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Investigating triple superphosphate for lead removal from aqueous solutions

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ABSTRACT

The aim of this research is to investigate monocalcium phosphate monohydrate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$] also called triple superphosphate (TSP) for the removal of lead (Pb) from aqueous solutions. In this study, TSP was selected amongst various phosphate-based materials and fertilizers to act as the source of orthophosphate (PO_4^{3-}) which is a powerful tool for metal fixation in soil and water. Thermodynamic equilibrium dissolution-precipitation relationships for the systems of $\text{Pb}-\text{H}_2\text{O}$ and $\text{Pb}-\text{PO}_4^{3-}-\text{H}_2\text{O}$ were drawn with the aid of Eh-pH stability diagrams to determine the predominance areas of different species. The lead phosphate compounds, identified through the stability area diagrams, were verified with the batch precipitation tests performed with standard solutions of lead and TSP at different conditions. It was observed that, depending upon solution conditions, TSP can precipitate 99.9% of the lead from the solution. Lead precipitates, analyzed by x-ray diffraction, showed the formation of lead phosphate compounds. The mechanism of TSP for the removal of lead from aqueous solutions is discussed.

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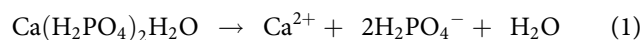
Triple superphosphate; lead removal; precipitation; stability; metal ions; Eh-pH diagram

Introduction

Lead (Pb) is a hazardous metal and release of Pb into the soil and water contaminates the environment. This contamination due to the mobility of Pb may result in serious consequences such as loss of ecosystems, human and animal health problems, economical losses.^[1,2] Accumulation of lead in the nature possesses more serious environmental and health problems than any other metals. Conventional methods for Pb removal from soil and wastewater are mainly fixation, precipitation, adsorption and ion-exchange.^[3] Various studies were performed on the effectiveness of Pb stabilization and parameters influencing Pb removal from soil and wastewater using phosphate-based materials and fertilizers.^[4–18] Researchers Hafsteinsdottir et al.^[7] and Valipour et al.^[19] stated that Pb precipitation from soil and water using TSP was cost effective.

Researchers in soil science have demonstrated the ability of TSP to dissolve and precipitate metals.^[20–24] When TSP is solubilized in aqueous environment, it provides orthophosphate (PO_4^{3-}) which is a powerful tool for metal fixation in soil and water. The mechanism of orthophosphate fixation includes dissolution, precipitation, ion exchange and sorption. These result in the formation of insoluble lead-phosphate minerals and precipitates, such as pyromorphites $\text{Pb}_5(\text{PO}_4)_3(\text{OH}, \text{Cl}, \text{F} \dots)$ and lead (II) phosphates PbHPO_4 and $\text{Pb}_3(\text{PO}_4)_2$.^[25–29]

In aqueous environment, TSP dissociates as:^[30]



The stability of metal ions in TSP solutions will be affected by many factors such as TSP and metal concentrations, pH, existence of other metals and ligands. In order to predict the feasibility of dissolution reactions and to determine which species and compounds are stable, a thorough analysis of the aqueous chemistry and thermodynamics is necessary. This study provides a background for the solution chemistry of TSP to precipitate (remove) lead from the wastewater and other polluted aqueous systems using stability diagrams (Eh-pH, $\text{Pb}-\text{H}_2\text{O}$ and $\text{Pb}-\text{PO}_4^{3-}-\text{H}_2\text{O}$) and presents discussions for the behavior of Pb in TSP solutions.

Materials and methods

Triple superphosphate (TSP) used in this study is a fertilizer and was obtained from Gübretaş in Turkey. Particle size of TSP is below 0.5 cm as received and ground to below 100 μm to use in the experiments. The moisture content was 2% as received. The standard stock solution of pure metal Pb^{2+} is at concentrations of 1000 mg/L as received from Merck KGaA company in Germany. From this concentration, a dilution was prepared with distilled water to give working concentrations of 10, 20, 50 mg/L.

Precipitation experiments and solution elemental concentrations

The precipitation experiments were carried out in accordance with USEPA.^[31] The effect of TSP was tested at two different amounts of 12.6 and 63 g (equivalent to 0.1 and 0.5 M or mol/L). First, TSP was solubilized in a glass beaker containing 500 mL of distilled water for 30 min by agitating with a magnetic stirring bar at room temperature. pH of the solution decreased to 3.4 with the addition of TSP. Then, the solutions of Pb^{2+} ions with different concentrations (10, 20, 50 mg/L), prepared from 1000 mg/L standard stock solution, were added into the TSP containing solution separately. pH of the solution did not change with time after addition of the standard solution of lead and remained stable during testing. Samples of 5 ml were taken at different time intervals of 0, 5, 10, 15, 30, 60, 120, 180 min and filtered immediately using 0.2 μ m syringe filters. Finally, the concentration of Pb in each sample was determined by the atomic absorption spectrometer (Perkin Elmer, model PinAAcle500) with measurement conditions of: Wavelength(nm), Slit: 286.31 nm, Lamp: Hallow Cathode Lamp (HCL), Air Flow 9.12 L/min, Acetylene Flow: 2.50 L/min. Appropriate external quality assurance and quality control (QA/QC) procedures are followed in the laboratory during sample preparation, digestion, instrument calibration and measurements to ensure the validity of the data collected. For the accuracy of the analysis, different standard solution of Pb concentrations (10, 20, 50 mg/L) were used to calibrate the spectrometer and the measurements were repeated 10 times in order to determine the limit of detection (LOD) and limit of quantification (LOQ) reliability.

Mineralogical (XRD) and chemical (XRF) analyses of TSP and Pb precipitate

Precipitation tests were performed with the standard solutions of pure lead (50 mg/L) and TSP (0.5 M) for 180 min to collect about 2 g of precipitate for XRD analysis. The obtained Pb precipitate was filtrated through a filter paper (Reeve angel - grade: 307; size:125 mm). It was then dried in an oven at 105 °C for 1 h, cooled in a desiccator and ground using a motor grinder (M G100/MG200). The dried Pb precipitate and raw TSP samples with a particle size less than 100 μ m were analyzed by Rigaku Miniflex x-ray diffractometer (D/Max 600, Cu K α radiation: 1.54059 Å, 33 KV, 15 m Å).

The raw TSP and Pb precipitate samples (particle size <100 μ m) were analyzed by x-ray fluorescence (XRF) spectrometer to identify the percent of their chemical elements. The spectrometer (Spectro iQ II model, Kleve, Germany) is equipped with a silicon drift detector and resolution 145 eV at 10,000 pulses and used an X-ray tube (25–50 kV) with a highly oriented pyrolytic graphite (HOPG) crystal for the measurement.

Construction of Eh-pH diagrams

In this paper, the solution chemistry of the lead with TSP is analyzed with aqueous stability diagrams. For a given

Table 1. Selected equilibrium reactions and constants for $Pb-PO_4^{3-}$, H_2O system.

No	Equilibrium reactions Lead	Log K
1	$Pb(c) \leftrightarrow Pb^{2+} + 2e$	4.33
2	$PbO(c) + 2H^+ \leftrightarrow Pb^{2+} + H_2O$	12.72
3	$Pb_3O_4(c) + 8H^+ + 2e \leftrightarrow 3Pb^{2+} + 4H_2O$	73.79
4	$PbO_2(c) + 4H^+ + 2e \leftrightarrow Pb^{2+} + 2H_2O$	49.68
5	$PbOH^+ + H^+ \leftrightarrow Pb^{2+} + H_2O$	7.70
6	$Pb(OH)_2^0 + 2H^+ \leftrightarrow Pb^{2+} + 2H_2O$	17.75
7	$Pb(OH)_3^- + 3H^+ \leftrightarrow Pb^{2+} + 3H_2O$	28.09
8	$Pb(OH)_4^{2-} + 4H^+ \leftrightarrow Pb^{2+} + 4H_2O$	39.49
9	$Pb_2(OH)^{3+} + H^+ \leftrightarrow 2Pb^{2+} + H_2O$	6.40
10	$Pb_3(OH)_4^{2-} + 4H^+ \leftrightarrow 3Pb^{2+} + 4H_2O$	23.89
11	$Pb_3(OH)_4^{4+} + 4H^+ \leftrightarrow 3Pb^{2+} + 4H_2O$	20.89
12	$Pb_6(OH)_8^{4+} + 8H^+ \leftrightarrow 6Pb^{2+} + 8H_2O$	43.58
13	$HPbO_2^- + 3H^+ \leftrightarrow Pb^{2+} + 2H_2O$	28.07
Lead-phosphate		
14	$Pb(H_2PO_4)_2(c) + 2H^+ \leftrightarrow Pb^{2+} + 2H_3PO_4^0$	-5.55
15	$PbHPO_4(c) + 2H^+ \leftrightarrow Pb^{2+} + H_3PO_4^0$	-2.10
16	$Pb_3(PO_4)_2(c) + 6H^+ \leftrightarrow 3Pb^{2+} + 2H_3PO_4^0$	-0.96
17	$Pb_4O(PO_4)_2(c) + 8H^+ \leftrightarrow 4Pb^{2+} + 2H_3PO_4^0 + H_2O$	6.54
18	$Pb_5(PO_4)_3OH(c) + 10H^+ \leftrightarrow 5Pb^{2+} + 3H_3PO_4^0 + H_2O$	2.31
19	$PbH_2PO_4^+ + H^+ \leftrightarrow Pb^{2+} + H_3PO_4^0$	0.65
20	$PbHPO_4^0(aq) + 2H^+ \leftrightarrow Pb^{2+} + H_3PO_4^0$	6.26

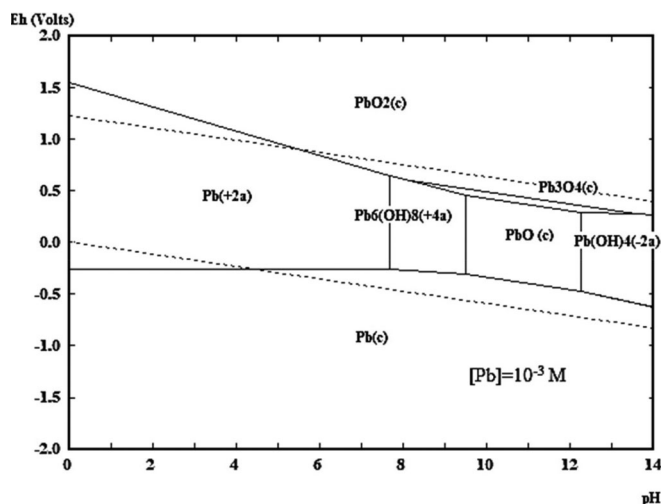


Figure 1. Eh-pH diagram for the $Pb-H_2O$ system, $[Pb] = 10^{-3} \text{ kmol.m}^{-3}$.

element, logarithmic activity-activity diagrams, such as Eh-pH, $\log \{\text{Metal}\}$ -pH and $\log \{\text{Ligand}\}$ -pH diagrams, predict the equilibrium states of all the possible reactions between the elements, its ions and its solid and gaseous compounds in the presence of water. These diagrams have direct significance to aqueous chemical processes in the fields such as environmental pollution control, geochemistry, corrosion science, hydrometallurgy, and mineral processing.

Eh-pH diagrams of $Pb-H_2O$ and $Pb-PO_4^{3-}-H_2O$ systems were constructed using the software HSC 6 Chemistry. The thermodynamic data were taken from the HSC database and from the literature.^[24,32–35] Thermodynamic data, used for the calculations, are given in Table 1. Even though thermodynamic calculations have some limitations, the constructed diagrams can serve as important guides for the removal of metal ions from solutions. The log K values are taken at 25 °C, 1 atm pressure and an ionic strength equal to zero. By using these constructed diagrams, the predominance areas of the different species and the solid/solution equilibria in the TSP solution can be shown and analyzed completely.

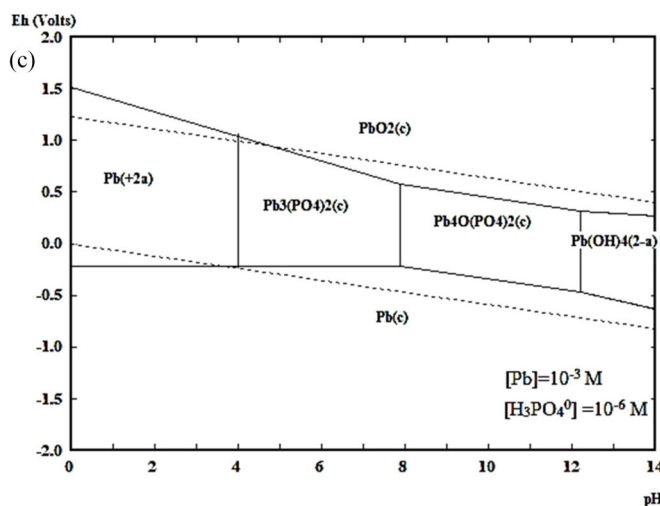
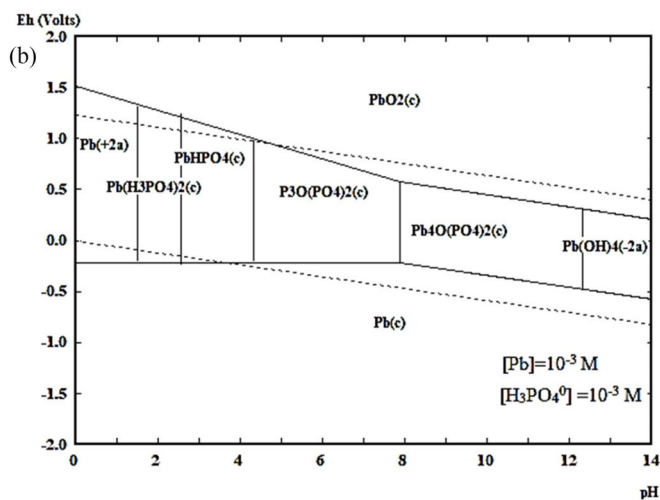
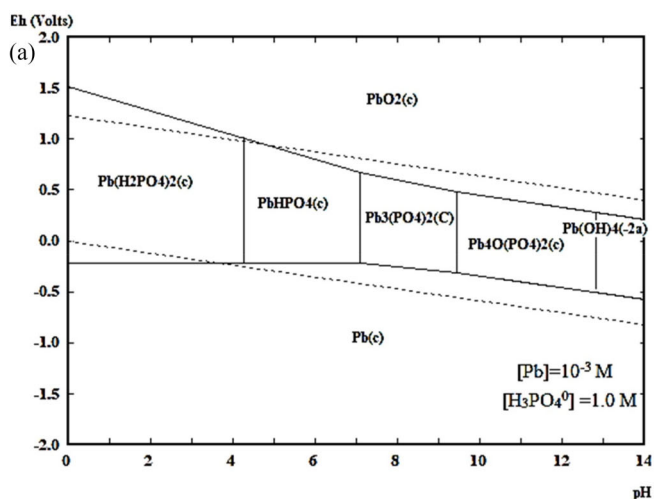


Figure 2. Eh-pH diagram for the $\text{Pb-PO}_4^{3-}\cdot\text{H}_2\text{O}$ system, $[\text{Pb}] = 10^{-3} \text{ kmol}\cdot\text{m}^{-3}$. 2a. $[\text{H}_3\text{PO}_4^0] = 1 \text{ kmol}\cdot\text{m}^{-3}$; 2b. $[\text{H}_3\text{PO}_4^0] = 10^{-3} \text{ kmol}\cdot\text{m}^{-3}$; 2c. $[\text{H}_3\text{PO}_4^0] = 10^{-6} \text{ kmol}\cdot\text{m}^{-3}$.

Results and discussions

Eh-pH diagram of $\text{Pb-H}_2\text{O}$ and $\text{Pb-PO}_4^{3-}\cdot\text{H}_2\text{O}$ system

Eh-pH diagram of $\text{Pb-H}_2\text{O}$ system with $[\text{Pb}] = 10^{-3} \text{ kmol}/\text{m}^3$ was constructed as shown in Figure 1. Here $[\text{Pb}]$ denotes the concentration of total dissolved metal ions in the system. The upper and lower dashed lines represent the range of

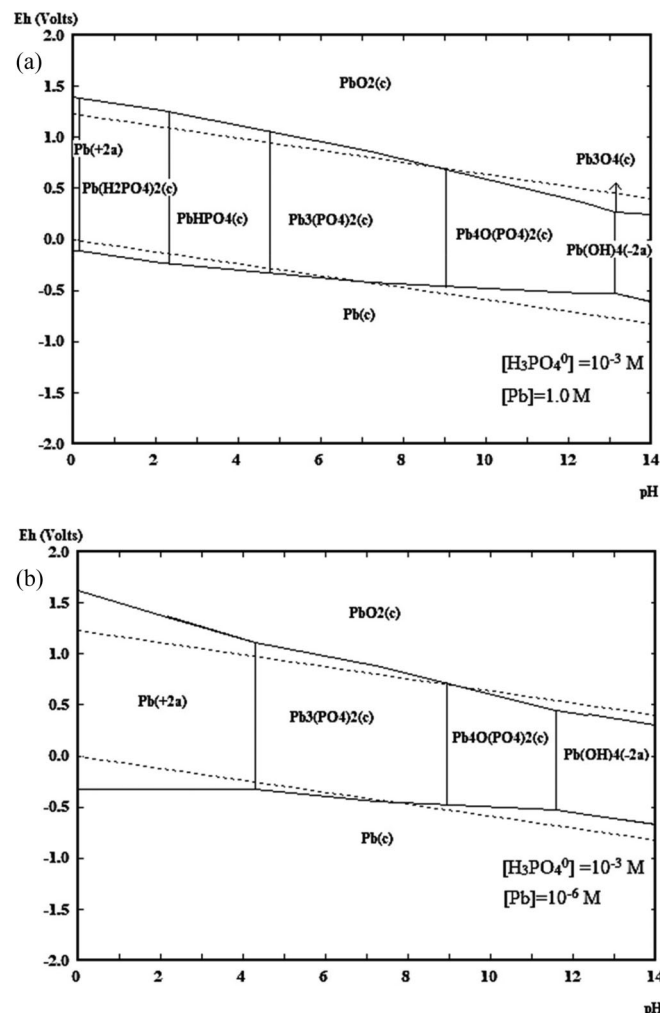


Figure 3. Eh-pH diagram for the $\text{Pb-PO}_4^{3-}\cdot\text{H}_2\text{O}$ system, $[\text{H}_3\text{PO}_4^0] = 10^{-3} \text{ kmol}\cdot\text{m}^{-3}$. 3a. $[\text{Pb}] = 1 \text{ kmol}\cdot\text{m}^{-3}$; 3b. $[\text{Pb}] = 10^{-6} \text{ kmol}\cdot\text{m}^{-3}$.

water stability. As seen from Figure 1, $\text{Pb}(+2a)$ and $\text{Pb}_6(\text{OH})_8(+4a)$ are predominant species below pH 9.5. Above pH 12.4 $\text{Pb}(\text{OH})_4(-2a)$ is the predominant soluble lead complex. Lead can be precipitated as lead oxide (PbO) between pH 9.5 and 12.4.

Eh-pH diagrams of $\text{Pb-PO}_4^{3-}\cdot\text{H}_2\text{O}$ system with different TSP and Pb concentrations are shown in Figures 2 and 3. As seen from Figure 2, when the total concentration of lead is fixed, the type and stability regions of lead complexes depend on TSP concentrations. At relatively high concentrations of the TSP ($[\text{H}_3\text{PO}_4^0] = 1 \text{ kmol}/\text{m}^3$), Pb^{2+} reacts with phosphate to form insoluble compounds of $\text{Pb}(\text{H}_2\text{PO}_4)_2(\text{c})$ and $\text{PbHPO}_4(\text{c})$ (Fig. 2a).

Similarly, $\text{Pb}_6(\text{OH})_8(+4a)$ reacts with phosphate and forms $\text{Pb}_3\text{O}(\text{PO}_4)_2(\text{c})$. At these conditions, Pb can be precipitated (removed) from the solution in both acidic and basic conditions ($4 < \text{pH} < 12.8$) as lead phosphates. Above pH 12.8, Pb forms soluble species of $\text{Pb}(\text{OH})_4(-2a)$. A decrease in TSP concentration reduces the stability region of $\text{Pb}(\text{H}_2\text{PO}_4)_2(\text{c})$ and $\text{PbHPO}_4(\text{c})$ compounds and they disappear (Fig. 2b and 2c). On the other hand, the stability region of $\text{Pb}_3\text{O}(\text{PO}_4)_2(\text{c})$ and $\text{Pb}_4\text{O}(\text{PO}_4)_2(\text{c})$ compounds increases and stays stable with a decrease in TSP concentration.

Figure 3a and 3b show high and low concentrations of lead at constant TSP concentrations. Again, lead phosphates cover most of the area in the Eh-pH diagram in the presence of TSP. Note that, from Figures 2 and 3, there is no lead oxide formation in the presence of TSP, except a very small region of $Pb_3O_4(c)$ and $PbO_2(c)$. Thus, lead phosphates do not dissociate, even at high pH values, i.e., TSP forms insoluble precipitates.

Pb removal from aqueous solution by TSP

The effects of two TSP concentrations (0.1 and 0.5 M) on lead removal were tested at three Pb concentrations (10, 20, 50 mg/L). The results, as seen in Figure 4, indicate that Pb removal efficiency depends on Pb and TSP concentrations

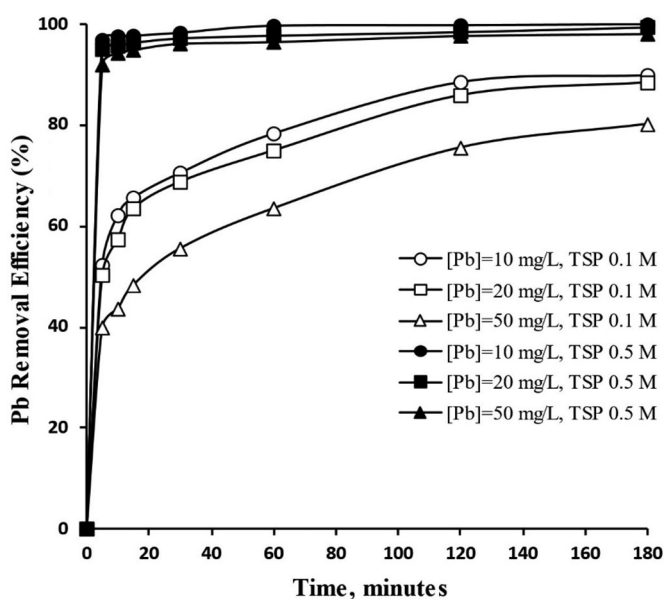


Figure 4. Influence of TSP concentrations (0.1, 0.5 M) on lead removal at different Pb concentrations (10, 20, 50 mg/L).

in the solution. The effectiveness of Pb removal increased with increasing TSP concentrations. The removal efficiency of lead for 50 mg/L Pb containing solution was 80.1% for 0.1 M TSP and 98.0% for 0.5 M TSP concentrations. The removal rate of lead decreases with low TSP and high Pb concentrations. The removal efficiencies at concentration of 0.1 M TSP were 89.9% for 10 mg/L of Pb, 88.4% for 20 mg/L of Pb and 80.1% for 50 mg/L of Pb at 180 min of reaction time. At concentration of 0.5 M TSP, the removal of Pb was effective at all three Pb concentrations. The addition of 0.5 M TSP removed 99.9% of the 10 mg/L Pb, 99.4% of the 20 mg/l Pb and 98.0% of the 50 mg/L Pb. At these conditions, pH of the solution was 3.4 in the presence of TSP additions and did not change with Pb additions and increasing reaction times.

The results agree with the Eh-pH diagrams showing the lead-phosphate compound formations at the same pH values as shown in Figure 2. Similar results were reported in the literature by Stanforth and Qui^[36] who indicated the effect of phosphate dosage for the immobilization of lead in the acid medium and by Chen et al.^[5,37] who exhibited the decrease of soil pH by the addition of soluble phosphoric amendments, the decrease in the mobility of Pb in the solution and a rapid formation of pyromorphite type lead-phosphate minerals.

Mechanism of TSP on Pb removal

The x-ray diffraction (XRD) analysis was conducted to confirm the identified lead phosphate compounds from stability diagrams. Lead precipitates, analyzed by XRD, showed the formation of the lead phosphate compounds as seen in Figure 5. The XRD analysis of raw TSP is presented in Figure 6 for comparison purposes. The main compounds observed in Pb precipitate sample were fluorapatite ($Ca_5(PO_4)_3F$), bassanite ($2CaSO_4 \cdot (H_2O)$) and quartz (SiO_2). In addition, some peaks show the formation of lead oxides

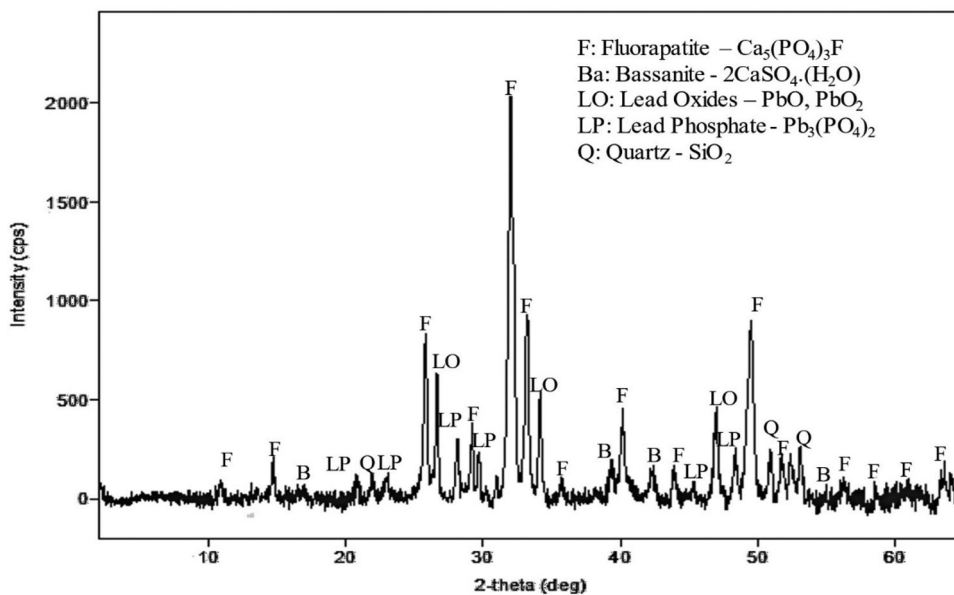


Figure 5. XRD pattern of Pb precipitated (removed from the solution) using TSP.

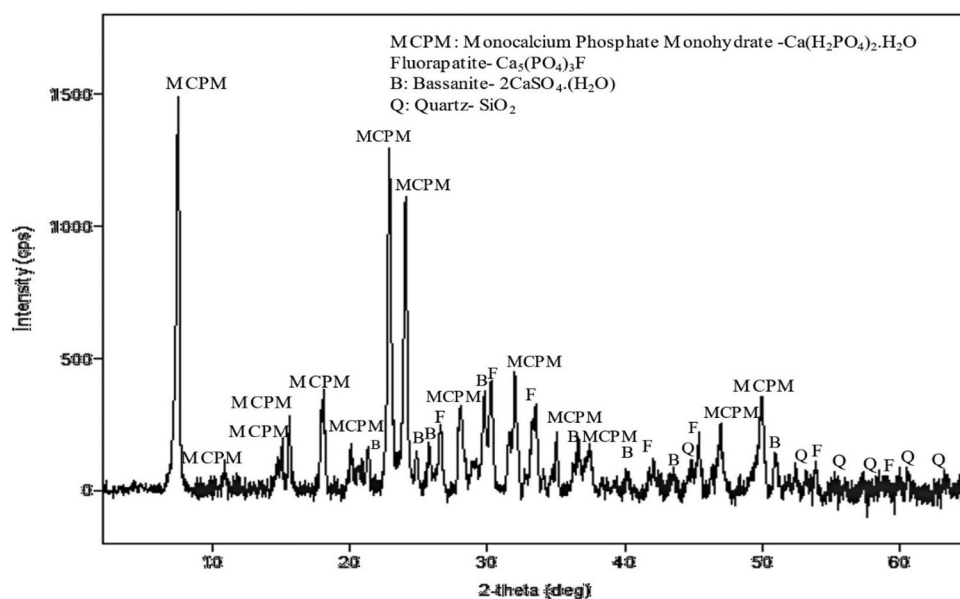
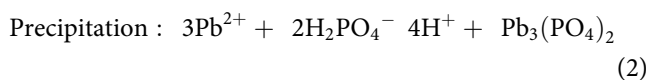


Figure 6. XRD pattern of raw TSP as received.

Table 2. Percentage of chemical elements detected by XRF in TSP and Pb precipitate sample.

Samples	Chemical Content (%)															
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	Fe ₂ O ₃	ZnO	Br	CaO	MnO	SrO	TiO ₂	PbO
TSP raw	47.55	7.03	3.42	<0.0011	27.23	0.52	0.044	<0.0012	0.11	0.013	0.0001	14.04	0.001	0.060	<0.0008	<0.0002
Pb precipitate	40.16	5.26	4.51	<0.0011	19.27	1.23	0.012	<0.0012	0.63	0.008	<0.00003	28.61	<0.014	0.039	<0.0008	0.097

(PbO, PbO₂) and lead phosphate (Pb₃(PO₄)₂) compounds. The formation of lead phosphate is a result of the dissolution of TSP and precipitation of Pb by TSP. The mechanism of the lead removal from aqueous solutions by TSP can be described by its dissolution (Equation (1)) and precipitation reaction (Equation (2)):



Similar results were reported in the literature, e.g., Sugiyama et al.^[38] demonstrated that the Pb stabilization by monocalcium phosphate monohydrate (Ca(H₂PO₄)₂.H₂O) was achieved through the dissolution and precipitation mechanism. Zhang and Ryan^[17] and Cao et al.^[39,40] also mentioned Pb immobilization with phosphate-based material hydroxyapatite and formation of hydroxylpyromorphite compounds.

The x-ray fluorescence (XRF) analysis indicated that TSP and Pb precipitate samples contain various chemical elements. As shown in Table 2, the analyzed elements are divided into 2 groups: major chemical oxides (Na₂O, P₂O₅, MgO, CaO) and minor chemical oxides (Al₂O₃, SiO₂, K₂O, Fe₂O₃, MnO, ZnO, SrO, TiO₂ and PbO). A study by Chauhan et al.^[41] reported that fertilizers depending on their origin contain 15 chemical elements as impurities. In this study, the same number of elements are determined in raw TSP sample. For Pb precipitate sample, except for calcium oxide, the concentration of all major elements decreased and a formation of new oxide (PbO) was observed. This phenomenon can be explained by the

reaction of oxide elements resulting from TSP with Pb to form lead oxide.

Conclusions

In this study, the solution chemistry of TSP [monocalcium phosphate monohydrate, Ca(H₂PO₄)₂.H₂O] was investigated for the removal of lead from the aqueous solutions using stability diagrams [Eh-pH, Pb-H₂O and Pb-PO₄³⁻-H₂O] and laboratory precipitation tests. The results of this study indicate that TSP can precipitate lead from an aqueous solution as metal phosphate compounds [(PbHPO₄(c), Pb(H₂PO₄)₂(c), Pb₃(PO₄)₂(c), Pb₄O(PO₄)₂(c)] in both acidic and basic conditions as identified through the stability diagrams. Lead phosphate species formed were insoluble (stable) in a wide range of pH and Eh values. It was observed that TSP could remove up to 99.9% of the Pb from the solution depending upon the solution conditions. The removal rate of lead decreases with low TSP and high Pb concentrations. The removal mechanism of lead by TSP includes the dissolution of TSP and the formation of lead phosphate compounds during the precipitation process. The lead phosphate compounds, identified through the stability area diagrams, were obtained with the batch tests and verified with the x-ray diffraction (XRD) analysis.

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Data availability statement

The data that support the findings of this study are available from the corresponding author, [M.C.S.G], upon reasonable request. Data were produced from chemical laboratory in Dokuz Eylül University, Mining Engineering Department.

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Appendix

Figure. 4S, Table. 4S1. Limit of detection (LOD) and Limit of quantification (LOQ) for the measurement with atomic absorption spectrometer.

Pb Standard Solutions	Measured concentrations (mg/L)										Mean	SD (±)	LOD	LOQ
10 mg/L	10.07	10.14	10.14	10.07	10.10	10.04	10.03	10.13	10.01	10.04	10.08	0.0481	0.1443	0.4809
20 mg/L	20.14	20.00	19.96	19.90	20.01	19.95	20.02	20.08	20.04	20.06	20.02	0.0693	0.2079	0.6931
50 mg/L	50.09	50.08	50.01	49.89	49.98	50.07	50.11	49.95	50.04	50.02	50.02	0.0690	0.2070	0.6899

Figure. 4S, Table. 4S2. Influence of TSP concentrations (0.1, 0.5 M) on lead removal at different Pb concentrations (10, 20, 50 mg/L).

Pb initial concentrations (mg/L)	TSP concentrations (M)	Lead removal efficiency with time (%)							
		0 min.	5 min.	10 min.	15 min.	30 min.	60 min.	120 min.	180 min.
10.0	0.1	0.00	52.2	62.1	65.6	70.5	78.3	88.5	89.9
	0.5	0.00	96.8	97.5	97.6	98.2	99.6	99.7	99.9
20.0	0.1	0.00	50.2	57.3	63.5	68.7	74.9	85.9	88.4
	0.5	0.00	95.0	95.7	96.3	97.2	97.8	98.5	99.4
50.0	0.1	0.00	39.8	43.6	48.3	55.5	63.4	75.5	80.1
	0.5	0.00	91.9	94.3	94.9	96.1	96.5	97.7	98.0