Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources

DOI: 10.31643/2027/6445.31
Mining & Mineral Processing

Activation of the mineralized mass of Central Kyzylkum using acidic wastewater from the oil and fat industry: Freundlich-based adsorption kinetics for fluorine release

[1*]Achilova S.S., [1]Saparbaeva N.K., [2] Matmuratov A.A., [3]Rustamova N.D., [4]Karimboyev O.Q.

[1]Urgench State University named after Abu Rayhon Biruni, Uzbekistan
[2]Mamun University, Khiva, Uzbekistan
[3]Urgench District General Secondary School No. 1, Uzbekistan
[4]Urgench State Pedagogical Institute, Uzbekistan

Corresponding author email: sanobar.a@urdu.uz

Received: *August 15, 2025*
Peer-reviewed: *October 16, 2025*
Accepted: *January 12, 2026*

ABSTRACT

This study investigates the simultaneous utilization of mineralized mass (MM) from Central Kyzylkum phosphorite waste and acidic wastewater (AWW) from the soapstock processing industry for efficient fluoride removal. The MM was chemically activated by AWW under controlled conditions, leading to surface modification, increased porosity, and enhanced active site heterogeneity. The chemical interaction between H^+ ions from AWW and fluorapatite in MM resulted in ion exchange, dissolution of phosphate groups, and the formation of volatile HF. Adsorption experiments were conducted at various MM: AWW ratios to determine the optimal operating parameters. Equilibrium data were fitted to the Freundlich isotherm model, confirming multilayer adsorption on heterogeneous surfaces. Kinetic analysis indicated that the pseudo-second-order (PSO) model provided the best fit, suggesting that chemisorption is the dominant rate-limiting mechanism. The Weber–Morris intra-particle diffusion model revealed that pore diffusion contributes to fluoride uptake but is not the sole controlling step. The synergy between isotherm and kinetic results supports a two-stage adsorption process involving rapid surface chemisorption followed by slower intraparticle diffusion. The developed method offers a dual environmental benefit by valorizing two industrial waste streams and reducing their ecological footprint. The produced sorbent showed high fluoride removal efficiency under simulated operational conditions. The process is simple, cost-effective, and compatible with existing industrial infrastructures. Large-scale application has the potential to reduce operational costs and promote circular economy principles. These findings provide a sustainable approach to water treatment in fluoride-affected regions while addressing industrial waste management challenges.

Keywords: fluoride removal, mineralized mass, acidic wastewater, Freundlich isotherm, adsorption kinetics, waste valorization.

	Information about authors:
Achilova Sanobar Sobirovna	*Doctor of Philosophy in Technical Sciences, Associate Professor at the Faculty of Chemical Technology, Urgench State University named after Abu Rayhon Biruni, Urgench, H. Olimjon Street 14, 220100, Uzbekistan. Email: sanobar.a@urdu.uz; ORCID ID: https://orcid.org/0000-0003-4691-0248*
Saparbaeva Nasiba Kamilovna	*Candidate of Chemical Sciences, Associate Professor at the Faculty of Chemical Technology, Urgench State University named after Abu Rayhon Biruni, Urgench, H. Olimjon Street 14, 220100, Uzbekistan. Email: nasiba.s@urdu.uz; ORCID ID: https://orcid.org/0009-0002-1942-8958*
Matmuratov Azizbek Abdikarimovich	*Doctor of Philosophy in Pedagogical Sciences, Associate Professor at the Department of Pedagogical Sciences, Mamun University, 220900, Bol-Khovuz Street 2, Qibla Tozabog MCG, Khiva, Uzbekistan. Email: my_darling90@mail.ru; ORCID ID: https://orcid.org/0009-0007-4177-3738*
Rustamova Nodira Davronbekovna	*English teacher, Urgench District General Secondary School No. 1, 220500, 1 Navruz Street, Urgench district, Uzbekistan. Email: nodira.rustamova1007@gmail.com*
Karimboyev Ogabek Qadamboyevich	*Assistant in the Faculty of Natural and Applied Sciences, Urgench State Pedagogical Institute 220100, 1-A, Gurlan str, Urgench, Uzbekistan.*

Introduction

The Central Kyzylkum phosphorites constitute the largest portion of Uzbekistan's phosphorite raw material base, with deposits in this region being extensively enriched in phosphate-bearing rocks [1]. Studies indicate that the average P_2O_5 content of Central Kyzylkum phosphorites is 16–17%, a level that necessitates industrial-scale beneficiation [2]. During the beneficiation process, large quantities of waste, referred to as "mineralized mass" (MM), are generated, containing 12–15% P_2O_5, along with CaO, MgO, F, and other components. According to statistical data, since the commencement of operations at the Central Kyzylkum phosphorite complex, millions of tons of MM waste have accumulated, with the total volume reaching 13–15 million tons [3]. These wastes are stored in open areas, posing a risk of environmental dispersion due to wind and rainfall [4].

Fluorine-containing compounds retained in the solid phase can be released into the atmosphere or water, posing ecological hazards, as elevated fluorine concentrations have adverse effects on human health and ecosystems [5]. The fluorapatite ($Ca_5(PO_4)_3F$) present in MM can decompose under acidic conditions, releasing fluoride ions [6]. Long-term open-air storage of such wastes can result in soil acidification and increased contamination with heavy metals and fluorine [7]. Therefore, the reduction or recycling of these wastes through environmentally safe methods is an urgent priority.

International practices employ various technologies for the processing of phosphorite wastes, including acid treatment, thermal activation, carbonate removal, and mechanochemical methods [8]. However, many of these technologies are not always economically viable due to high energy requirements or large acid consumption. Furthermore, the presence of fluorine in the wastes increases the technological complexity of many processing operations [6].

In the context of Uzbekistan, large-scale industrial practices for the effective utilization of MM wastes have not yet been implemented [4]. Recycling MM by integrating it with other industrial wastes represents a promising direction both ecologically and economically [3]. For example, the high acidity of acidic wastewater (AWW) from the fat-and-oil industry can partially decompose the fluorapatite in MM [5]. The mechanisms of fluorine removal in this process can be attributed to pH variation, ion exchange, and chemical decomposition [7]. Modeling the interaction between the two types of waste makes it possible to evaluate and optimize process efficiency [6]. The Freundlich adsorption model is among the effective approaches for describing fluorine removal in such systems. Studies have shown that fluorine removal during the acidification of phosphorite waste is sensitive to pH, temperature, mixing intensity, and mass ratios. Therefore, modeling fluorine removal from Central Kyzylkum MM by mixing it with AWW, using the Freundlich model, holds significant scientific and practical relevance for the fields of environmental protection, waste utilization, and industrial symbiosis [[6], [8]].

During the process of separating fatty acids from soapstock in the fat-and-oil industry, the resulting acidic wastewater—commonly referred to as “acidulated soapstock wastewater” (AWW)—is characterized by a high organic load (e.g., fats, glycerol, phospholipids, phosphatides, pigments, etc.) and low pH values, which significantly complicate both biological and chemical treatment systems [9]. The elevated chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of these wastewaters slow down biological purification processes, thereby reducing overall treatment efficiency [10]. Extremely low pH values, such as those in the range of 0.7–1.2, have also been reported. Under such acidic conditions, both organic and mineral fractions remain in a free state, leading to corrosion and aggregation issues in treatment equipment [10]. Furthermore, the presence of surfactants (e.g., sulfates, lauryl sulfates, etc.) exerts a negative impact on microbial activity and destabilizes flocculation mechanisms during treatment processes [[11], [12]]. When such surfactants enter soil or groundwater, they may exert toxic effects on humans and animals—for instance, the activity of anionic surfactants can damage the gill tissues of aquatic organisms and disrupt microbial reproduction [12].

In addition, the high organic matter content can deplete oxygen in soils, create anaerobic conditions, and generate unfavorable environments in root zones [13]. When these wastewaters infiltrate soils, direct filtration and percolation processes are impaired, increasing the risk of groundwater contamination [[11], [13]]. Moreover, elevated concentrations of phosphates and nitrates in such effluents intensify the risk of eutrophication, leading to algal blooms and the formation of hypoxic “dead zones” in aquatic environments [[13], [14]]. These phenomena pose direct threats to ecological balance, aquatic biodiversity, and human health [14]. Consequently, the efficient treatment and utilization of acidic wastewaters from the fat-and-oil industry constitute a pressing and complex scientific–engineering challenge for ensuring environmental safety.

Fluorine is a widely distributed element in the environment, and its compounds are encountered in various industrial processes, particularly in phosphorite and aluminum production, as well as in certain chemical fertilizers. The introduction of fluoride ions into ecosystems via water, air, or soil directly affects their biological balance [15].

Numerous studies have reported that excessive fluoride concentrations in drinking water can cause dental fluorosis and, in severe cases, skeletal fluorosis in humans [[16], [17]]. Dental fluorosis is characterized by enamel brittleness, discoloration, and compromised aesthetics, while skeletal fluorosis leads to hardening of bone tissue and reduced joint mobility [18]. In animals, high fluoride doses slow growth rates and impair reproductive functions [15]. From an ecosystem perspective, excessive fluoride reduces photosynthetic activity in aquatic plants, decreases plankton and fish populations, and, in soils, diminishes microbial activity while limiting nutrient uptake in plants. Therefore, controlling fluoride removal during waste processing plays a crucial role in ensuring environmental sustainability. The reduction of fluoride in industrial wastes not only mitigates pollution sources but also helps preserve drinking water quality. Furthermore, managing the natural cycle of fluoride prevents its excessive accumulation in soil and water systems. From the standpoint of maintaining ecological balance and safeguarding public health, monitoring fluoride concentrations, reducing pollution sources, and implementing efficient utilization technologies remain urgent priorities [18].

The Freundlich isotherm expresses the equilibrium of adsorption from solution to solid phase in an empirical manner and, by accounting for surface energetic heterogeneity, is widely applicable to numerous real systems [[19], [20]]. Its general form is as follows:

$$q_e = K_F \cdot C_e^{\frac{1}{n}}$$

In the Freundlich isotherm, K_F represents the affinity between the adsorbent and the adsorbate, while $\frac{1}{n}$ expresses surface heterogeneity and adsorption favorability; when $\frac{1}{n} < 1$, the process is generally considered “favorable” [[19], [20], [21]].

Logarithmic linearization ($\log q_e = \log K_F + \frac{1}{n} \log C_e$) is often employed to estimate the parameters; however, modern guidelines recommend the use of non-linear fitting to minimize errors [[20], [21]]. The Freundlich model does not accurately describe saturation at high concentrations; therefore, extended isotherms such as Langmuir–Freundlich (Sips) or Redlich–Peterson are sometimes used [[19], [20]]. Nevertheless, in many systems, the Freundlich model provides reliable correlations within low-to-moderate concentration ranges due to its two-parameter simplicity and physically meaningful coefficients [[19], [20]].

In adsorption kinetics characterization, pseudo-first-order (PFO) and pseudo-second-order (PSO) models are most commonly applied; PSO often provides a better fit when chemical interactions—such as surface complexation or ion exchange—predominate [[22], [23]]. As demonstrated by Azizian, the origins of the PFO and PSO models can be interpreted as different limiting cases of the general Langmuir kinetic approach, thereby clarifying their respective domains of applicability [22]. To distinguish mass transfer limitations, the Weber–Morris intraparticle diffusion model ($q_t = k_i \cdot d \cdot t^{\frac{1}{2}} + C$) and the Boyd model are frequently used as diagAWWtic tools [24]. Recent analyses have highlighted cases of misinterpretation of the intraparticle diffusion model and provided guidelines for its correct application and solution methods (e.g., multi-stage linear plots, physical interpretation of the intercept) [24].

When selecting models and determining parameters, it is recommended to compare the results of linear and non-linear fitting using statistical indicators such as R^2, RMSE, X^2, and AIC, as linearization may distort weighting and lead to incorrect estimates of K_F and $\frac{1}{n}$ [[20], [24]].

Freundlich parameters can be temperature-sensitive; therefore, evaluating thermal effects via the van’t Hoff approach and repeating isotherm fitting at different temperatures is advisable [6]. In multicomponent mixtures or systems with strong competitive adsorption, the flexibility of the three-parameter Sips (Langmuir–Freundlich) model can be advantageous, although care must be taken to avoid improper linearization [[1], [8]]. From an experimental design perspective, it is recommended to first assess the time to equilibrium using PFO/PSO fitting, and then separately analyze intraparticle and film diffusion stages [23].

In our system (interaction of MM with AWW in the presence of fluoride-bearing species), the equilibrium sorption capacity is described using the Freundlich model, while the time dependence is characterized by the PSO model combined with intraparticle diffusion diagAWWtics. This approach allows separation of the initial rapid film transfer stage from the subsequent pore diffusion/reaction stages [22]. Ultimately, the correct interpretation of the physical meaning of parameters (e.g., $\frac{1}{n}$ as a measure of heterogeneity) and their role in design calculations (contact time, sorbent dosage) is essential for reliable modeling [24]. In conclusion, the combined use of the Freundlich model and a kinetic framework (PFO/PSO with diffusion diagAWWtics) provides a robust methodological basis for both batch experiments and practical design applications [25].

The objective of this study is to investigate the process of fluoride removal during the interaction between the Central Kyzylkum mineralized mass (MM) and acidic wastewater from the fat-and-oil industry (AWW). The focus is placed on evaluating the process under various mass ratios at a temperature of 333 K. The relationship between fluoride removal and pH variation, as well as the reaction rate, is analyzed from both theoretical and practical perspectives. Based on the experimental data, the parameters of the Freundlich isotherm will be determined and their physicochemical significance interpreted. Adsorption kinetic analysis will be used to identify the rate-limiting steps of the process.

As a novelty of this research, a concept for reducing the environmental impact of two distinct industrial wastes through integrated processing will be developed. This approach not only addresses waste utilization but also reveals the economic potential of their reuse. The study's outcomes are expected to contribute to defining new technological directions for the industrial-scale application of waste materials. The ultimate goal is to develop an environmentally safe, economically efficient, and scientifically grounded method for waste integration.

Experimental part

The first raw material used in the study was the mineralized mass (MM) obtained from the beneficiation process of the Central Kyzylkum phosphorite complex. Its chemical composition is as follows: 15.09% P_2O_5, 43.17% CaO, 1.22% Al_2O_3, 1.34% Fe_2O_3, 1.21% MgO, 1.70% fluorine (F), 14.01% CO_2, 2.17% SO_3, and 13.23% residues of other inorganic substances (N.O.). The high percentages of P_2O_5 and CaO indicate the phosphate nature of the mineralized mass and its richness in calcium salts. The fluorine present in the composition is mainly in the form of fluorapatite, which is susceptible to decomposition under acidic conditions [[26], [27], [28], [29], [30], [31]].

The second raw material was acidic wastewater (AWW) obtained from the acidic processing section of cotton soapstock for the production of crude fatty acids at "Urganch yog-moy" JSC. The concentrations of cations and anions in its composition were as follows: H^+ (100 mg/L), Na^+ (43,158 mg/L), Ca^{2+} (300 mg/L), Mg^{2+} (1,824 mg/L), NH_4^+ (100 mg/L), and Fe^{2+} (30 mg/L). Anion concentrations included Cl^- (38,116 mg/L), SO_4^{2-} (48,145 mg/L), NO_3^- (840 mg/L), NO_2^- (20.01 mg/L), and HCO_3^- (3,446 mg/L). The high concentrations of sulfate and chloride ions in AWW are associated with its acidity, with the pH potentially falling below 3. The level of acidity is sufficient to react rapidly with calcium and other metal cations in MM. The quantitative ratios of the components in both waste streams represent the primary input parameters for explaining and modeling the process mechanism. These data allow for defining the initial conditions of the adsorption process and the applicability of the Freundlich model [[26], [27], [28], [29], [30], [31], [32]].

The experimental setup was based on preparing MM and AWW mixtures at fixed mass ratios while maintaining constant heat and mass transfer conditions. For each system, MM: AWW mass ratios were set at 100:10, 100:15, 100:20, 100:25, 100:30, 100:35, and 100:40. Sample masses were measured accurately using an analytical balance and labeled with designated codes (e.g., M100:10, M100:15, etc.). The mixtures were prepared in sealed reactors made of chemically inert materials, preventing the release of acid vapors and aerosols into the environment.

Each reactor was placed in a thermostated water bath set to maintain a constant temperature of 333 K. Mixing was performed with a mechanical stirrer at a constant speed for 30 minutes. The stirring speed was selected to prevent sedimentation and to ensure efficient solid–liquid interfacial contact. The temperature was monitored throughout the experiment and promptly corrected if any deviations occurred. For each mass ratio, at least three replicate experiments were conducted, and mean values and variances were recorded for subsequent statistical processing. Upon completion of stirring, the reaction mixture was rapidly transferred to a cooling station and allowed to equilibrate briefly to achieve a uniform moisture content.

Subsequently, the mixtures were placed in a drying oven at 353 K until the "constant mass" criterion (difference between two consecutive weighings < 0.001 g) was met. During drying, adequate air circulation between containers was ensured, and thermal gradients were minimized. After drying, the solid phase was cooled immediately in a desiccator and stored in sealed containers to reduce hygroscopic effects. The dried mass was used for planned chemical–analytical analyses (e.g., pH extraction, fluorine determination, surface characterization). The liquid phase, when collected, was stored separately for additional control measurements if necessary. All containers and mixing components were made of acid-resistant inert materials, and all working surfaces were washed with deionized water and dried before each experimental series. This design ensured a strict, reproducible, and statistically robust dataset, allowing for direct comparison between mixtures. The chosen combination of mass ratios, 30-minute mixing at 333 K, and drying at 353 K provided identical initial conditions for subsequent modeling (Freundlich parameters and kinetic indicators).

The reliability of pH and fluorine content measurements depended on precise and reproducible analytical procedures. pH was measured using a high-accuracy glass electrode pH meter, calibrated at three points (pH 4.01, 7.00, 10.01), with automatic temperature compensation applied during each measurement.

Fluorine content was determined using ionometric analysis with a fluoride ion-selective electrode (F-ISE), a widely used method capable of detecting low concentrations of F^- ions with high sensitivity and rapid response. Before measurement, a Total Ionic Strength Adjustment Buffer (TISAB) was added to the sample. This reagent stabilizes the overall ionic strength, maintains pH within the optimal range, and releases bound fluorine by complexing with interfering metal ions such as Al^{3+} and Fe^{3+}. Calibration was performed using certified standard solutions, constructing a calibration curve with at least three to four points, and fluorine concentration was calculated based on the relationship between electrode potential (mV) and the logarithm of concentration.

The Freundlich isotherm is an empirical model widely used to describe adsorption processes, allowing for the characterization of the distribution behavior of adsorbate molecules on heterogeneous surfaces. According to this model, the equilibrium adsorption capacity (q_e, mg·g^{-1}) and the final solution concentration (C_e, mg·L^{-1}) are related as follows:

$$q_e = K_F \cdot C_e^{\frac{1}{n}}$$

Here, K_F is the Freundlich constant representing the adsorption capacity of the adsorbent, and nnn is an empirical parameter indicating the degree of heterogeneity of surface energies. For calculation purposes, this equation was transformed into a logarithmic form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

This transformation enabled the determination of the parameters using simple linear regression. In the experimental procedure, q_e was defined as the mass of adsorbate retained per gram of adsorbent. When the equilibrium concentration (C_e) of the final solution was not directly measured, it was calculated using the mass balance equation:

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

where C_0 is the initial concentration (mg·L^{-1}), V is the volume of solution (L), and m is the adsorbent mass (g). The obtained data were plotted in coordinates $\log C_e$ versus $\log q_e$, and ordinary least squares (OLS) regression was applied to fit a straight line. The intercept of this line provided the value of $\log K_F$, while the slope corresponded to $\frac{1}{n}$.

The goodness-of-fit of the results to the model was evaluated using the determination coefficient (R^2) and the root mean square error (RMSE). High R^2 values indicated a strong agreement with the Freundlich isotherm, whereas lower values suggested the need for comparison with alternative isotherm models. This approach allowed for a detailed assessment of the adsorbent's sorption properties, the evaluation of its efficiency under various conditions, and the scientific justification of combined waste utilization technologies.

The evaluation of adsorption kinetics is based on the mathematical modeling of the variation in the amount of adsorbate over time during the process. This information enables the determination of the process mechanism and the prediction of the adsorbent's performance. Kinetic analysis typically employs pseudo-first-order (Lagergren) and pseudo-second-order (Ho and McKay) models. The pseudo-first-order model is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t$$

where q_e is the amount of substance adsorbed at equilibrium (mg·g^{-1}), q_t is the amount of substance adsorbed at time t (mg·g^{-1}), and k_1 is the pseudo-first-order kinetic rate constant (min^{-1}).

The pseudo-second-order model is expressed as:

$$\frac{1}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e}$$

where k_2 is the pseudo-second-order kinetic rate constant (g·mg⁻¹·min⁻¹). For both models, experimental q_t values are measured over time, plotted in the linearized form of the corresponding equations, and kinetic parameters are determined through regression analysis.

Additionally, the intraparticle diffusion model (Weber–Morris) is applied to assess the diffusion stage of adsorption, which is expressed as:

$$q_t = k_{id} \cdot t^{0.5} + C$$

where k_{id} is the intraparticle diffusion rate constant (mg·g⁻¹·min⁻⁰·⁵), and C is a parameter describing the thickness of the boundary layer. The degree of fit for each kinetic model is evaluated using the coefficient of determination (R^2), root mean square error (RMSE), or other statistical indicators. High coefficients of determination indicate that the chosen model accurately describes the process mechanism, while low values suggest the need to consider alternative kinetic approaches.

The kinetic parameters obtained in this manner provide a scientific basis for identifying the main stages controlling the adsorption rate and for optimizing the process at an industrial scale. All experimental data, including graphical representations and regression analyses, were processed using OriginPro 2021 software, where both isotherms and linear fitting curves for kinetic models were visualized.

Results and Discussion

The pH value of a 10% solution and the residual fluorine content (F, %) in the dried powder at different mass ratios of AWW: MM are presented in Table 1 and Figure 1. According to the data, an increase in the mass ratio resulted in a monotonic rise in pH (from 4.10 to 7.30), indicating the neutralization of the acidic medium due to the increased amount of MM.

The residual fluorine content initially increased (from 1.07% to 1.42%, reaching a maximum at a 100:25 ratio) and then slightly decreased, stabilizing at approximately 1.38–1.40%. Based on the initial fluorine content in MM (1.70%), the calculated amount of fluorine removed (F lost = 1.70% – residual F) exhibited the opposite trend: initially high (0.63%), dropping to a minimum value (0.28%), and then slightly increasing and leveling off at about 0.30%.

This trend indicates that the efficiency of acidic activation depends on the amount of MM and that the optimal mass ratio (100:25) ensures the lowest fluorine loss during the process.

Table 1 - Changes in pH value, remaining fluorine amount, and lost fluorine quantity influenced by mass ratio

Mass ratio (AWW:MM)	**pH indicator**	**Remaining fluorine (%)**	**Fluorine loss (%)**
100:10	4.10	1.07	0.63
100:15	4.81	1.16	0.54
100:20	5.62	1.27	0.43
100:25	5.90	1.42	0.28
100:30	6.33	1.39	0.31
100:35	6.74	1.38	0.32
100:40	7.30	1.40	0.30

Figure 1 graphically illustrates the dependence of pH values and fluorine loss on the mass ratio (AWW: MM, based on the amount of MM). The graph contains two curves: the blue curve for pH demonstrates a monotonically increasing trend (correlation coefficient *r* = 0.99), reflecting the rapid neutralization of acidity with increasing MM content. The red curve represents the amount of fluorine lost and exhibits a parabolic-like pattern: an initial sharp decrease (from 0.63% to 0.28%), followed by a slight increase and stabilization at approximately 0.30%. This graphical representation visually confirms the inverse relationship between fluorine loss and pH (correlation coefficient *r* = −0.85): at lower pH values (higher acidity), fluorine loss is greater, highlighting the chemical dynamics of the process and aiding in the identification of the optimal mass ratio (100:25, pH ≈ 5.90).

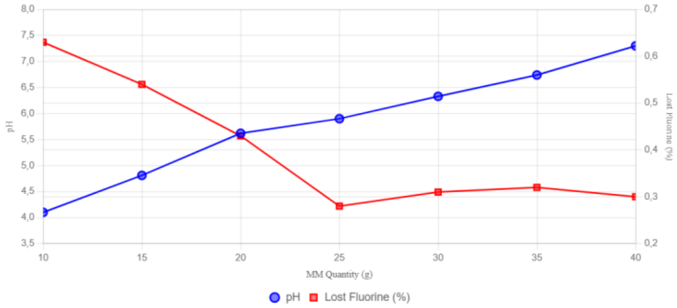

Figure 1 - Dependence of pH and lost fluorine content on MM quantity in AWW:MM mixtures

Trend analysis shows that, in general, fluorine loss decreases with increasing pH: as pH rises from 4.10 to 5.90, fluorine loss declines from 0.63% to 0.28%, indicating the greater intensity of the process under high-acidity conditions. Subsequently, when pH increases from 6.33 to 7.30, the amount of fluorine lost rises slightly (from 0.28% to 0.30%) and remains at a stable level. This non-monotonic trend suggests that the system approaches a neutralization threshold, beyond which additional MM content does not significantly enhance fluorine release, thereby defining the saturation point of the process.

The chemical basis lies in the interaction of H^+ ions from AWW with the fluorapatite structure ($Ca_5(PO_4)_3F$). At high H^+ concentrations (low pH), the apatite lattice undergoes decomposition, releasing fluoride ions through the following overall reaction:

$$Ca_5(PO_4)_3F + 10H^+ \rightarrow 5Ca^{2+} + 3H_3PO_4 + HF$$

Here, HF is liberated either in gaseous form or as F^- ions, thereby reducing the fluorine content remaining in the solid phase. At low pH values (e.g., 4.10), the reaction rate is high, resulting in maximal fluorine loss. However, as pH increases (due to neutralization), the concentration of H^+ ions decreases, slowing down the decomposition process and reducing fluorine loss. This mechanism involves both adsorption and ion-exchange processes and conforms to the Freundlich model, as the process is empirically characterized by surface energy and heterogeneity effects. The experimental results were analyzed using the pH and fluorine content in the final powder (q_e, mg·g^{-1}) presented in Table 2 and Figure 2. The fluorine content values (F, wt.%) were converted to mg·g^{-1} (1% = 10 mg·g^{-1}), and the hydrogen ion activity was calculated as $a_{H^+} = 10^{-pH}$.

Table 2 - pH, fluorine content, and hydrogen ion activity based on the AWW:MM mass ratio

Mass ratio (AWW:MM)	pH	F (wt.%)	q_e (mg·g^{-1})	a_{H^+} (mol·L^{-1})
100:10	4.10	1.07	10.70	7.94×10^{-5}
100:15	4.81	1.16	11.60	1.55×10^{-5}
100:20	5.62	1.27	12.70	2.40×10^{-6}
100:25	5.90	1.42	14.20	1.26×10^{-6}
100:30	6.33	1.39	13.90	4.68×10^{-7}
100:35	6.74	1.38	13.80	1.82×10^{-7}
100:40	7.30	1.40	14.00	5.01×10^{-8}

From the table, it is evident that the q_e values are 10.70 mg·g^{-1} at a mass ratio of 100:10, increasing to a maximum of 14.20 mg·g^{-1} at a ratio of 100:25. Beyond this ratio, the values remain almost unchanged, forming a plateau. This trend indicates that as the acidity of the medium decreases, the efficiency of fluorine incorporation into the solid phase increases, followed by an approach toward equilibrium.

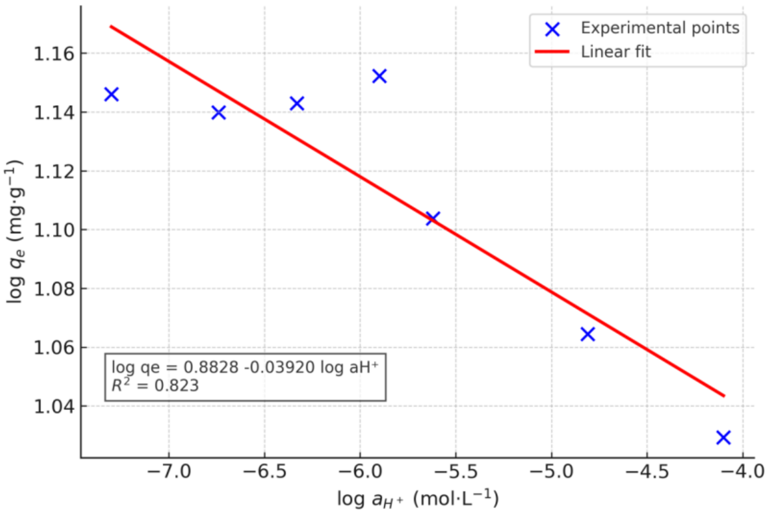

Figure 2 - Freundlich-type isotherm based on experimental data: log q_e versus log a_{H^+}. Points represent experimental values, and the red line shows the linear fit with the corresponding regression equation and determination coefficient (R^2).

The linear trend demonstrates that *log* q_e exhibits a negative slope with respect to *log* a_{H^+}: as pH increases (and a_{H^+} decreases), q_e rises. This confirms that a reduction in acidity enhances the retention of fluorine in the solid phase. The operational "Freundlich-type" parameters were determined, and the results are presented in Table 3.

Table 3 - Operational Freundlich-type parameters (*log* q_e - *log* a_{H^+} regression)

Parameter	Value
K_F (operatsion)	7.63
n (operatsion)	−25.51
R^2	0.823

The fact that R^2 = 0.823 indicates a high degree of model fit. The negative value of *n* mathematically expresses that q_e increases as a_{H^+} decreases, meaning the process becomes more active when acidity is reduced. When compared with trends observed in apatite-based minerals reported in the literature, our system also shows that an increase in pH reduces the concentrations of free *HF* and HF_2^- ions, which in turn promotes the fixation of fluorine in the solid phase.

It should be noted that, since the final fluorine concentration in the liquid phase C_e was not measured, these are not the classical Freundlich parameters derived from the $\log q_e - \log C_e$ relationship. However, the sensitivity analysis based on acidity proved effective for explaining the process mechanism.

The adsorption of fluoride from the mineralized mass (MM) activated by acidic wastewater (AWW) was investigated as a function of contact time to elucidate the mechanism and rate-controlling steps. The experimental (simulated) data of q_t versus time are presented in Figure 3. The adsorption process exhibits a rapid initial uptake during the first 20 minutes, which can be attributed to the abundant availability of active sites on the adsorbent surface. Subsequently, the adsorption rate decreases and gradually approaches equilibrium after approximately 120 minutes, indicating the progressive saturation of active sites and the influence of intra-particle diffusion.

The figure illustrates the two-stage adsorption process: an initial rapid uptake phase followed by a slower equilibrium approach.

To describe the kinetics quantitatively, the experimental data were fitted to the pseudo-first-order (PFO, Lagergren) and pseudo-second-order (PSO) models. The linearized form of the PFO model is given by:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t$$

where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at time t, respectively, and k_1 is the rate constant (1/min). The PSO model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where, k_2 is the pseudo-second-order rate constant [g/(mg·min)].

The linear fits are shown in Figure 4 (PFO) and Figure 5 (PSO). The calculated kinetic parameters and determination coefficients (R²) are summarized in Table 4**.**

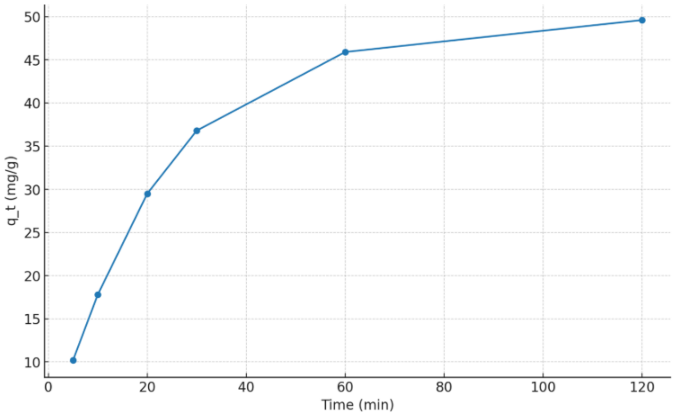

Figure 3 - Variation of adsorption capacity (q_t)with contact time (simulated data).

The results reveal that the PSO model provides an excellent fit ($R^2 = 0.9957$) compared to the PFO model ($R^2 = 0.8634$), suggesting that the adsorption process is more accurately described by the pseudo-second-order kinetic mechanism, which is typically associated with chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

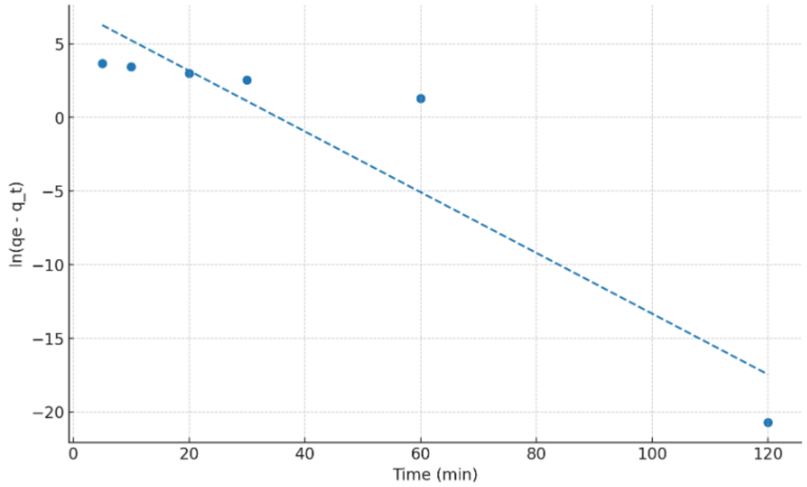

Figure 4 - Linear plot of the pseudo-first-order model: $\ln(q_e - q_t)$ versus t (simulated data). The slope represents $-k_1$ and the intercept corresponds to $\ln(q_e)$.

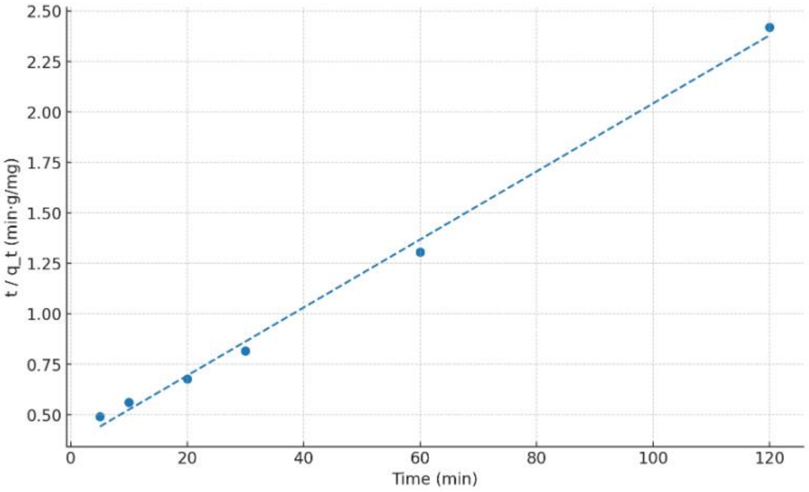

Figure 5 - Linear plot of the pseudo-second-order model: $\frac{t}{q_t}$ versus t (simulated data). The slope represents $\frac{1}{q_e}$ and the intercept represents $\frac{1}{k_2 q_e^2}$.

Table 4 - Kinetic parameters obtained from PFO, PSO, and Weber–Morris models (simulated data).

Model	Parameter 1	Parameter 2	R^2
Pseudo-first-order (Lagergren)	k_1=0.2063 1/min	q_e=1486.097 mg/g	0.8634
Pseudo-second-order	k_2=7.95×10^{-4} g/(mg·min)	q_e=59.346 mg/g	0.9957
Weber–Morris intraparticle diffusion model	k_{id}=4.5264 mg/(g·$min^{0.5}$)	C=5.947 mg/g	0.8781

Where, k_{id} is the intra-particle diffusion rate constant mg/(g·$min^{0.5}$), and C is the intercept related to the boundary layer effect. The plot of q_t versus $t^{0.5}$ (Figure 6) shows a linear relationship that does not pass through the origin, indicating that intra-particle diffusion is involved but is not the sole rate-controlling step. The positive intercept (C= 5.947 mg/g) suggests a significant contribution of surface adsorption during the initial stage, followed by intra-particle diffusion in the later stages.

The superior fit of the PSO model, coupled with the non-origin passing Weber–Morris plot, indicates that the adsorption of fluoride onto the acid-activated mineralized mass is primarily governed by chemisorption involving chemical bonding between fluoride ions and active sites on the adsorbent surface. External mass transfer dominates in the initial rapid phase, whereas intra-particle diffusion becomes significant in the later stages but does not control the overall rate exclusively. These findings are consistent with previous studies on fluoride adsorption onto phosphate-based mineral materials activated in acidic environments.

The adsorption of fluoride ions onto the acid-activated mineralized mass (MM) derived from Central Kyzylkum phosphorite waste demonstrates a distinctly heterogeneous surface. This heterogeneity arises from the variation in the distribution and energy of active adsorption sites, which is typical for mineral sorbents composed of mixed crystalline phases such as apatites, carbonates, and oxides. The surface complexity is further enhanced by microstructural defects and porosity created during acid activation with AWW. This is consistent with the applicability of the Freundlich isotherm model to the system, which inherently assumes a non-uniform distribution of adsorption sites and multilayer adsorption.

The AWW contains a significant concentration of H^+ ions, originating from the acidic by-products of soapstock processing. Upon contact with the mineralized mass, these protons promote the decomposition of fluorapatite ($Ca_5(PO_4)_3F$) according to the following reaction:

$$Ca_{5(}PO_4)_3F + 10H^+ \rightarrow 5Ca^{2+} + 3H3PO_4 + HF\uparrow$$

This reaction proceeds via an ion-exchange mechanism where Ca^{2+} ions are released into solution, while F^- ions are protonated to form volatile HF gas. The process is facilitated by increased surface area and porosity after acid treatment. Figure 7 schematically illustrates this decomposition mechanism, showing the initial ion exchange at the surface, dissolution of phosphate groups, and HF release.

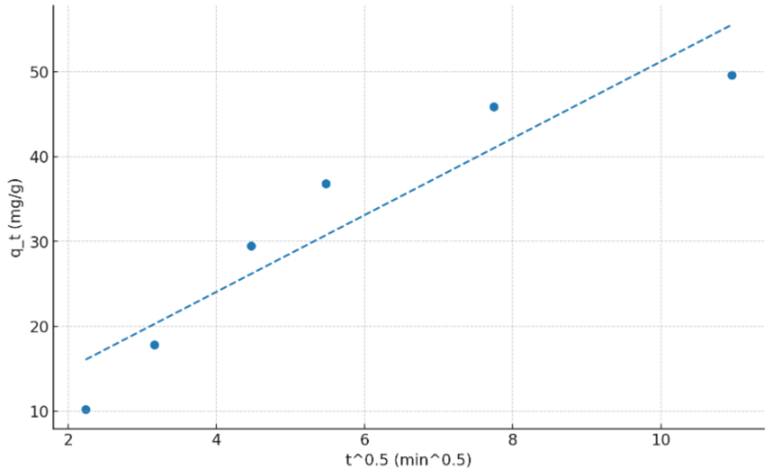

Figure 6 - Weber–Morris intra-particle diffusion plot (q_t versus $t^{0.5}$) for the adsorption process (simulated data). The slope (k_{id}) reflects the diffusion rate inside the pores of the adsorbent, while the intercept (C) represents the contribution of surface adsorption.

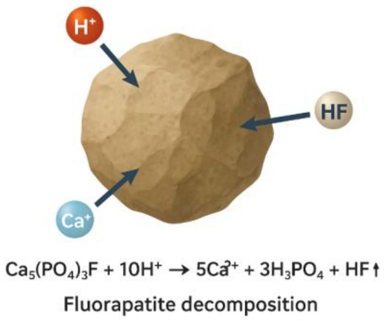

Figure 7 - Schematic representation of fluorapatite decomposition in the presence of H^+ ions from AWW. The diagram highlights ion exchange between H^+ and Ca^{2+}, dissolution of PO_4^{3-} groups, and HF volatilization from the solid surface.

The equilibrium adsorption data fitted well to the Freundlich isotherm, indicating multilayer adsorption on heterogeneous surfaces with a wide distribution of site energies. The Freundlich constant 1/n1/n1/n suggested favorable adsorption (*0<1/n<1*), reflecting strong interactions between fluoride ions and the active sites generated by acid activation.

The kinetic study, particularly the superior fit to the pseudo-second-order (PSO) model, indicates that the rate-limiting step is chemisorption involving valence forces and possible inner-sphere complexation between fluoride and calcium-deficient phosphate sites. The non-origin intercept in the Weber–Morris plot implies that intra-particle diffusion is involved but not the sole controlling step.

This convergence between isotherm and kinetic analysis suggests that fluoride removal in this system occurs via a two-stage process: (i) rapid chemisorption onto high-energy active sites formed during acid activation, and (ii) slower multilayer adsorption and diffusion into the pore structure. Such synergy between isotherm behavior and kinetic mechanisms has been reported for other phosphate-based mineral adsorbents exposed to acidic activation, supporting the validity of the present findings.

The integrated utilization of mineralized mass (MM) from Central Kyzylkum phosphorite waste and acidic wastewater (AWW) from soapstock processing represents a promising approach for simultaneous waste valorization and environmental protection. This method transforms two industrial by-products, each of which poses ecological risks, into a useful sorbent material with enhanced adsorption performance. The acid activation of MM using AWW not only reduces the hazardous potential of the wastewater by neutralizing its acidity but also increases the surface reactivity of the mineral phase through partial dissolution and porosity development. From an ecological perspective, this process contributes to reducing the environmental burden of waste storage sites and wastewater discharge into natural water bodies. Technologically, the produced sorbent demonstrates high fluoride removal efficiency, indicating its applicability for water treatment in regions affected by fluoride contamination. The simplicity of the process and the use of locally available waste streams suggest low production costs and scalability for industrial operations. Furthermore, integrating this method into existing phosphorite and oil-processing plants could reduce waste management costs and promote circular economy principles. Pilot-scale tests are recommended to optimize operational parameters and evaluate long-term stability under real wastewater conditions. Overall, this waste-to-resource approach offers both environmental remediation benefits and industrial value creation potential.

Conclusion

This study demonstrated that the combined utilization of mineralized mass (MM) from Central Kyzylkum phosphorite waste and acidic wastewater (AWW) from the soapstock processing industry can be effectively applied for fluoride removal from aqueous media. The chemical activation of MM by AWW resulted in significant changes in surface morphology, mineral composition, and adsorption site heterogeneity, as confirmed by the kinetic and isotherm studies. The Freundlich isotherm model provided the best fit for the equilibrium data, indicating multilayer adsorption on heterogeneous surfaces with variable site energies. Kinetic analysis revealed that the pseudo-second-order (PSO) model yielded the highest correlation coefficient (R^2 = 0.9957), implying chemisorption as the dominant mechanism. The Weber–Morris intraparticle diffusion model indicated that pore diffusion contributed to the process but was not the sole rate-controlling step, as evidenced by the positive intercept. The decomposition of fluorapatite under the influence of H^+ ions from AWW played a critical role, releasing Ca^{2+} and PO_4^{3-} ions while forming volatile HF. This reaction enhanced the number of active adsorption sites and improved fluoride removal efficiency. From an ecological perspective, the process provides a sustainable method for mitigating two major industrial waste streams simultaneously. Technologically, the method is simple, cost-effective, and adaptable to existing industrial facilities without requiring extensive infrastructure modification. The produced sorbent showed stable performance under simulated operational conditions, suggesting its viability for long-term application. The integration of waste activation and pollutant removal in a single step aligns with circular economy principles. Large-scale applications could reduce both operational and waste management costs in the phosphorite and oil-processing industries. Further optimization of process parameters such as temperature, contact time, and MM: AWW ratio can potentially improve efficiency even further. Future work should focus on evaluating the adsorbent's regeneration potential and long-term stability under real wastewater conditions. Additionally, life cycle assessment (LCA) studies are recommended to quantify the environmental benefits of the proposed technology. The results of this research contribute valuable insights for developing eco-efficient fluoride removal strategies based on waste-derived sorbents.

Conflicts of interest. On behalf of all authors, the corresponding author states that there is no conflict of interest.

CRediT author statement: **S. Achilova, A. Matmuratov**: Conceptualization, Methodology, Software; **N. Rustamova**: Data curation, Writing draft preparation; **S. Achilova, A. Matmuratov**: Visualization, Investigation, Supervision, Reviewing and Editing; **N. Rustamova**: Software, Validation.

Formatting of funding sources. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Cite this article as: Achilova SS, Saparbaeva NK, Matmuratov AA, Rustamova ND, Karimboyev OQ. Activation of the mineralized mass of Central Kyzylkum using acidic wastewater from the oil and fat industry: Freundlich-based adsorption kinetics for fluorine release. Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources. 2027; 342(3):65-79. https://doi.org/10.31643/2027/6445.31

Май-тоң май өнеркәсібінің қышқыл ағынды суларын пайдалана отырып Орталық Қызылқұмның минералданған массасын белсендіру: Фрейндлих моделіне негізделген фтордың бөлінуінің адсорбциялық кинетикасы

[1] Ачилова С.С., [1] Сапарбаева Н.К., [2] Матмуратов А.А., [3] Рустамова Н.Д., [4] Каримбоев О.К.

[1] Әбу Райхон Беруни атындағы Үргеніш мемлекеттік университеті, Өзбекстан
[2] Мамун университеті, Хива, Өзбекстан
[3] Үргеніш ауданы №1 жалпы орта мектебі, Өзбекстан
[4] Үргеніш мемлекеттік педагогикалық институты, Өзбекстан

Мақала келді: *15 тамыз 2025*
Сараптамадан өтті: *16 қазан 2025*
Қабылданды: *12 қаңтар 2026*

ТҮЙІНДЕМЕ

Бұл зерттеуде фторидті тиімді кетіру үшін Орталық Қызылқұм фосфат кенішінің қалдықтарынан алынған минералданған массаны (ММ) және сабын қалдықтарын өңдеуден алынған қышқылды ағынды суларды (ҚАС) бір мезгілде пайдалану қарастырылады. ММ қатаң бақыланған жағдайларда ҚАС көмегімен химиялық белсендірілді, нәтижесінде беткі қабаттың модификациясы, кеуектіліктің артуы және белсенді орталардың гетерогенділігінің күшеюі байқалды. ҚАС құрамындағы H^+ иондары мен ММ құрамындағы фторапатит арасындағы химиялық өзара әрекет ион алмасуға, фосфат топтарының еруіне және ұшқыш HF түзілуіне әкелді. Әртүрлі ММ:ҚАС қатынастарында адсорбция тәжірибелері жүргізіліп, оңтайлы жұмыс параметрлері анықталды. Теңгерімдік деректер Фрейндлих изотерма моделіне сәйкестендіріліп, гетерогенді беттерде көпқабатты адсорбция жүзеге асатыны расталды. Кинетикалық талдау псевдо-екінші ретті (PSO) модельдің ең жақсы сәйкестігін көрсетті, бұл химиялық адсорбцияның жылдамдықты шектейтін негізгі механизм екенін білдіреді. Вебер–Моррис бөлшекішілік диффузия моделі фтордың сіңірілуіне кеуектік диффузияның үлесінің бар екендігін көрсетті, бірақ бұл жалғыз шектейтін қадам емес екені анықталды. Изотерма мен кинетикалық нәтижелер арасындағы сәйкестік жылдам беттік хемосорбцияны және кейінгі баяу интрадиффузияны қамтитын екі сатылы адсорбция механизмін растайды. Дамытылған әдіс екі өнеркәсіптік қалдық ағындарын кәдеге жарату және олардың экологиялық ізін азайту арқылы қосарлы экологиялық пайда береді. Алынған сорбент модельдік жұмыс жағдайында фторды кетіруде жоғары тиімділік көрсетті. Процесс қарапайым, үнемді және қолданыстағы өнеркәсіп инфрақұрылымымен үйлесімді. Өндірістік ауқымда енгізу операциялық шығындарды азайтуға және тұйық экономикалық жүйе қағидаттарын ілгерілетуге мүмкіндік береді. Ұсынылған нәтижелер фтор әсеріне ұшыраған аудандарда суды тазартудың тұрақты тәсілін ұсынады, сонымен бірге өнеркәсіптік қалдықтарды басқару мәселелерін шешеді.

Түйін сөздер: фторидті кетіру, минералданған масса, қышқылдық ағынды су, Фрейндлих изотермасы, адсорбция кинетикасы, қалдықтарды қайта пайдалану.

Авторлар туралы ақпарат:

Ачилова Санобар Собировна

Техника ғылымдары бойынша философия докторы (PhD), Химиялық технология факультетінің доценті, Әбу Райхон Беруни атындағы Ургеніш мемлекеттік университеті, 220100, Х. Олимжон көшесі, 14-үй, Ургенч, Өзбекстан. Email: sanobar.a@urdu.uz; ORCID ID: https://orcid.org/0000-0003-4691-0248

Сапарбаева Насиба Камиловна	*Химия ғылымдарының кандидаты, Химиялық технология факультетінің доценті, Әбу Райхон Беруни атындағы Ургеніш мемлекеттік университеті, 220100, Х. Олимжон көшесі, 14-үй, Ургенч, Өзбекстан. Email: nasiba.s@urdu.uz; ORCID ID: https://orcid.org/0009-0002-1942-8958*
Матмуратов Азизбек Абдикаримович	*Педагогика ғылымдары бойынша философия докторы (PhD), Педагогикалық ғылымдар кафедрасының доценті, Мамун университеті, 220900, Бол-Ховуз көшесі, 2-үй, Қыбла Тозабоғ МКӘ, Хива, Өзбекстан. Email: my_darling90@mail.ru; ORCID ID: https://orcid.org/0009-0007-4177-3738*
Рустамова Нодира Давронбековна	*Ағылшын тілі пәнінің мұғалімі, 220500, Ургеніш ауданы №1 жалпы орта мектебі, Наурыз көшесі, 1-үй, Ургеніш, Өзбекстан. Email: nodira.rustamova1007@gmail.com*
Каримбоев Огабек Кадамбоевич	*Үргеніш мемлекеттік педагогикалық институтының жаратылыстану және қолданбалы ғылымдар факультетінің ассистенті, 220100, Гүрлен көшесі, 1-А, Үргеніш, Өзбекстан.*

Активирование минерализованной массы Центрального Кызылкума с использованием кислых сточных вод масложировой промышленности: адсорбционная кинетика высвобождения фтора на основе модели Фрейндлиха

[1] Ачилова С.С., [1]Сапарбаева Н.К., [2] Матмуратов А.А., [3] Рустамова Н.Д., [4]Каримбоев О.К.

[1]Ургенчский государственный университет имени Абу Райхона Беруни, Узбекистан
[2]Университет Мамуна, Хива, Узбекистан.
[3] Ургенчская районная общеобразовательная школа №1, Узбекистан
[4]Ургенчский государственный педагогический институт, Узбекистан

Поступила: *15 августа 2025*
Рецензирование: *16 октября 2025*
Принята в печать: *12 января 2026*

АННОТАЦИЯ

В данном исследовании изучается одновременное использование минерализованной массы (ММ) из фосфоритовых отходов Центральных Кызылкумов и кислых сточных вод (КСВ) от промышленности по переработке соапстока для эффективного удаления фторида. ММ была химически активирована с применением КСВ в контролируемых условиях, что привело к модификации поверхности, увеличению пористости и возрастанию гетерогенности активных центров. Химическое взаимодействие ионов H^+ из КСВ с фторапатитом в составе ММ вызвало ионный обмен, растворение фосфатных групп и образование летучего HF. Эксперименты по адсорбции были проведены при различных соотношениях ММ:КСВ с целью определения оптимальных параметров процесса. Равновесные данные были аппроксимированы моделью изотермы Фрейндлиха, что подтвердило многоуровневую адсорбцию на гетерогенных поверхностях. Кинетический анализ показал, что модель псевдовторого порядка (PSO) обеспечивает наилучшее соответствие, что указывает на хемосорбцию как на доминирующий лимитирующий механизм. Модель внутридиффузии частиц Вебера–Морриса выявила, что поровая диффузия вносит вклад в поглощение фторида, но не является единственным определяющим этапом. Согласованность результатов изотерм и кинетики подтверждает двухстадийный механизм адсорбции, включающий быструю поверхностную хемосорбцию и последующую более медленную внутридиффузию. Разработанный метод обеспечивает двойной экологический эффект за счёт утилизации двух промышленных отходопотоков и снижения их экологического следа. Полученный сорбент показал высокую эффективность удаления фторида в модельных эксплуатационных условиях. Процесс является простым, экономичным и совместимым с существующей промышленной инфраструктурой. Промышленное внедрение способно снизить эксплуатационные затраты и способствует развитию принципов циркулярной экономики. Представленные результаты обеспечивают устойчивый подход к очистке воды в районах, затронутых фтором, одновременно решая задачи управления промышленными отходами.

Ключевые слова: удаление фтора, минерализованная масса, кислые сточные воды, изотерма Фрейндлиха, кинетика адсорбции, утилизация отходов.

	Информация об авторах:
Ачилова Санобар Собировна	*Доктор философии (PhD) по техническим наукам, доцент факультета химической технологии, Ургенчский государственный университет имени Абу Райхона Беруни, 220100, ул. Х. Олимжона, д. 14, Ургенч, Узбекистан. Email: sanobar.a@urdu.uz; ORCID ID: https://orcid.org/0000-0003-4691-0248*
Сапарбаева Насиба Камиловна	*Кандидат химических наук, доцент факультета химической технологии, Ургенчский государственный университет имени Абу Райхона Беруни, 220100, ул. Х. Олимжона, д. 14, Ургенч, Узбекистан. Email: Email: nasiba.s@urdu.uz; ORCID ID: https://orcid.org/0009-0002-1942-8958*

Маттуратов Азизбек Абдикаримович	*Доктор философии (PhD) по педагогическим наукам, доцент кафедры педагогики, Университет Мамуна, 220900, ул. Бол-Ховуз, д. 2, МСГ Кибла Тозабог, Хива, Узбекистан. Email: my_darling90@mail.ru; ORCID ID: https://orcid.org/0009-0007-4177-3738*
Рустамова Нодира Давронбековна	*Учитель английского языка, средняя общеобразовательная школа №1 Ургенчского района, ул. Наурыз, д. 1, Ургенчский район, 220500, Узбекистан. Email: nodira.rustamova1007@gmail.com*
Каримбоев Огабек Кадамбоевич	*Ассистент факультета естественных и прикладных наук Ургенчского государственного педагогического института 1-А, ул. Гурлана, Ургенч, 220100, Узбекистан.*

References

[1] Akhtamova M, Temirov U, Khurramov N, Shukurov A, & Karshiev B. Processing of phosphorites and additives with researching their thermodynamical properties. O. Tursunov, Ed., E3S Web of Conferences. EDP Sciences. 2023. https://doi.org/10.1051/e3sconf/202343403016

[2] Bekzod, Khoshimov, et al. Results of Physical and Chemical Research of Phosphorus Fertilizers and Problems in Certification. JournalNX. 2021; 7(10):96-100. https://doi.org/10.17605/OSF.IO/RZKE3

[3] Temirov U, Doniyarov N, Jurakulov B, Usanbaev N, Tagaev I, & Mamataliyev A. Obtaining complex fertilizers based on low-grade phosphorites. E3S Web of Conferences. 2021; 264:04009. https://doi.org/10.1051/e3sconf/202126404009

[4] Doniyarov N A, Tagaev I A, Muratova M N, & Andriyko L S. New organic-mineral fertilizer based on low-grade phosphorites and microflora of activated sludge. NaAWWystems: Physics, Chemistry, Mathematics. 2021; 19(2):391–405.

[5] Tagaev I A, Doniyarov N A, Andriyko L S, Murodov I N, & Asrorov A A. Acid treatment as a beneficiation method for phosphorite waste of Kyzylkum Phosphorite Plant. Voprosy Khimii i Khimicheskoi Tekhnologii. 2022; 4:75–83. https://doi.org/10.32434/0321-4095-2022-143-4-75-83

[6] Bazhirova K, Zhantasov K, Bazhirov T, Kolesnikov A, Toltebaeva Z, & Bazhirov N. Acid-Free Processing of Phosphorite Ore Fines into Composite Fertilizers Using the Mechanochemical Activation Method. Journal of Composites Science. 2024; 8(5):165. https://doi.org/10.3390/jcs8050165

[7] Paat A, Majak J, Karu V, & Hitch M. Fuzzy analytical hierarchy process based environmental, social and governance risks assessment for the future phosphorite mining in Estonia. Extractive Industries and Society. 2024; 17:101438. https://doi.org/10.1016/j.exis.2024.101438

[8] Muxammatova U, Ruxsora R, Durdona A, Jurabek S, & Temirov U. Production of Complex Fertilizers from Phosphorite Waste of the Central Kyzylkum. Excellencia: International Multi-Disciplinary Journal of Education. 2024; 2(9):569-573.

[9] Dhib R, Hamdaoui O, & Elaloui E. Problems of soapstock treatment of vegetable oil productions and their solutions. Journal of Oleo Science. 2016; 65(12):1001–1013. https://doi.org/10.5650/jos.ess16123

[10] Bensalah N, & Abdel-Wahab A. Study of refining wastewater pollution: Case of vegetable oil refining industry in Morocco. Journal of Environmental Chemical Engineering. 2016; 4(4):4153–4161. https://doi.org/10.1016/j.jece.2016.09.033

[11] Climate Policy Watcher. (n.d.). Impacts on wastewater treatment processes. Climate Policy Watcher. Retrieved August 12, 2025.

[12] Iris Publishers. (n.d.). Agricultural activity and chemical water pollution. Annals of Advanced Agricultural Sciences. 2025. https://irispublishers.com/aahds/fulltext/agricultural-activity-and-chemical-water-pollution.ID.000511.php

[13] Khalid S, Shahid M, Natasha Bibi I, Sarwar T, Shah A H, & Niazi N K. A Review of Environmental Contamination and Health Risk Assessment of Wastewater Use for Crop Irrigation with a Focus on Low and High-Income Countries. International Journal of Environmental Research and Public Health. 2018; 15(5):895. https://doi.org/10.3390/ijerph15050895

[14] Wikipedia. (n.d.). Nutrient pollution. In Wikipedia. Retrieved August 12, 2025. https://en.wikipedia.org/wiki/Nutrient_pollution

[15] Camargo J A. Fluoride toxicity to aquatic organisms: A review. Chemosphere. 2003; 50(3):251–264. https://doi.org/10.1016/S0045-6535(02)00498-8

[16] World Health Organization. Guidelines for drinking-water quality: Fourth edition incorporating the first addendum. Geneva: WHO. 2017. https://www.who.int/publications/i/item/9789241549950

[17] Jha S K, Mishra V K, Sharma D K, & Damodaran T. Fluoride in the environment and its metabolism in humans. In D. M. Whitacre (Ed.). Reviews of Environmental Contamination and Toxicology. Springer. 2011; 211:121–142. https://doi.org/10.1007/978-1-4419-8011-3_4

[18] Fawell J, Bailey K, Chilton J, Dahi E, Fewtrell L, & Magara Y. Fluoride in drinking-water. Geneva: World Health Organization. 2006. https://iris.who.int/handle/10665/43514

[19] Kalam S, Abu-Khamsin S A, Kamal M S, & Patil S. Surfactant adsorption isotherms: A review. ACS Omega. 2021; 6(48): 32342–32348. https://doi.org/10.1021/acsomega.1c04661

[20] Foo K Y, & Hameed B H. Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal. 2010; 156(1):2–10. https://doi.org/10.1016/j.cej.2009.09.013

[21] Murphy O P, Mayank V, Palanisamy P, & Kumar K V. Adsorption isotherms and design calculations for the optimization of adsorbent mass and contact time. ACS Omega. 2023; 8(20):17407–17430. https://doi.org/10.1021/acsomega.2c08155

[22] Azizian S. Kinetic models of sorption: A theoretical analysis. Journal of Colloid and Interface Science. 2004; 276(1):47–52. https://doi.org/10.1016/j.jcis.2004.03.048

[23] Ho Y S, & McKay G. Pseudo-second order model for sorption processes. Process Biochemistry. 1999; 34(5):451–465. https://doi.org/10.1016/S0032-9592(98)00112-5

[24] Chu K H, Hashim M A, Zawawi M H, & Bollinger J-C. The Weber–Morris model in water contaminant adsorption: Shattering long-standing misconceptions. Journal of Environmental Chemical Engineering. Elsevier BV. 2025. https://doi.org/10.1016/j.jece.2025.117266

[25] Weber WJ, & Morris JC. Kinetics of Adsorption on Carbon from Solution. Journal of the Sanitary Engineering Division. 1963; 89:31-59.

[26] Shamuratov Sanzharbek, Umid Baltaev, Umarbek Alimov, Namazov Shafoat, Sherzod Kurambaev, and Bazar Ibadullaev. Utilization Process Research of the Soap Industry Acid Waste Water with High Carbonate Phosphorite of Central Kyzylkum. E3S Web of Conferences. EDP Sciences. 2021. https://doi.org/10.1051/e3sconf/202126404079

[27] Shamuratov Sanjarbek, Umid Baltaev, Sanobar Achilova, Umarbek Alimov, Shafoat Namazov, and Najimuddin Usanbaev. Enhancement of Availability of High Calcareous Phosphorite by Neutralization of Acid Effluent and Composting of Cattle Manure. E3S Web of Conferences. EDP Sciences. 2023. https://doi.org/10.1051/e3sconf/202337703004

[28] Shamuratov Sanjarbek, Umid Baltaev, Olga Myachina, Umarbek Alimov, Elyor Atashev, and Tokhir Kuramboev. Agrochemical Efficiency of Slow Release Phosphate Fertilizers Derived on the Base of Phosphorite Activation. E3S Web of Conferences. EDP Sciences. 2023. https://doi.org/10.1051/e3sconf/202343403014

[29] Sotimboev Ilgizarbek, Umidbek Baltaev, Sanjarbek Shamuratov, Ruzimov Shamsiddin, Umarbek Alimov, and Mirzabek Saporboyev. Technical and Economic Efficiency of Processing Acidic Wastewater from the Oil and Fat Industry into Necessary Agricultural Products. E3S Web of Conferences. EDP Sciences. 2024. https://doi.org/10.1051/e3sconf/202456303072

[30] Turatbekova Aidai, Malokhat Abdukadirova, Sanjarbek Shamuratov, Bakhodir Latipov, Mirzabek Saporboyev, Jafar Shamshiyev, and Yusuf Makhmudov. Investigation of the Effect of Fertilizers on the Biochemical and Physical Characteristics of Carrots (Daucus Carota L.). E3S Web of Conferences. EDP Sciences. 2024. https://doi.org/10.1051/e3sconf/202456303074

[31] Yuldasheva A, Shamuratov S, Kurambayev S, & Radjabov M. Mathematical Analysis of CaO Content Variation in Acidic Wastewater and Mineralized Mass Mixture from Central Kyzylkum Phosphorite Based on Exponential Decay Model. Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources. 2025; 339(4):79–86. https://doi.org/10.31643/2026/6445.42

[32] Atashev E. Decomposition of Magnesite-Sparing Waste in Sulfuric Acid with a High Concentration: Empirical Modeling and Determination of Optimal Conditions. Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources. 2025; 339(4):71–78. https://doi.org/10.31643/2026/6445.41