions is very doubtful. Since, after using the collectors, the phosphate part becomes contaminated and additional cleaning is required. A promising method of recycling cottrel dust is processing it for fertilizer. The abundance of phosphorus anhydride in the composition (up to 30%), fine structure, and excess amount can serve as an alternative to traditional phosphate raw materials [14]. Scientists from the Bekhturov Institute of Chemical Sciences have proposed a method for processing cottrel dust into fertilizers. The method is based on mixing cottrel dust and quicklime at a solid/liquid ratio = 1/(2.5-3) [15]. Also, cottrel dust can be used in the ore preparation process at the Electric Furnace Process as an additive to increase the phosphorus component. About 0.13–0.15 tons of cottrel dust are formed per ton of product in the form of yellow phosphorus [16]. To date, Kazphosphate LLP has technological regulations for the disposal of cottrel dust in the form of phosphorus-potassium fertilizers. However, it will not be possible to effectively process this accumulated waste over many years of operation of the phosphorus plant for fertilizers in a few years. The currently known methods of their processing are questionable due to economic unprofitability and have not been fully evaluated for environmental and agrochemical efficiency.

In this regard, the search and creation of new effective methods for the disposal of phosphorus sludge and cottrel dust is an urgent task. The task is solved by the fact that we propose the processing of the above-mentioned waste with humic acid to obtain mineral fertilizer. This study is a logical continuation of the early work, according to the research plan: Stage 1: a comprehensive study of the structure and composition of phosphoric sludge and cottrel dust [17]; Stage 2: the development of a method for obtaining humic acid from brown coal mining waste [18]; Stage 3: a study of the process of humic acid decomposition of phosphoric sludge and cottrel dust. Step-by-step, long-term research has allowed us to obtain new scientific information on the processing of waste of technogenic origin.

2. Results and Discussion

2.1. Features in the Chemical Composition and Phase Structure of the Initial Materials

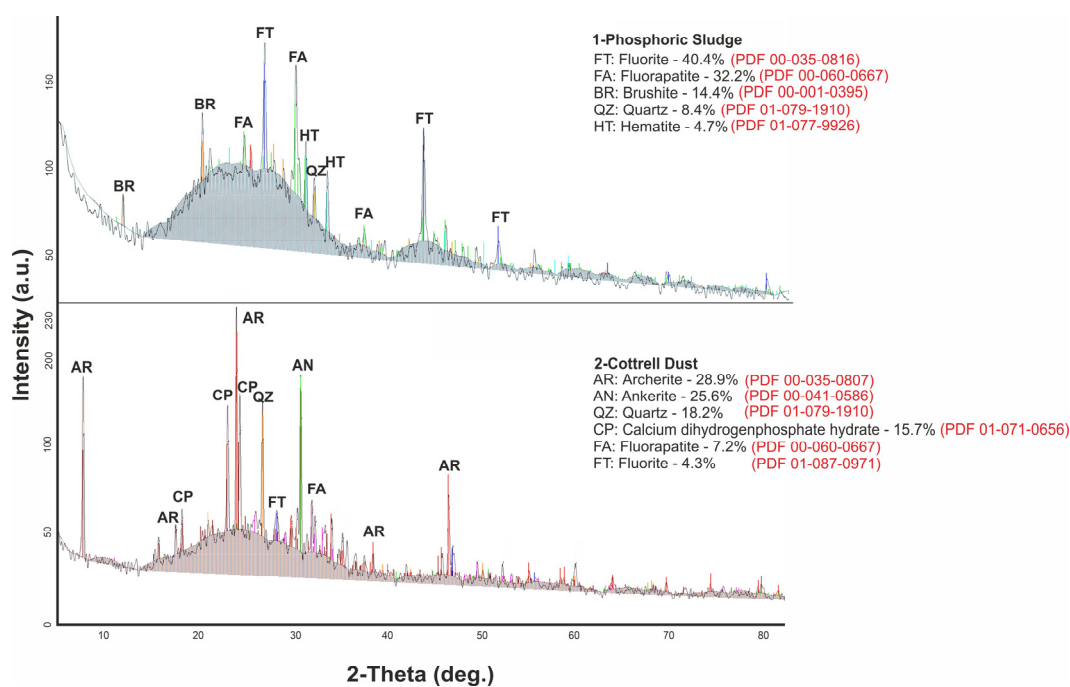
From the data given in Table 1, it can be seen that the studied samples do not differ significantly from each other in chemical composition and are close to the initial phosphate raw materials with inclusions of the components of the charge mass—quartzite and coke. The average content of P_2O_5 will qualify them as poor raw materials but suitable for processing into fertilizer products, since about half of the phosphorus in them is already in an assimilable form. This makes it possible to count on a reduced consumption of decomposing acids during the processing of phosphoric sludge and cottrel dust. The average chemical composition ($n = 8$) is given in Table 1.

Table 1. Average chemical composition of phosphorus sludge and cottrel dust.

Compounds	P ₂ O ₅ Total	P ₂ O ₅ Assimilable	K ₂ O	SiO ₂	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	C
Phosphorus Sludge	11.01%	6.06%	4.50%	13.62%	27.13%	1.57%	0.90%	0.39%	14.82%
Standard Deviations (<i>n</i> = 8)	0.59	0.74	1.08	1.04	0.52	0.29	0.67	0.07	1.01
Cottrel dust	24.12%	15.67%	7.16%	9.17%	17.96%	0.89%	0.78%	0.45%	26.09%
Standard Deviations (<i>n</i> = 8)	0.88	0.69	0.95	0.83	0.58	0.97	0.54	0.12	1.15
Karatau phosphorites (for comparison) [19,20]	33.08%	-	-	2.68%	34.36%	6.90%	2.40%	1.63%	13.66%

A comparative analysis of the data in Table 1 with known information on the chemical composition of Karatau phosphorites [19,20] shows that a noticeable decrease in the concentration of P₂O₅, CaO, and Al₂O₃ and a significant increase in the content of K₂O, SiO₂, MgO, and C are observed in phosphorus sludge and cottrel dust. It follows that their fertilizing value for P₂O₅ is lower than that of phosphorite, and in terms of K₂O content, they differ favorably from the latter. In addition, an increase in the content of silicon oxide and magnesium oxide and the appearance of free carbon make it necessary to take these features during their humic acid leaching.

For a detailed study of the structure of the raw materials, X-ray diffraction analysis was used; XRD results are shown in Figure 1.

**Figure 1.** XRD patterns of phosphorus sludge and cottrel dust.

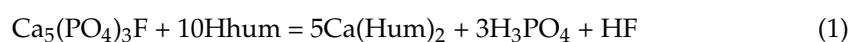
The phase composition of phosphoric sludge is characterized mainly by calcium fluoride and fluorapatite, with maxima $d = 3.14992 \text{ \AA}$, $1.931193 \text{ \AA}$, and $2.797436 \text{ \AA}$, respectively. The same compounds are found in the composition of cottrel dust but have a lower d value. According to Duisembiev et al. [21], it is believed that the phase composition of phosphorus sludge and cottrel dust is quite diverse and depends on the composition of the charge, the mode of thermal preparation, and the conditions for the reduction of phosphorus in the furnace. Phosphorus occurs in their composition in the form of ortho- and polyphosphates of potassium, calcium, and magnesium. This also explains the increased content of the assimilable form of phosphorus. The silicon compounds in both samples are assigned to

quartz. According to studies [22], the quartz in these compounds is acid-insoluble and amorphous, which is a consequence of the heat treatment of the charge material.

Based on the above, it can be said that phosphoric sludge and cottrel dust have an amorphous structure. Since no sharp diffraction peaks are observed, the diffraction pattern is typically featureless and exhibits broad, weak diffraction peaks. This in turn indicates that these materials can be treated with solutions of weak acids.

2.2. Experimental Data of Humic Acid Leaching

After careful study of the composition and structure of phosphorus sludge and cottrel dust, it can be said that they have the same phosphate part in the form of $\text{Ca}_5(\text{PO}_4)_3\text{F}$. This is necessary to describe the chemical reaction of humic acid decomposition. At the same time, the molecular formula of humic acid itself is unknown. In this case, the process of acid decomposition of the phosphate part of phosphoric sludge and cottrel dust can be represented as follows



It follows from the above reaction that the products of humic acid (HA) decomposition can be calcium humate in the form of an insoluble residue and phosphoric acid in the liquid phase. The formation of hydrogen fluoride in this reaction is impossible since in this case the fluoride compounds are presented in the form of calcium fluoride (from the XRD analysis). Humic acid cannot decompose calcium fluoride (CaF_2) because calcium fluoride is a very stable compound with a high lattice energy, which makes it difficult to break down. Humic acid, on the other hand, is an organic acid with relatively low reactivity towards inorganic compounds like calcium fluoride. In addition, the bond between calcium and fluoride in CaF_2 is a strong ionic bond, which requires a significant amount of energy to break. As a result, even under normal conditions, humic acid is not able to decompose calcium fluoride, and the compound remains intact in the solid phase.

Phosphoric sludge (PS) and cottrel dust (CD) with particle sizes of 0.100–0.315 mm were used for experimental studies. Figure 2 and Table 2 show the results of experimental studies that took the following factors into account: time, temperature, PS-CD/HA ratio, and pH of HA.

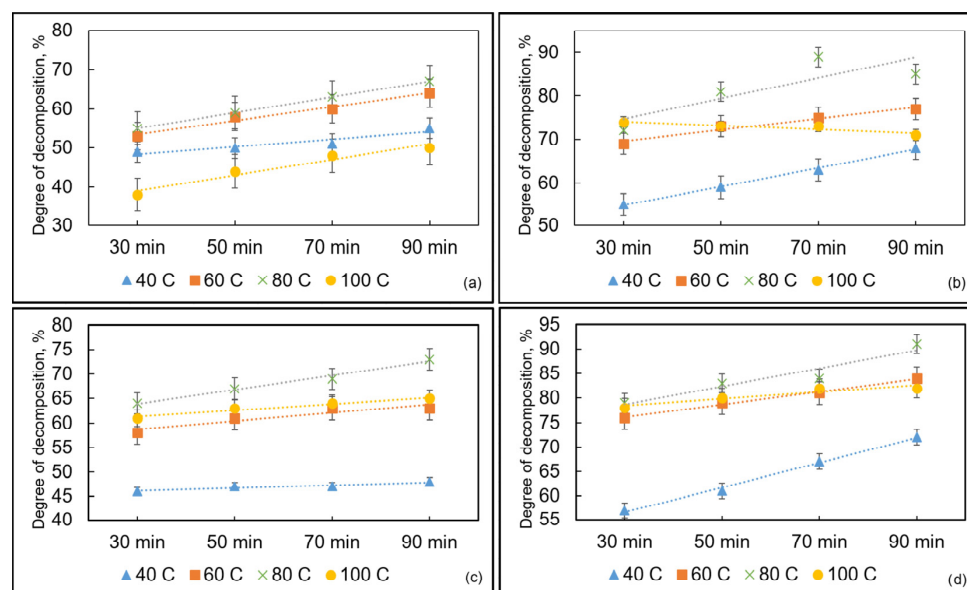


Figure 2. Plots of degree of composition vs. time at various conditions: (a) PS-CD/HA ratio = 1/1, pH = 1.92; (b) PS-CD/HA ratio = 1/2, pH = 1.92; (c) PS-CD/HA ratio = 1/1, pH = 1.5; (d) PS-CD/HA ratio = 1/2, pH = 1.5.

Table 2. Equation and confidence value of the linear approximation from Figure 2.

Temp.	(a)	(b)	(c)	(d)
40 °C	$y = 1.9x + 46.5$	$y = 4.3x + 50.5$	$y = 0.6x + 45.5$	$y = 5.1x + 51.5$
	$R^2 = 0.8699$	$R^2 = 0.9968$	$R^2 = 0.9010$	$R^2 = 0.9946$
60 °C	$y = 3.5x + 50$	$y = 2.6x + 67$	$y = 1.7x + 57$	$y = 2.6x + 73.5$
	$R^2 = 0.9761$	$R^2 = 0.9657$	$R^2 = 0.8627$	$R^2 = 0.9941$
80 °C	$y = 4x + 51$	$y = 4.7x + 70$	$y = 2.9x + 61$	$y = 3.7x + 75$
	$R^2 = 0.9102$	$R^2 = 0.7957$	$R^2 = 0.9836$	$R^2 = 0.9157$
100 °C	$y = 4x + 35$	$y = -0.9x + 75$	$y = 1.3x + 60$	$y = 1.4x + 77$
	$R^2 = 0.9524$	$R^2 = 0.8526$	$R^2 = 0.9657$	$R^2 = 0.8909$

As can be seen from the experimental data, time, temperature, pH, and the solid/liquid ratio varied during the acid decomposition of phosphoric sludge and cottrel dust. In Figure 2a,b, the pH value is 1.92. With a difference in the solid/liquid ratio, the maximum value of the degree of decomposition reaches up to 89% with a PS-CD/HA ratio = 1/2. In comparison to Figure 2a, $\alpha = 67\%$, an increase in the time and temperature of the process in both cases leads to a decrease in the α -value. This is explained by a growth in the proportion of the formation of insoluble CaHPO_4 , which blocks the decomposed grains of the initial phosphate with a dense crystalline film. In this case, the reaction mass is saturated with the production liquid-phase acid, which in turn proves the course of the acid leaching reaction. Further, the rate of the humic acid decomposition process decreases due to the accumulation of reaction products in the solution and a decrease in acid activity. To overcome this barrier, a more acidic humic acid (pH = 1.5) was used with the same experimental parameters. As a result, it was determined that, as in the first case, with a PS-CD/HA ratio = 1/1 (Figure 2c), α reaches only 73%. Apparently, the amount of humic acid needed for decomposition is not enough. Also, at a PS-CD/HA ratio = 1/2 (Figure 2d), the concentration of humic acid has a significant effect on the decomposition process. At the same time, with increasing acid concentration, the degree of decomposition rises, reaching the maximum degree of conversion of P_2O_5 total phosphoric sludge to the assimilable form of P_2O_5 in the final product at 91%. This indicates a relatively high reactivity of the phosphate part of phosphorus sludge and cottrel dust, which, as we previously found (Section 2.1), have an amorphous structure. Consequently, compared with natural phosphate raw materials, these phosphorus-containing wastes have a low apparent activation energy.

2.3. Processing of Experimental Data by the Method of Formal Kinetics

Reaction kinetics in a heterogeneous fluid-spherical particle system refers to the study of chemical reactions that occur between the fluid and the solid particles in the system. In this system, the reaction rate can be described by the Ginstling-Brounstein rate equation, which relates the reaction rate to the concentration of the reactants and other system parameters. In a heterogeneous fluid-spherical particle system, the reaction can occur both on the surface of the particles and in the fluid phase. The reaction rate on the particle surface can be described using surface reaction kinetics, while the reaction rate in the fluid phase can be described using fluid reaction kinetics. The overall reaction rate in the system can be obtained by combining the surface and fluid reaction rates, taking into account the mass transfer of reactants between the particle surface and the fluid phase. The effect of temperature and time on the degree of decomposition (α) of phosphoric sludge and cottrel dust during humic acid decomposition and the results of processing experimental data in relation to the equation of reaction kinetics of heterogeneous processes (2) [23] are shown in Figure 3

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = k \cdot t, \quad (2)$$

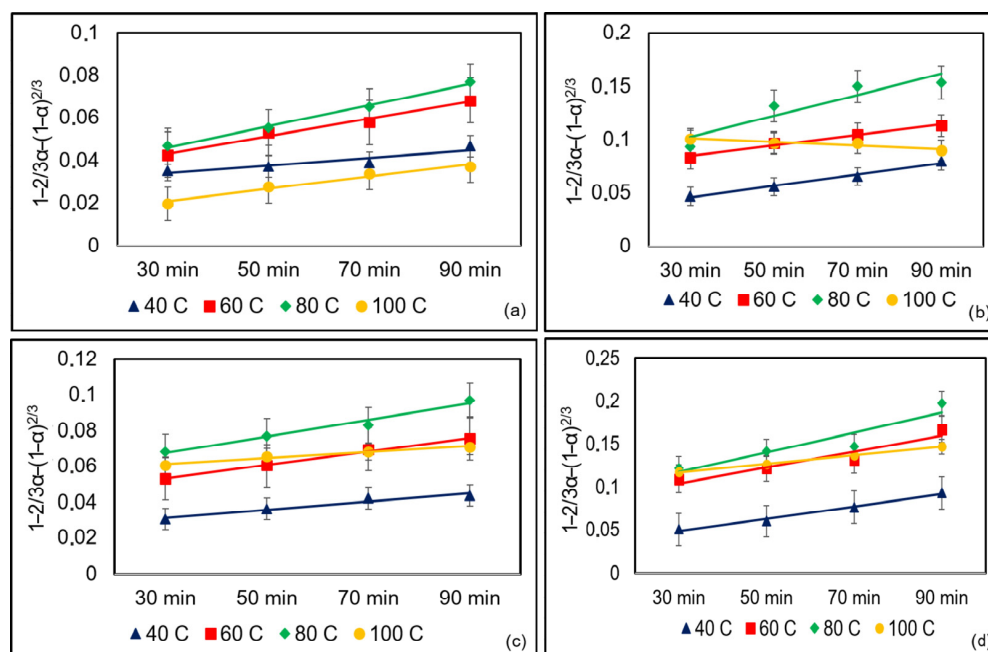


Figure 3. Plots of $1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}}$ vs. time at various conditions: (a) PS-CD/HA ratio = 1/1, pH = 1.92; (b) PS-CD/HA ratio = 1/2, pH = 1.92; (c) PS-CD/HA ratio = 1/1, pH = 1.5; (d) PS-CD/HA ratio = 1/2, pH = 1.5.

The determination of the rate constant of the chemical reaction was carried out graphically. According to the tangent of the angle of the straight lines to the abscissa axis shown in Figure 3, the reaction rate constants are found (Table 3).

Table 3. Reaction rate constant and confidence value of the linear approximation from Figure 3.

Temp.	(a)	(b)	(c)	(d)
40 °C	$k = 3.69 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.8577$	$k = 5.78 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.9856$	$k = 1.54 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.9528$	$k = 8.65 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.9858$
60 °C	$k = 7.49 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.9806$	$k = 4.34 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.9795$	$k = 4.56 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.9941$	$k = 1.54 \times 10^{-4} \text{ min}^{-1}$ $R^2 = 0.9075$
80 °C	$k = 9.72 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.9964$	$k = 2.12 \times 10^{-4} \text{ min}^{-1}$ $R^2 = 0.8676$	$k = 3.74 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.9731$	$k = 8.29 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.8728$
100 °C	$k = 3.58 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.9735$	$k = 6.34 \times 10^{-6} \text{ min}^{-1}$ $R^2 = 0.8606$	$k = 9.34 \times 10^{-6} \text{ min}^{-1}$ $R^2 = 0.9715$	$k = 4.37 \times 10^{-5} \text{ min}^{-1}$ $R^2 = 0.9993$

As can be seen from the above table, with an increase in temperature to 80 °C, there is a shift of the maximum towards a higher rate, i.e., there is a sharp increase in the number of molecules with speeds much higher than the average. If we take into account that the maximum increase in the degree of decomposition is achieved at 80 °C in cases (b) and (d) (Figure 2), then the results differ when calculating the reaction rate constants. So in case (b), at 80 °C, $k = 2.12 \times 10^{-4} \text{ min}^{-1}$, and this indicator reduces with increasing temperature. Also in the case of (d), the maximum value of $k = 1.54 \times 10^{-4} \text{ min}^{-1}$ reaches 60 °C; a further rise in temperature leads to a sharp fall in the speed of the process. To explain this phenomenon, it is necessary to determine the activation energy of each process and consider the data obtained from the point of view of the theory of the activated complex and the frontal movement of the reaction zone.

The activation energy of the process is a characteristic of the reaction and determines the effect of temperature on the reaction rate. In the case of complex reactions or reactions occurring in several stages, E_a has no strict physical meaning and is a function of the activation energy of individual stages, usually called the apparent activation energy [24]. The apparent activation energy of the process of humic acid decomposition of phosphoric sludge and cottrel dust is shown graphically. For these purposes, a graph of the $\ln k$ dependence on $1/T$ is plotted, as shown in Figure 4.

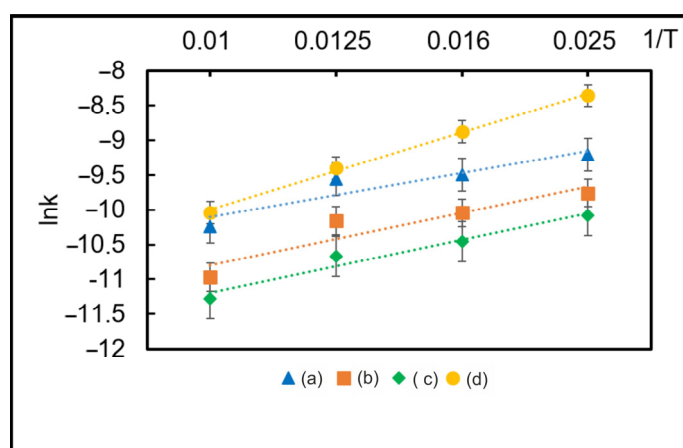


Figure 4. Arrhenius plot for the humic acid leaching of PS and CD: (a) PS-CD/HA ratio = 1/1, pH = 1.92; (b) PS-CD/HA ratio = 1/2, pH = 1.92; (c) PS-CD/HA ratio = 1/1, pH = 1.5; (d) PS-CD/HA ratio = 1/2, pH = 1.5.

Based on Figure 4 and Formula (4), the apparent activation energy of the process was calculated (Table 4)

$$E_a = R \cdot \tan \alpha, \quad (3)$$

where E_a —apparent activation energy; R —gas constant (8.314 J/mol·K); $\tan \alpha$ —the tangent of the angle of inclination of the resulting straight line.

Table 4. Apparent activation energy and reliability parameters of the linear approximation.

(a)	$E_a = 9.04 \text{ kJ/mol}$	$y = 0.3154x - 10.414$ $R^2 = 0.8712$
(b)	$E_a = 11.82 \text{ kJ/mol}$	$y = 0.3742x - 11.168$ $R^2 = 0.8671$
(c)	$E_a = 12.90 \text{ kJ/mol}$	$y = 0.3809x - 11.575$ $R^2 = 0.9611$
(d)	$E_a = 26.73 \text{ kJ/mol}$	$y = 0.5573x - 10.559$ $R^2 = 0.9972$

Statistical analysis of the found activation energy values by the least squares method: correlation coefficient—0.99; linear correlation coefficient—0.984, i.e., on the Cheddock scale, the relationship between the signs is noticeable and direct; the approximation error is 5.4%.

From the point of view of the activated complex theory, the process under study is formed as an intermediate state in all chemical reactions. It is considered a molecule that exists only temporarily and is destroyed at a certain speed. In our case, this complex is formed from such interacting molecules, whose energy is sufficient for them to be able to come close to each other according to the scheme



This scheme has a relationship with the reaction (1), where calcium humates, as expected, are a solid, insoluble residue, while phosphoric acid belongs to the liquid phase. At the same time, the activated complex in the form of CaHPO_4 has an intermediate structure between reagents and products. The activation energy of the reaction is the additional energy that the reacting molecules must acquire in order to form the activated complex necessary for the reaction to proceed [25]. According to this theory, the indicated values of the apparent activation energy characterize the process as being limited by the diffusion rate. Also, when describing a specific diffusion region from the point of view of a model with a frontal displacement of the reaction zone, the process of humic acid decomposition is internal diffusion (Figure 5). This means that the penetration of humic acid to the surface of PS/CD occurs through the layer formed by CaHPO_4 . This area is typical for all cases. Then, in order to increase productivity, it is necessary to strive to eliminate the inhibitory effect of diffusion stages. By increasing the time, the temperature of the process, and the concentration of the acid, they were able to achieve a maximum degree of decomposition of up to 91% (Figure 2d). Despite this, it can be said that the E_a values found are much lower than those of the treatment of natural phosphates with mineral acids, as noted above. Data on the acid processing of phosphorus-containing waste have not been found; however, there is information about the processing of phosphate ore with mineral acids. For example, phosphate ore from Huidong, Sichuan Province, China, was subjected to hydrochloric acid treatment (temperature: 10 °C, HCl concentration: 0.488 mol·L⁻¹, time: 2 min). The apparent activation energy of this process was 41.99 kJ/mol [26]. Another mineral acid is sulfuric acid. It was used to process phosphorite from Mazıdağı, Mardin, Turkey (temperature: 14–70 °C, acid concentration: 40–98%, time: 10–75 min). At the same time, the kinetic model used in this work is similar to ours. The activation energy of sulfuric acid treatment of phosphate raw materials was 29.66 kJ/mol [27]. Comparing the obtained data on humic acid leaching, it can be said affirmatively that this process is energy efficient due to the fact that the temperature is lower than when treated with mineral acids.

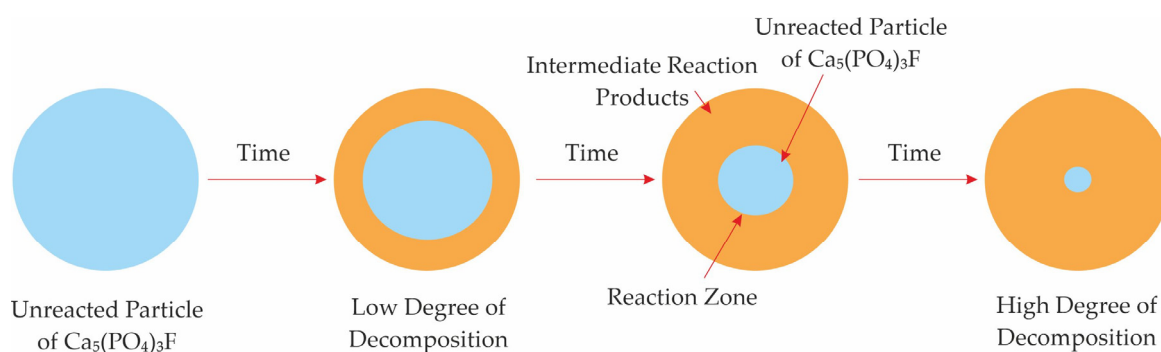


Figure 5. According to the model of a particle with a non-interacting nucleus, the reaction proceeds on its outer surface, and the reaction zone moves frontally into the particle, leaving behind the particle substance completely converted into reaction products.

After calculating the apparent activation energy (E_a), the kinetic model for the studied processes can be described by the following Equations (4)–(7)

$$\text{For (a): } 1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = 2.07 \times 10^3 e^{-9.04/RT} \cdot t, \quad (4)$$

$$\text{For (b): } 1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = 6.58 \times 10^3 e^{-11.82/RT} \cdot t, \quad (5)$$

$$\text{For (c): } 1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = 3.35 \times 10^3 e^{-12.90/RT} \cdot t, \quad (6)$$

$$\text{For (d): } 1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} = 4.55 \times 10^3 e^{-26.73/RT} \cdot t, \quad (7)$$

2.4. Description of the Chemical Composition and Phase Structure of the Obtained Products

The composition of the filtrate in the form of phosphoric acid and insoluble residue was analyzed for the content of the main compounds. At the same time, the insoluble residue was dried at 110 °C to a constant weight. The ratio of phosphoric acid-insoluble residue, according to the results of the experiments, was 1/4. If we take into account that the reaction mass was initially 450 g at a PS-CD/HA ratio = 1/2, then after leaching the ratio of the liquid and solid phases, respectively, is 87 g/363 g. The average chemical composition of phosphoric acid and insoluble residue is given in Table 5.

Table 5. Average chemical composition of phosphoric acid and insoluble residues.

P ₂ O ₅ Total	P ₂ O ₅ Assimilable	K ₂ O	SiO ₂	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	C
Phosphoric acid								
29.19%	26.56%	18.14%	-	10.07%	0.19%	0.07%	0.06%	-
Production phosphoric acid (for comparison) [28]								
29–30%	-	0.03–0.04%	0.6–0.9%	0.1–0.2%	0.1–0.3%	0.3–0.4%	0.3–0.4%	-
Insoluble residue								
14.12%	8.91%	2.07%	20.83%	33.13%	2.12%	0.94%	0.78%	37.91%

From the chemical analysis data, it can be seen that the total P₂O₅ content is 29.19%, while the assimilable P₂O₅ is 26.56%. Total P₂O₅ content refers to the amount of phosphorus pentoxide (P₂O₅) present in a sample. It represents the total amount of phosphorus available in the sample. Assimilable P₂O₅ refers to the portion of the total P₂O₅ that is readily available for plant uptake. This is the portion of the total P₂O₅ that can be absorbed and utilized by the plant for growth and development. The difference between total P₂O₅ content and assimilable P₂O₅ is that total P₂O₅ content represents the total amount of phosphorus present, while assimilable P₂O₅ represents the portion of that phosphorus that is available for plant uptake.

The insoluble residue also contains phosphorus pentoxide in both forms. The content of potassium is more dominant in phosphoric acid, while the content of the remaining compounds prevails in the insoluble residue. This is most likely due to the salting out process. For a complete structural analysis, an XRD of both products presented in Figure 6 should be considered.

The XRD-identified compounds are monetite and potassium dihydrophosphate, with 65.2% and 34.8%, respectively. The formation of monetite may be explained by the evaporation of the acid produced for these analyses. After all, it is known that monetite reacts with atmospheric water to form brushite [29]. The same compound is found in the composition of an insoluble residue with an amount of about 11.7%. As in the phase structure of the feedstock, low intensity is also observed here, which in turn allows us to draw conclusions about the amorphous structure of the insoluble residue. The presence of synclinal fluorapatite is explained by the fact that humic acid does not completely decompose the phosphate part of phosphorus sludge and cottrel dust. In addition, silicon-containing compounds are presented in the form of quartz and calcium silicon carbide. That is, carbon is associated with silicon and calcium. Also, fluoride compounds in the form of calcium fluoride do not react with humic acid and remain as part of an insoluble residue. Magnesium, aluminum, and iron compounds have not been identified, possibly due to their small amounts.

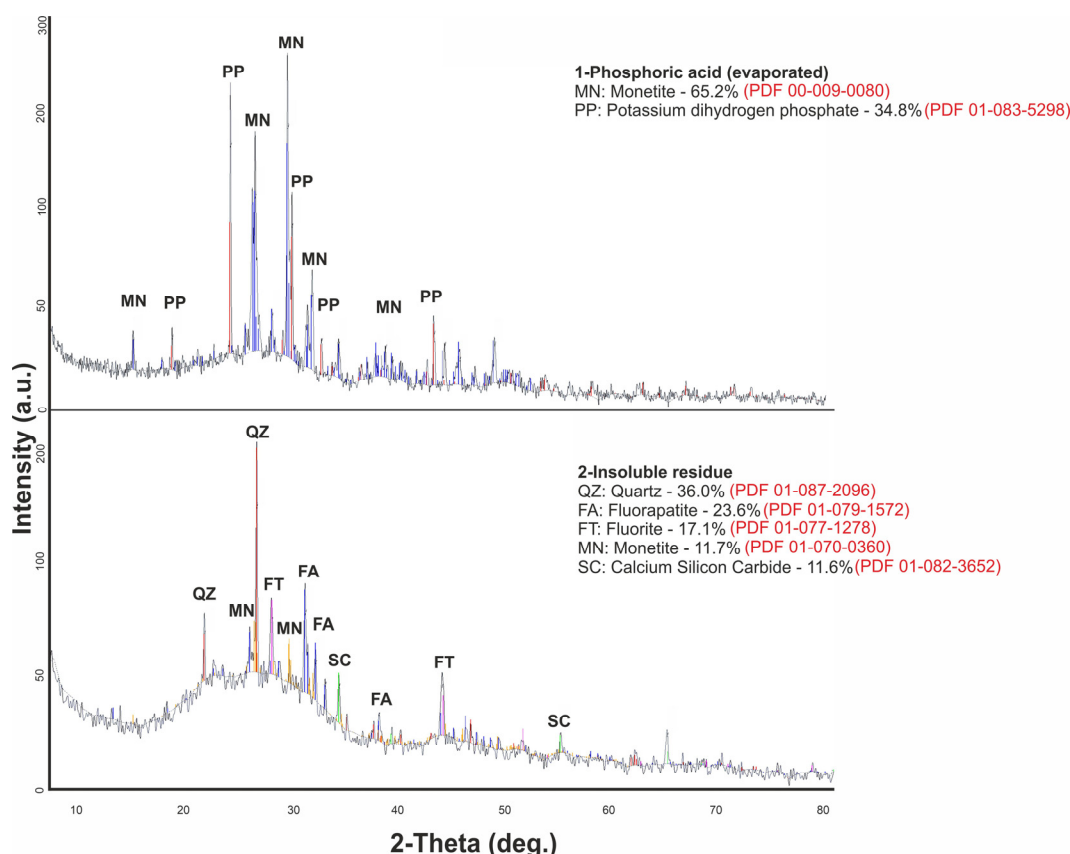


Figure 6. XRD patterns of phosphoric acid (evaporated) and insoluble residue.

The humic acid leaching method of processing phosphoric solid waste differs from traditional methods in several ways [30], as follows:

- Chemical composition: Humic acid is a naturally occurring organic compound, whereas traditional methods often use strong mineral acids like sulfuric acid. This difference in chemical composition can result in different leaching efficiencies and environmental impacts. For example, with the traditional method of sulfuric acid treatment of phosphate raw materials, phosphogypsum is formed as a by-product [31]. The problem of its disposal and neutralization has not yet been solved.
- Environmental impact: Humic acid is considered environmentally friendly, as it is biodegradable and does not produce toxic by-products. Traditional methods, on the other hand, can produce hazardous byproducts and have a higher carbon footprint.

Overall, the humic acid leaching method offers potential advantages over traditional methods in terms of efficiency, environmental impact, cost, and selectivity, making it a promising alternative for the processing of phosphoric solid waste.

3. Materials and Methods

Samples of phosphorus-containing waste were taken from the sludge accumulators of Kazphosphate LLP (Taraz, Kazakhstan).

The phase composition was studied using a Bruker D8 diffractometer (Germany). It uses X-rays to excite the atoms in a sample and measure the diffraction pattern of the X-rays as they pass through the sample (shooting angle 3–180°). The diffraction pattern can be used to determine the crystal structure of the sample and its atomic arrangements. The Bruker D8 diffractometer is equipped with a high-power X-ray source, a detector, and a goniometer (sample stage) that allows for precise positioning of the sample in the X-ray beam.

The obtained data were interpreted in the Diffrac Plus Search database. The software provides a search function that can match the peaks in the diffraction pattern to those in

the database and provide a list of possible matches. The database of PDF2 radiographic standards was also used, containing about 450,000 cards of radiographs of known compounds, each of which contains diffraction, crystallographic, and bibliographic data, as well as experimental conditions.

The chemical composition was studied according to well-known methods:

Determination of phosphoric anhydride by photometry (Trilon B) [19]. In this case, P_2O_5 (phosphorus pentoxide) is a chemical compound used to measure the amount of phosphorus in fertilizers. “Total P_2O_5 ” refers to the total amount of P_2O_5 in a fertilizer, which includes both soluble and insoluble forms of phosphorus. This measurement represents the total potential available phosphorus for plant growth.

The steps for the Trilon B determination method are as follows: preparing a sample solution by dissolving a weighed amount of fertilizer in a suitable solvent; adding Trilon B reagent to the sample solution and stirring to allow for complete reaction; adding an indicator to the reaction mixture to form a colored complex; measuring the absorbance of the colored complex at a specific wavelength $\lambda = 440$ nm using a spectrophotometer (alphanumeric LCD with backlight); calculating the total P_2O_5 by comparing the absorbance of the sample to that of a reference standard. This method is relatively simple, easy to perform, and provides accurate results in a relatively short amount of time.

“Assimilable P_2O_5 ” or “available P_2O_5 ” refers to the portion of the total P_2O_5 in the fertilizer that can be taken up by plants and used for growth. It is the amount of phosphorus that is readily soluble in soil and can be absorbed by plant roots.

The determination of assimilable P_2O_5 (Phosphorus Pentoxide) in fertilizers using Trilon B is a colorimetric method that measures the portion of the total P_2O_5 in the fertilizer that can be taken up by plants and used for growth [32].

The steps for the Trilon B determination method are similar to the method for total P_2O_5 .

Potassium by the FPA-2-01 flame photometer (Russia), silicon by gravimetry, calcium and magnesium by the Kvant-2m1 atomic absorption spectrophotometer (Russia), aluminum and iron by complexometry, and carbon by the gas volume method.

Humic acid used for decomposition was synthesized from brown coal mining waste (Lenger, South Kazakhstan) according to the method [18]. Acidic characteristics of humic acid: pH = 1.5–1.92. To measure the pH of humic acid, a 160-MI brand pH meter was used, where its electrode was placed in a solution and a reference electrode was used to complete the circuit.

The experiments were carried out according to the method of multifactorial planning. The conditions for the humic acid decomposition of phosphorus-containing waste were as follows: The time interval was 30–100 min, the temperature was 40–90 °C, the ratio of phosphoric sludge/cottrel dust was 1:2, and the ratio of a mixture of phosphoric sludge and cottrel dust/humic acid was 1:1 and 1:2, respectively. The experimental setup is shown in Figure 7.

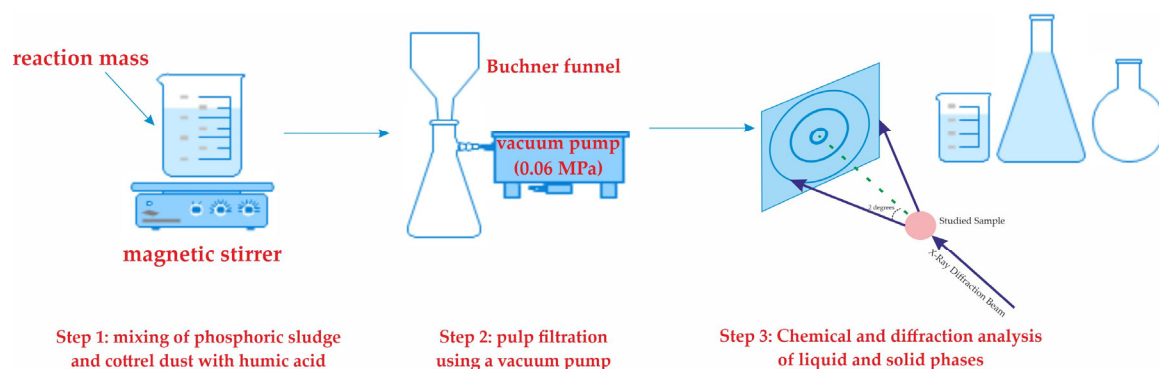


Figure 7. Experimental setup and sequence of experiment execution.

A magnetic stirrer of the IKA brand was used to stir the reaction mass. Filtration was carried out using a KNF vacuum filter at a pressure of 0.06 MPa. Glassware has been used as reaction vessels and Erlenmeyer flasks for sampling, chemical analysis, and solution heating.

The efficiency of the process was estimated by the degree of decomposition, which is calculated by Formula (8)

$$\alpha = P_2O_5_{\text{assimil.}}/P_2O_5_{\text{total}}(\%), \quad (8)$$

Differences were analyzed via two-tailed paired student *t*-test using Microsoft Excel software, *p* values < 0.05 were considered as statistically significant.

4. Conclusions

In conclusion, the scientific novelty of this study lies in the application of humic acid as a leaching agent for the processing of phosphoric solid waste. Studying the process of leaching phosphoric sludge and cottrel dust with humic acid, it can be concluded that, according to this method, it is possible to obtain production phosphoric acid with enhanced Ca and K impurities. This, in turn, can serve as an alternative to the traditional method of its production. Studying the kinetic laws of the process, it was determined that the process is limited by diffusion, including being in the internal diffusion region. When recalculating the degree of decomposition, which was the main estimate of the entire process and reached up to 91%, the apparent activation energy was 26.73 kJ/mol. Based on the results of experimental studies, kinetic models are proposed for different conditions. The optimal parameters of the investigated process are as follows: process temperature—80 °C; PS-CD/HA ratio = 1/2; time: 90 min.

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