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Çinko Ekstraksiyon Atığı Kullanılarak Sulu Çözeltilerden Fosfat Gideriminin Araştırılması

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Öz

Çinko üretim tesislerinde açığa çıkan ve içerdikleri metaller nedeniyle tehlikeli atık olarak sınıflandırılan katı liç artıklarının çevre ve insan sağlığına zarar vermeden ekonomik olarak değerlendirilmesi atık yönetimi açısından önemlidir. Bu kalıntıların bertarafı çoğu zaman özel teknolojiler gerektirse de, bu teknolojilerin pahalı olması ve bazı durumlarda yasal yaptırımların yetersiz kalması nedeniyle tehlikeli atıklar çevreye veya çöp depolama alanlarına bırakılmaktadır. Bu nedenle bu kalıntıların değerlendirilerek sanayiye kazandırılması ekonomik ve çevresel açıdan önemlidir. Bu çalışmada, Kayseri Çinkur işletmesinden getirilen çinko ekstraksiyonu üretimi sırasında oluşan kurşun keki kullanılmıştır. Bu atık, çinko ve demirin yanı sıra yüksek miktarda kurşun da içerdiğinden, sulu çözeltilerden fosfatın uzaklaştırılması koşulları araştırıldı. Elde edilen toplu test sonuçları kullanılarak fosfat giderme adsorpsiyon izotermleri elde edildi. Ayrıca fosfat giderimine ilişkin bazı termodinamik büyüklükler de hesaplanmıştır. Deney sonucunda sulu çözeltilerden P giderim veriminin önemli ölçüde çözelti pH'ına ve atık kurşun keki dozuna bağlı olduğu belirlendi. Ayrıca sulu çözeltilerden fosfat gideriminin Langmuir ve Freundlich izotermine uyduğu belirlendi. Ayrıca 120 dakikalık bir süre sonunda fosfat adsorpsiyon dengesinin kurulduğu gözlendi. pH’ı 7.69 olan 100 mg/L fosfat çözeltisinin herhangi bir ilave olmaksızın 20 g/L kurşun keki ile karıştırılması ve 120 dakika süreyle temas ettirilmesiyle fosfatın yaklaşık %74’ü adsorpsiyonla etkili bir şekilde giderilebilir.

Anahtar kelimeler: Ekstraksiyon kalıntısı, Liç, Kurşun, Fosfat adsorpsiyonu, Atık

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[*] Yazışılan yazar

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Investigation of Phosphate Removal from Aqueous Solutions Using Zinc Extraction Waste

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Abstract

It is important for waste management to economically evaluate the solid leach residues released in zinc production facilities and classified as hazardous waste due to the metals they contain, without harming the environment and human health. Although the disposal of these residues often requires special technologies, hazardous wastes are left to the environment or landfills due to the expense of these technologies and the inadequacy of legal sanctions in some cases. For this reason, it is important from an economic and environmental perspective to evaluate these residues and bring them into the industry. In this study, lead cake formed during zinc extraction production, brought from Kayseri Çinkur enterprises, was used. Since this waste contains high amounts of lead as well as zinc and iron, the conditions for removing phosphate from aqueous solutions were investigated. Phosphate removal adsorption isotherms were obtained using the obtained batch test results. Additionally, some thermodynamic quantities regarding phosphate removal were calculated. As a result of the experiment, it was determined that the P removal efficiency from aqueous solutions significantly depends on the solution pH and the dose of waste lead cake. It was also determined that phosphate removal from aqueous solutions obeyed the Langmuir and Freundlich isotherm. Additionally, it was observed that phosphate adsorption equilibrium was established after a period of 120 min. By mixing 100 mg/L phosphate solution with pH 7.69 with 20 g/L lead cake without any addition and contacting for 120 minutes, approximately 74% of the phosphate can be effectively removed by adsorption.

Keywords: Extraction residue, Leaching, Lead, Phosphate adsorption, Waste

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[*] Corresponging auther

1. Introduction

Eutrophication can be defined as the deterioration of water quality as a result of the enrichment of water with nutrients and the active development of plant life, adversely affecting the ecological balance of water. The limiting nutrient in most freshwater lake and river reservoirs is phosphorus, and the migration of these elements from anthropogenic sources into waters accelerates the eutrophication process, which proceeds very slowly during the natural aging of lakes. As a result of this event occurring in the lake environment, the dissolved oxygen present is consumed significantly by the algae formed. Depletion of dissolved oxygen can lead to fish mortality, and some blue-green algae can cause poisoning of fish and sometimes livestock [1-6].

Considering these bad effects of phosphates in waters, it becomes necessary to prevent their passage into waters as much as possible. For this, first of all, phosphate sources for waters must be determined well and phosphates must be removed to a significant extent before being discharged from these sources into surface waters [7-9].

Important sources of phosphorus transfer to surface waters are runoff from agricultural areas and farm areas, domestic and industrial wastewater, and urban drainage seepage. A significant portion of phosphates pass through point sources such as domestic and industrial flows. These sources can be controlled more easily than non-point sources [10-12].

Research has shown that the phosphorus concentration in domestic wastewater is around 5-30 mg-P/L. Currently used treatment techniques are suitable for the treatment of wastewater with these concentration limits. However, the treatment of water containing high phosphate, such as boiler water and some food industry wastewater, requires special techniques. Much research has been done on the treatment of wastewater containing normal levels of phosphate. Economical treatment processes are needed for special wastewaters with high phosphate content. In existing phosphate treatment technologies, manufactured chemicals are generally used. However, using waste from another industry with low economic value in the treatment may make the process attractive in terms of cost [13-17].

At the end of the production process in zinc production facilities, a mixture containing precious metals is formed. For the production of metallic zinc, these mixtures are leached with dilute sulfuric acid solution, and then the solid residue, which is insoluble in acid and rich in other components, especially lead, is filtered through filters. Depending on the composition of the raw material used, the content of the zinc extraction waste may consist of approximately 16% lead, 5% zinc, as well as precious metals such as manganese, cadmium, silver and gold.

The high amount of zinc production and the limited storage areas cause facility waste problems. As a result of production in the zinc zinc production facility, there is an excessive amount of zinc in it and the inability to use this solid residue in the system creates problems in terms of economy and environment. The failure to develop a sustainable waste utilization approach to waste negatively affects the competitiveness of the zinc production facility.

In this study, the removal of phosphate from waters with high orthophosphate concentration was investigated by using filtration residue cakes containing significant amounts of lead compounds, which are released during the production of zinc from carbonate ores by the leaching-electrolysis method. Preliminary tests have shown that a significant amount of phosphorus can be removed by treating solutions with high concentrations of phosphate (100-200 mg-P/L) with these wastes.

A large amount of residue called rotary filter cake is formed in ÇİNKUR facilities in Kayseri. In this study, the possibilities of using this residue in the treatment of waters containing high levels of phosphate were investigated. In the experimental section, the results of the experiments on the effects of factors such as pH, time, concentration and temperature on the adsorption of phosphate from water using this cake were given and discussed. Additionally, some thermodynamic parameters were determined by applying the obtained results to adsorption isotherms.

2. Materials and Methods

2.1. Supply and Preparation of Lead Cake

In the experiments, zinc production residue lead cake obtained from Kayseri Zinc-Lead Enterprise Inc. was used. This cake, which formed after the leaching process, was first washed with distilled water 5 times to remove metal sulfates that could dissolve and pass into the environment. It was partially dried at room temperature and then dried in an oven at 105°C, passed through a -200 mesh sieve and stored in capped plastic bottles. The XRD and SEM-EDX results are given in Figure 1, Figure 2 and Figure 3. Chemical analysis of the zinc extraction residue was carried out by the $LiBO_2$ dissolution-HNO_3 solubilization method [8, 9].

2.2. Preparation of Phosphate Solution

Phosphate solutions used in the experimental study were prepared from Na_2HPO_4 salt. For this purpose, 14.314 g of 80% pure Na_2HPO_4 salt was weighed, dissolved in some water, and then its volume was made up to 500 mL. The standard stock solution at a concentration of 5000 mg-P/L prepared in this way was diluted appropriately and used in the experiments. Dilutions were made with distilled water.

2.3. Experimental Study

In the study, first the effects of adsorbent amount and time on the efficiency of phosphate removal were examined. For this, phosphate solutions were prepared at a concentration of 100 mg-P/L from the standard stock solution. 100 mL of these solutions were placed in 150 mL conical flasks, varying amounts of lead cake were added to them, varying between 0.5-5 g, and they were sealed and placed in a shaking incubator (ZCHENG 200D) at 25°C. The samples were shaken at 400 oscillations/minute for periods ranging from 10 to 240 min. After shaking, the mixtures were filtered through blue band filter paper. pH measurement, phosphorus, zinc, lead, manganese, iron, cadmium and cobalt analyzes were performed on the filtrates. Removal percentages were calculated taking into account the phosphorus concentration.

To determine the effect of phosphate concentrations, phosphate removal experiments were performed for varying periods of time with phosphate solutions with initial concentrations of 100, 125, 150 mg-P/L. Then, in order to examine the effect of initial pH on phosphate removal, experiments were carried out with phosphate solutions at a concentration of 100 mg-P/L, pH varying between 3-12. Finally, an isotherm study was conducted with phosphate solutions with concentrations varying between 25-125 mg-P/L, at the appropriate pH and equilibration time determined by previous experiments. All experiments were carried out on two parallel samples, and results within ± 5% agreement were considered correct and averaged.

2.4. Phosphate Analyzes

Phosphorus analyzes in the filtrates obtained during the experiments were carried out spectrophotometrically according to the Ascorbic Acid method [18].

2.5. Metal Analysis

All metal analyzes were carried out with an atomic absorption spectrophotometer (Perkin elmer aanalyst 400). As a result of the analyzes performed using appropriate standards and diluting to the determination range, the leaching percentages of metals from the zinc extraction residue were calculated by backcalculating from the determined metal concentrations.

3. Results and Discussions

The composition of lead cake used as an adsorbent in phosphate adsorption is given in Table 1. As seen in the table, the sample used contains 15.8% Pb, 8.5% Zn and 5.3% Fe as the main components. The idea that certain materials can remove anionic complex ions from wastewater due to the presence of polyvalent metal ions is supported by multiple research findings. Polyvalent metal ions can indeed interact with anionic species, facilitating their removal through various mechanisms, such as adsorption, electrochemical processes, and the formation of inner-sphere complexes.. In this study, the removal of phosphate from aqueous media using lead cake was investigated.

In some preliminary studies, it was found that lead cake effectively removed low concentrations of phosphate from aqueous environments. For this reason, it was thought that it would be more advantageous to remove the high concentration of phosphate in the aqueous environment with lead cake. In line with this idea, the first experiments were carried out with phosphate solutions at a concentration of 100 mg-P/L in order to reveal the effect of the amount of lead cake on phosphorus removal depending on time. 100 mL of phosphate solution was mixed with lead cake in amounts ranging from 0.5 to 5 g and shaken for periods ranging from 10 to 240 minutes. The phosphorus removal percentage calculated from analyzes and measurements and the metal ion concentrations that dissolve from the cake and pass into solution are given in Figure 4.

Table 1. Chemical composition of the lead cake used in the experiments.

Component	Composition
Pb	% 15.80
Zn	% 8.50
Fe	% 5.30
Ca	% 1.30
Mn	2155 mg/kg
Cd	318 mg/kg
Cu	2280 mg/kg
Ni	475 mg/kg
Cr	249 mg/kg

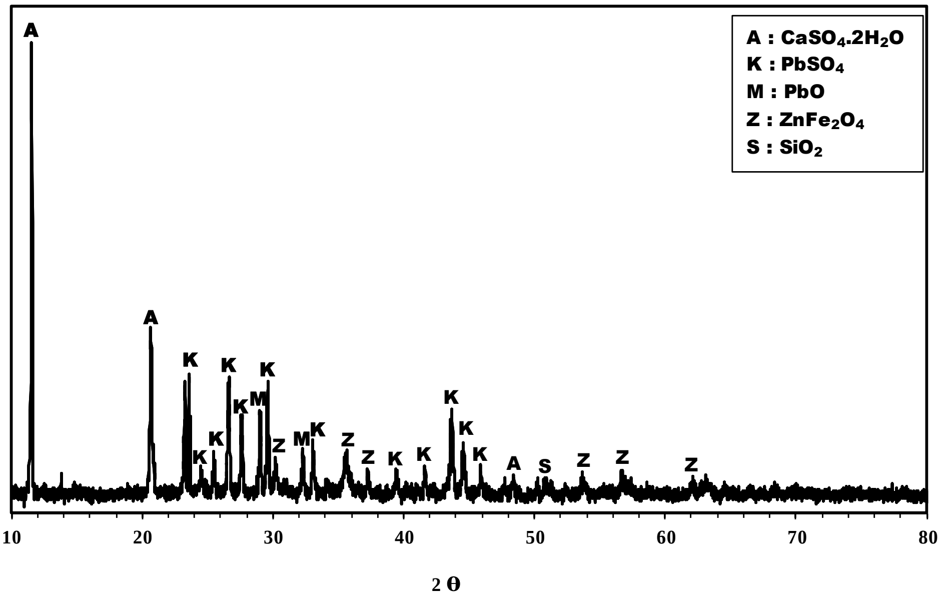

Figure 1. XRD diagram of the lead cake used in the experiments.

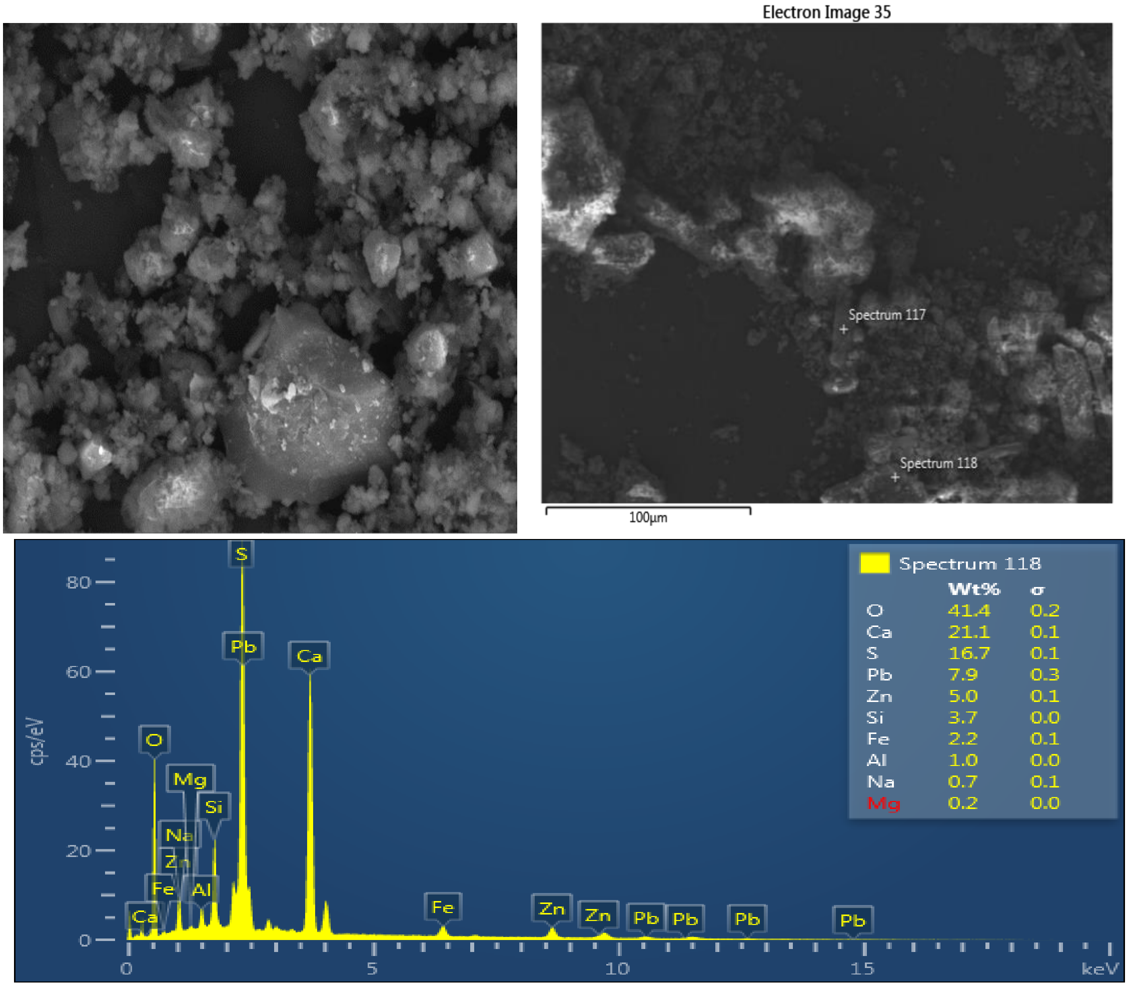

Figure 2. SEM image and EDX evaluation of the lead cake used in the experiments

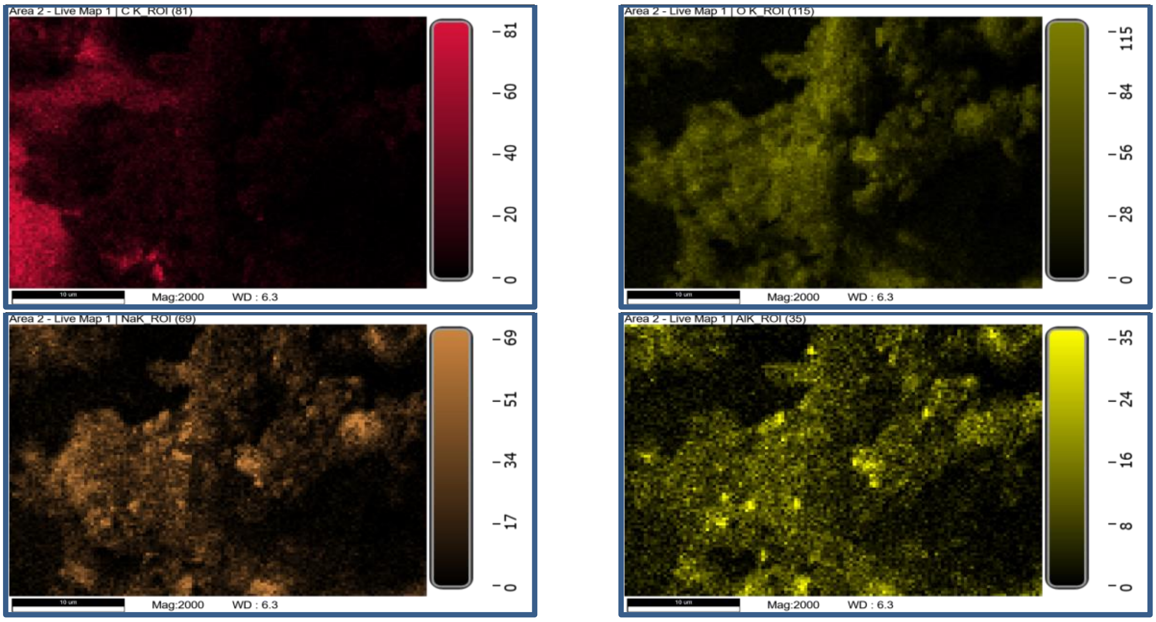

Figure 3. SEM image and EDX evaluation of the lead cake used in the experiments

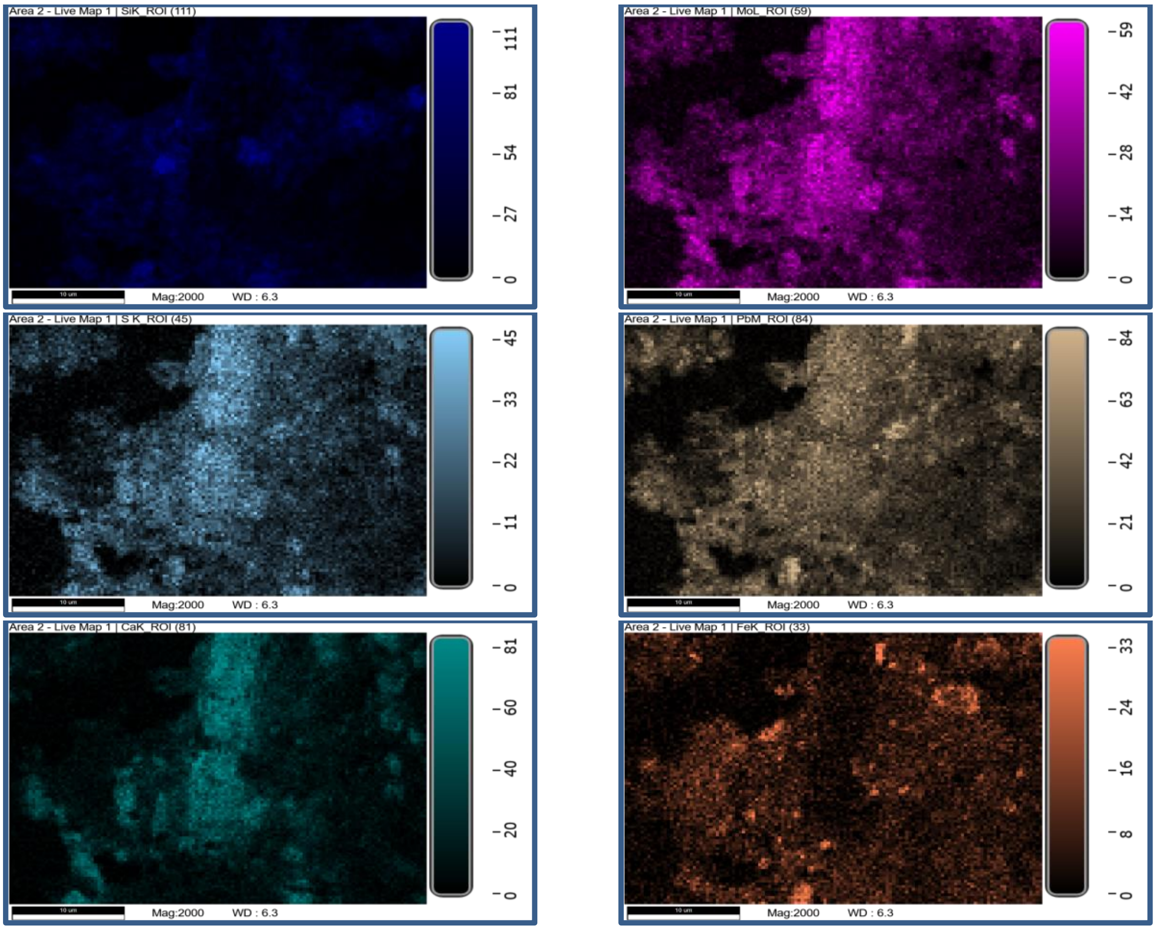

Figure 3. SEM image and EDX evaluation of the lead cake used in the experiments (Continue)

It can be said that with increasing lead cake amount and time, the phosphorus removal efficiency generally increases and an equilibration time is reached at the end of a reaction time of approximately 120 min for all cake amounts. Figure 4 shows that the concentration of metal ions that dissolve from the lead cake into the solution environment increases depending on the amount of cake. Considering the phosphorus removal percentage, it can be said that a dose of 50 g/L lead cake is suitable to remove phosphorus at a concentration of 100 mg/L. However, in order for a treatment process to be applicable, it is required that the treatment in question be carried out in the most effective way and that no other pollution occurs in the process. This is why the concentrations of metal ions in the lead cake that pass into solution must be taken into account. Figure indicates that much higher amounts of Zn and Pb pass into the solution when the 50 g/L lead cake dose is used. For example, in the experiment conducted with a 30 g/L lead cake dose, where the phosphorus removal percentage is relatively high at the end of the equilibration period, 0.82 mg/L lead and 1.02 mg/L zinc pass into the solution, while with a 50 g/L dosage, 0.94 mg/L lead and 18.20 mg. It can be seen that /L zinc passes. In order not to cause any further pollution, it can be said that it would be more appropriate to use cake at a dosage of 30 g/L to remove phosphorus at a concentration of 100 mg/L.

In the second stage, the effect of ambient pH on phosphate removal was examined. For this, phosphate solutions at a concentration of 100 mg/L, the initial pH of which was adjusted between 3-12 using NaOH and H_2SO_4, were shaken for 120 min using cake at a dosage of 30 g/L. The results obtained are seen in figure 4.

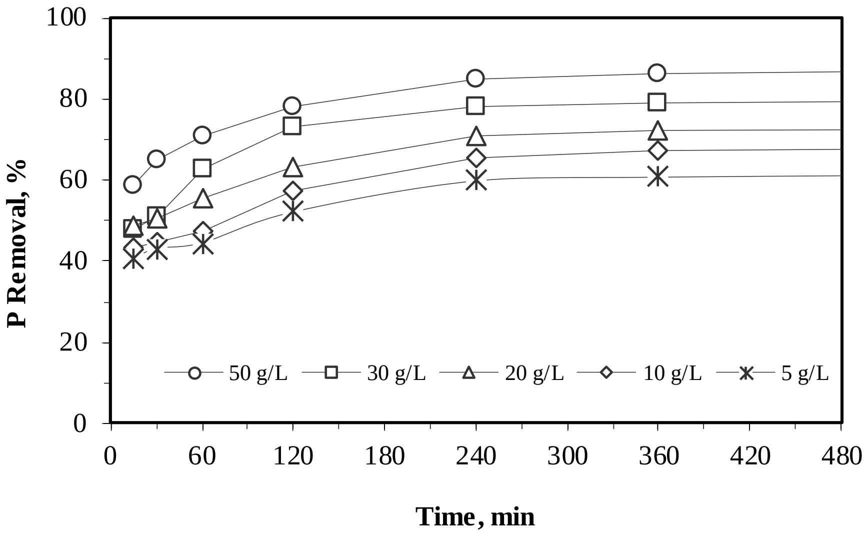

Figure 4. Results of experiments conducted with different doses of lead cake for different periods of time. [25°C; 100mg-P/L; 100 mL; pH: 7.69]

The percentage of phosphate removal increased significantly due to the increase in initial pH. While 2-20% of the total phosphorus can be removed in the pH<6 region, more than 80% of the total phosphorus can be removed at pH>9. It can be seen that at the original pH of the solution, 7.69, approximately 75% of the phosphorus is removed. On the other hand, it is seen that the concentration of Pb ion, which dissolves from the cake and passes into the solution, increases with increasing pH. Zinc passes into solution more at low pH.

Very low and high pH values have no practical applicability due to both acid and base consumption and deterioration of the neutral properties of water. It can be seen from Figure 5 that the most effective phosphorus removal is at pH>10. However, in this case, it is seen that Pb and Zn pass into the solution well above their concentration limits. It can be said that it is more suitable in terms of process economy and applicability to carry out the process at its own pH in order to prevent such secondary pollution and eliminate alkali consumption. For this reason, experiments examining the effects of other parameters on phosphate adsorption were carried out at the original pH of the solution.

Figure 6 shows the effect of initial phosphate concentration on phosphate adsorption. As the phosphate concentration increases, the removal percentage decreases, but the amount of phosphate removed per unit adsorbent (lead cake) increases. Additionally, after approximately 100-120 minutes, an equilibration period is reached for all concentrations. For example, in phosphate solutions at a P concentration of 100 mg/L, an adsorption of approximately 74.98% occurs after 120 minutes of equilibration, while this value becomes 66.17% and 48.98% for concentrations of 125 and 150 mg-P/L, respectively.

The data obtained as a result of contacting phosphate solutions with different initial concentrations with cake at a dosage of 30 g/L, at optimum pH and for 120 min, were applied to Langmuir and Freundlich isotherms (equations 1 and 2).

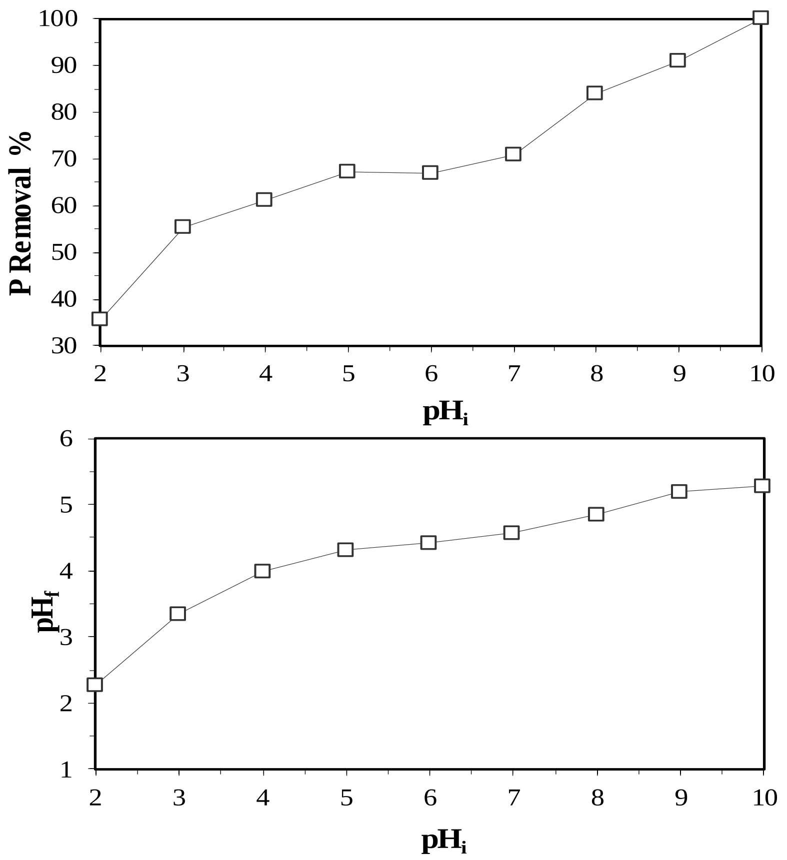

Figure 5. Experimental results examining the effect of initial pH on phosphate adsorption with lead cake. [25°C; 100 mL; 30 g/L lead cake; 100mg-P/L; 120 minutes contact time]

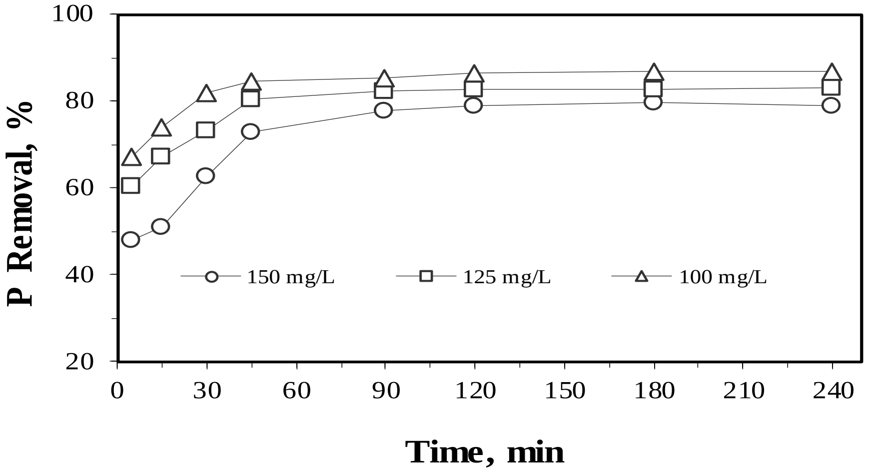

Figure 6. Effect of initial phosphorus concentration on phosphate adsorption by lead cake. [25°C; 30 g/L lead cake; 100 mL; pH: 7.69].

Langmuir isotherms obtained after phosphate adsorption at different temperatures are given in Figure 7. b and Q_0 values were calculated from the slope and shift of the isotherms using linear regression. By plotting ln b values against 1/T values according to Equation 3, the adsorption enthalpy was found to be -11.5941 kJ/mol. Adsorption free enthalpy and entropy changes at different temperatures were calculated using Equations 4 and 5. The results are seen in table 2.

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \qquad (1)$$

$$\ln(x/m) = \ln K_f + \frac{1}{n} \ln C_e \qquad (2)$$

$$\ln b = \ln b' - \Delta H/RT \qquad (3)$$

$$\ln(1/b) = \Delta G/RT \qquad (4)$$

$$\Delta G = \Delta H^o - T\,\Delta S \qquad (5)$$

In the equations, x: The amount of adsorbed substance (mg), m: The amount of adsorbent (g), C_e: The equilibrium concentration of the adsorbed substance in the solution (mg/L). K_f (mg/g) is the Freundlich constant, which is a measure of adsorption capacity. The other Freundlich constant n is dimensionless. qmax: Maximum adsorption capacity, (mg/g), b: A constant related to adsorption energy, (l/mg). T is the absolute temperature (K) and R is the universal gas constant (8.314 $Jmol^{-1}K^{-1}$). Thermodynamic parameters of the adsorption process, such as free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) change, can be calculated with the above equations.

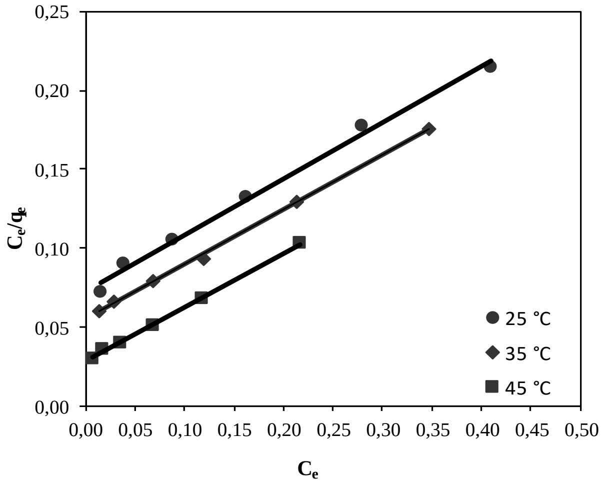

Figure 7. Langmuir isotherm for phosphate adsorption with lead cake. [pH: 7.69; 100 mL; 25-125 mg-P/L; 120 min contact time; 30 g/L lead cake].

The negative sign of the adsorption enthalpy calculated for phosphate adsorption indicates that the adsorption event is exothermic. In addition, in the temperature studies carried out while obtaining the isotherms, the decrease in the percentage of phosphate removal with increasing temperature proves that the phenomenon is exothermic. Table 2 shows that the free enthalpy change of phosphorus adsorption with lead cake is negative. This shows that the adsorption of phosphate to the cake is a spontaneous event.

Table 2. Langmuir constants and Thermodynamic constants.

	Langmuir			
Temperature, °C	**b**	**q_{max}**	**ΔG (kJ/mol)**	**ΔS (kJ/mol)**
25	0.3371	2.6441	5.479	0.02
35	0.2312	2.3463	5.433	
45	0.1049	2.2104	5.109	

The isotherm data obtained for each temperature were applied to the Freundlich equation. The lines obtained by plotting ln(x/m) values against lnC values show that the results are applicable to the Freundlich isotherm (Figure 8). Freundlich constants obtained depending on temperature are given in T Table 3. As can be seen from the table, Freundlich constant k_f, which is a measure of adsorption capacity, decreases with increasing temperature.

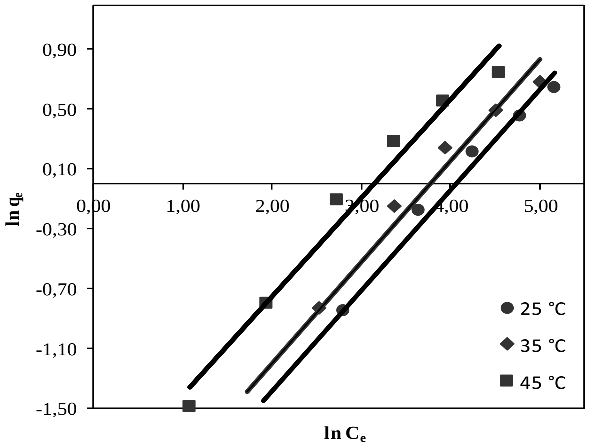

Figure 8. Freundlich isotherm for phosphate adsorption with lead cake. [pH: 7.69; 100 mL; 25-125 mg-P/L; 120 min contact time; 30 g/L lead cake].

Table 3. Freundlich constants.

Temperature, °C	n	1/n	K_f
25	2.41	0.42	0.66
35	3.18	0.32	0.69
45	2.64	0.37	0.44

The maximum monolayer capacity obtained from Langmuir isotherms is 2.644 mg/g at 25°C with an initial concentration range of 25-125 mg-P/L and a dose of 30 g/L. As the temperature increases, the adsorption capacity decreases and the phosphate adsorption capacity at 45°C is 2.210 mg/g.

4. Conclusions

The study investigating the phosphate adsorption properties of lead cakes, which are the residual materials after zinc extraction from carbonate ores, yielded significant insights into their potential application for wastewater treatment. This analysis draws from multiple research articles to provide a comprehensive understanding of the mechanisms and factors influencing phosphate adsorption by such lead cakes.In the equilibration time study conducted with solutions prepared from orthophosphate at a concentration of 100 mg-P/L, at a dose of 30 g/L lead cake and at 25°C, it was found that equilibrium was achieved after 120 minutes. Under these conditions, approximately 75% of the phosphate in the environment is removed. As a result of experiments conducted at different pH values, it was found that lead cake removes more phosphate as pH increases. Phosphate removal efficiency is higher in strongly alkaline environments (pH 10-12). However, this has no practical significance. As a result of experiments conducted with solutions at different temperatures and different initial phosphate concentrations, phosphate removal complies with the Langmuir and Freundlich isotherms in the concentration range of 25-125 mg-P/L. In the calculations made regarding this; Langmuir monolayer adsorption capacity was found to be 2.6441 mg/g adsorbent at 25°C. Adsorption efficiency decreases depending on temperature. The fact that the adsorption enthalpy is negative indicates that the event is exothermic. The fact that the free enthalpy changes are negative indicates that the adsorption of orthophosphate onto the lead cake is a spontaneous event.

As a final result, it can be said that orthophosphate effectively adsorbs lead cake. However, even though soluble zinc and lead residues have been removed by prior washing, zinc and lead ions may pass from the lead cake into the solution medium. As a matter of fact, the results show this. Therefore, this material cannot be used to remove phosphate from wastewater. Because this time, there is a need to remove these secondary pollutants. In cases where the presence of lead and zinc ions in the environment does not pose a problem, it can be taken into consideration in phosphate removal.

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6. Author Contribution Statement

Feride N. Turk: Investigation, Conceptualization, Data curation, Validation, Formal analysis, Methodology, Visualization, Writing - review & editing, Writing – original draft.

6. Ethics Committee Approval and Conflict of Interest

There is no need for an ethics committee approval in the prepared article. There is no conflict of interest with any person/institution in the prepared article.

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