FEASIBILITY STUDY INTO THE POSSIBILITY OF MANGANESE ORE ENRICHMENT WASTE USE FOR SORBENT MATERIAL DEVELOPMENT

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ABSTRACT

This study explores the synthesis of sorption-active phosphate materials from manganese ore enrichment tailings of the Zhairem deposit. The initial tailings, predominantly composed of calcite (76.4 %), quartz (16.4 %), and braunite, were characterized by XRD and EPMA. Acid-thermal treatment with phosphoric acid followed by calcination at 200 - 800°C yielded calcium - manganese phosphate materials. Phase transformations were monitored via XRD, showing formation of crystalline phosphates at 200 - 600°C and a glassy phase at 800°C. The product synthesized at 600°C demonstrated the lowest water solubility (9.91 %), highest pore volume (0.175 $cm^3 g^{-1}$), and optimal sorption capacity for Ni^{2+} (0.2934 mg-eq g^{-1}), which increased to 0.4697 mg-eq g^{-1} after 0.4 wt. % of HCl activation. The enhanced performance is attributed to the formation of low-solubility polyphosphates and well-developed porous structures. SEM confirmed porous morphology at 600°C and denser, glassy structure at 800°C. The synthesized material showed no toxic elements such as Pb, Cd, or As, making it suitable for environmental applications. The findings indicate that Zhairem tailings are a promising raw material for producing effective sorbents for heavy metal removal, especially after acid activation. The optimal product is the calcium-manganese phosphate synthesized at 600°C.

Keywords: *technogenic raw materials, ore enrichment wastes, silicophosphates, sorbents, structural analysis.*

INTRODUCTION

The advancement of a competitive national economy necessitates the implementation of cutting-edge technologies, particularly in the development of nanostructured inorganic materials for multifunctional applications. In Kazakhstan, as well as in neighbouring and distant countries, significant efforts are being directed toward the development and production of such materials, including sorbents and porous ceramics [1, 2].

Porous sorbents and membranes are traditionally synthesized by sintering powders with specific particle sizes - such as quartz, glass, and metal oxides - together with binders like liquid glass, clay minerals (e.g., kaolinite, montmorillonite), aluminophosphate binders, or polymers [3 - 6]. By varying powder dispersion, binder composition, additives, and thermal treatment parameters, it is possible to obtain ceramic membranes with tailored porosity and permeability characteristics [4, 5]. Wilson et al. developed a microporous crystalline aluminosilicate zeolite, UZM-4, featuring a three-dimensional network of AlO_2 and SiO_2 tetrahedra. This zeolite remains thermally stable up to 600°C and is synthesized by heating a mixture of aluminum and silicon sources with organic reagents (e.g., protonated amines or quaternary ammonium bases) at temperatures ranging from 85°C to 225°C. The material is suitable for various hydrocarbon conversion processes, including

hydrocracking and isomerization [7]. Another work presents a method for synthesizing low-silica zeolites and high-purity gmelinite with a SiO_2/Al_2O_3 ratio of ~10 or less. The process involves the initial formation of Na-gmelinite at 80 - 100°C, followed by calcination of M-gmelinite (where M represents elements such as Na, Li, Ca, Ba, or Mg), and its transformation into M-AFI zeolite [8]. A patented approach for forming macroscopic aggregates of fine-crystalline aluminosilicate zeolite involves reacting an alkaline salt solution (pH ≥ 12) with a silicate source and an electrolyte salt (e.g., phosphates, carbonates, or sulfates). The addition of an aluminum source - such as Al_2O_3, dried silica-alumina gels, or clay-yields zeolite aggregates 1-5 μm in size. After washing to reduce SiO_2 inclusions to 20 %, the material can be used in water softening applications [9]. Researchers have also patented a catalyst composition primarily based on large-pore zeolites, supplemented with silicoaluminophosphates possessing a zeolite-type structure. These contain Si, Al, and P in mole percentages of 0.2 - 40, 30 - 49.9, and 10 - 49.9, respectively, and can be synthesized from microemulsion systems containing surfactants [10].

A method for producing metalloaluminosilicate compositions involves combining a silicon dioxide source with an aqueous acidic solution of a metal (other than Si or Al), followed by mixing with an aluminium source to form a gel. This gel undergoes hydrothermal crystallization to form a metalloaluminosilicate in which the metal is incorporated into the aluminosilicate framework [11]. Additionally, a silicophosphate adsorbent has been developed by mixing sodium silicate, aluminium sulfate, and calcium dihydrogen phosphate solutions. The process involves precipitation at pH 6 - 7, followed by washing, filtration, and calcination [12].

A method for obtaining adsorbents and catalysts based on mixed phosphates and metal oxides has been proposed, allowing the production of materials with enhanced adsorption-structural properties and improved thermal stability [13]. The production is carried out as follows. Orthophosphoric acid is added to a mixture of cadmium and aluminum salts, the pH of the mixture is brought to 2 - 3. After the precipitate has formed, the pH of the mixture is brought to 8 - 9 with intensive stirring, the precipitate is aged, washed, dried, formed into granules and calcined at 400 - 800°C. The ratio of cadmium, aluminium and phosphorus in the synthesis is 1:(0.4 - 3):(0.2 - 0.4) (in terms of oxides). The specific surface area of the obtained adsorbents is 78 - 130 $m^2 g^{-1}$, the adsorption capacity is 0.43 - 0.95 $cm^3 g^{-1}$. Effective pore radius 108 - 391 Å.

The sorption capacity of opoka, tripoli, quartzite, limestone, diatomite, dolomite, and ferruginous sandstone toward non-ionic surfactants was studied in the other research [14]. The advantage of opoka over other natural ones was shown. Based on the studies, the opoka of the Saratov region can be recommended for additional purification of wastewater from non-ionic surfactants.

Waste from pulp and paper enterprises, specifically airfountain drying fiber, is proposed as a sorbent that enables a higher rate of oil spill absorption, ease of collection, and efficient separation of the adsorbed oil (with an oil return rate of 70 %) [15].

A method is described in which natural clay material is mixed with a medium aluminium salt and caustic soda, while aluminium hydroxide or silicon oxide is simultaneously added to the reaction mixture; this is followed by thermal steam treatment and subsequent thermal activation, after which the product is combined with aluminosilicate hydrogel to form a homogeneous mass [16]. In this case, aluminium sulfate is used as the average aluminium salt. The possibility of purifying water from dissolved iron impurities using heat-treated carbonate and silicate rocks was demonstrated by the authors [17]. Moreover, heat treatment of dolomite $CaMg(CO_3)_2$ in the temperature range of 500 - 900°C has a significant effect on the degree of extraction of iron compounds, in contrast to heat-treated diopside $CaMg(SiO_3)_2$. An increase in the degree of sorption of iron compounds on diopside is possible after alkaline modification.

Recent studies confirm the growing relevance of such sorbents. For example, granular sorbents with enhanced porosity and heavy metal removal efficiency were developed by modifying bentonite with aluminium and iron polyhydroxocations [18]. The effectiveness of Ukrainian aluminosilicates functionalized with polymers for removing toxic metals was also demonstrated [19]. Additionally, an automated sorption treatment system was introduced to improve the efficiency of mine wastewater purification processes [20].

Despite the wide variability in the composition of inorganic porous materials, most sorbents are

synthesized from oxides and salts of aluminium, silicon, and phosphorus [4 - 6, 11]. Common approaches include sol-gel methods or precipitation, followed by hydrothermal treatment. The overall synthesis process is typically complex and multistage, involving successive steps of washing, filtration, and drying. Notably, there is a lack of systematic research on the development and characterization of such materials derived from ore enrichment waste in the Republic of Kazakhstan as well as in neighbouring and distant countries.

At present, there is no comprehensive research in Kazakhstan or abroad focusing on the use of ore beneficiation waste for the synthesis of such materials and the investigation of their sorption properties. Thus, the study of the synthesis mechanisms of sorbents based on mining waste in Kazakhstan is of critical importance. It represents a significant step toward building a competitive industrial sector and enabling Kazakhstan's integration into the global community of technologically advanced nations.

EXPERIMENTAL

Tailings from the enrichment of manganese ores from the Zhairem deposit were selected as objects of research.

The phase composition was determined by X-ray diffraction using a DRON-3 diffractometer with Cu_{Ka} radiation and a β-filter under the following operating conditions: 35 kV, 20 mA, 2θ scan mode at 2° min^{-1}, with a time constant of 2 s. Semi-quantitative phase analysis was carried out using the method of equal-weight portions and artificial mixtures. Phase identification was performed based on the PDF-2 ICDD database and standard reference patterns of pure minerals.

The elemental composition of the materials was examined by electron probe microanalysis (EPMA) using a JEOL-733 electron microscope equipped with an X-ray analyser.

The synthesis of sorption materials based on the enrichment waste of manganese ore from the Zhairem mine was carried out using the acid-thermal method. For the synthesis, the required amount of phosphoric acid was calculated based on the content of acid-absorbing components based on the results of the material composition of the initial enrichment waste samples. Then, wet grinding of the sample with a size of +0 - 10 μm was carried out, the wet product was dried at 105°C for an hour, and then calcined at temperatures of 200°C, 400°C, 600°C and 800°C.

Losses of mass during synthesis were determined by the difference in mass between the initial dried semi-finished product and the heat-treated sample (Eq. (1)):

$$SFPL = \frac{100 \cdot (m_0 - m_f)}{m_0} \quad (1)$$

where: SFPL- semi-finished product losses, rel. %; m_o - mass of the original sample before heat treatment, g; m_f - mass of the obtained product, g.

The solubility of the synthesized materials was assessed by the mass loss of the products upon dissolution in water. Samples weighing 1 g, taken with an accuracy of 0.0001 g, were dissolved in 100 mL of distilled water and stirred on a shaker for 30 min. After that, the solution was filtered, the undissolved residue was dried and weighed. Solubility was calculated using Eq. (2) in rel. %:

$$S = \frac{(m_0 - m_1) \cdot 100}{m_0} \quad (2)$$

where: S - solubility, rel. %; m_o - mass of sample before dissolution, g; m_1 - mass of a substance after dissolution, g.

The total pore volume of the synthesized porous materials was determined using a known method, for which 10 cm^3 of a sorbent of known mass were boiled for 15 min with 100 cm^3 of distilled water, followed by cooling and bringing the volume to the initial value [21]. Then the suspension was filtered on a Buchner funnel with a vacuum of 8 kPa for 3 min (until a free-flowing state). The wet sorbent was weighed and the mass of water in the pores was determined by the difference. The total pore volume was determined using Eq. (3) in $cm^3\,g^{-1}$:

$$\Sigma V = \frac{m_1 - m_2}{dHOH \cdot m_2} \quad (3)$$

where: ∑V- the total pore volume, $cm^3\,g^{-1}$; m_1 - the weight of the sorbent soaked in water, g; m_2 - the weight of the dry sorbent, g; dHOH - the density of water, g cm^{-3}.

The sorption capacity of the synthesized materials was evaluated using model solutions of nickel salts at a concentration of 0.05 mol L^{-1}. Nickel chloride ($NiCl_2$) was selected for the sorption experiments, as

the precipitation of nickel hydroxide ($Ni(OH)_2$) from dilute solutions occurs in the pH range of 7 - 8, making chemical precipitation ineffective for wastewater treatment containing Ni^{2+} ions. This necessitates the application of sorption or ion-exchange techniques.

The sorption experiments were conducted under static conditions at room temperature using the separate weighed portions method [21]. A 100 mL aliquot of the metal salt solution was mixed with a known weight of the sorbent and agitated for 30 min on a shaker. After the process, the liquid phase was separated from the solid by filtration through a "blue ribbon" filter paper. The degree of nickel ion removal was assessed by a gravimetric method involving dimethylglyoxime [22]. In an ammonia medium, nickel ions react with dimethylglyoxime to form a light red, water-insoluble complex, which, after filtration and drying at 110°C, yields a stable compound used for gravimetric quantification. The residual concentration of Ni^{2+} was calculated using the following Eq. (4):

$$X = \frac{0.2032 \cdot m \cdot 1000}{V} \quad (4)$$

where: X - the residual concentration of Ni^{2+}, mg L^{-1}; m - the mass of nickel dimethylglyoximate, mg; V - the volume of the sample taken for analysis, mL; 0.2032 - the conversion factor for nickel dimethylglyoximate to nickel.

RESULTS AND DISCUSSION

Using X-ray diffraction analysis performed on three parallel samples obtained by quartering the initial process sample of manganese ore beneficiation tailings at Zhairem deposit, it was found that the main mineral phases are (wt. %): calcite $CaCO_3$ - 76.4; quartz SiO_2 - 16.4; albite $Na(AlSi_3O_8)$ - 4.9 and braunite $(Mn_2O_3)_3MnSiO_3$ - 2.4. The results of the material analysis correlate with the X-ray diffraction data and show that the main components of the gravity concentration waste are calcium, silicon and manganese (Table 1). The studies also showed that such harmful impurities as lead, cadmium, arsenic, antimony and barium are absent in the studied concentration tailings. Therefore, it was proposed to consider the possibility of obtaining new inorganic phosphate materials based on these wastes, the synthesis of which was carried out by the acid-thermal method.

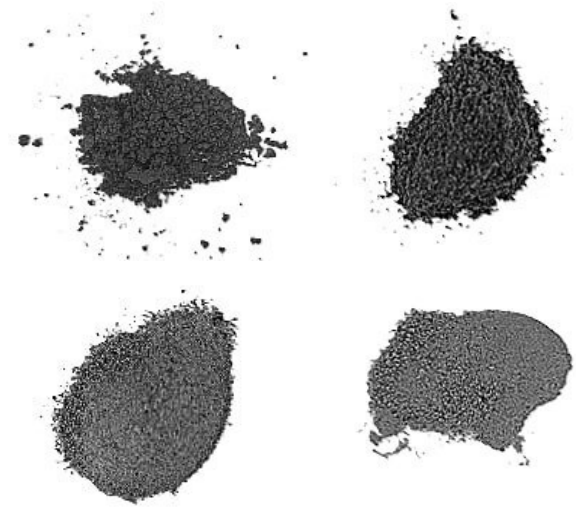

Fig. 1. Calcium–manganese phosphate materials synthesized at (a) 200°C, (b) 400°C, (c) 600°C and (d) 800°C from tailings of the Zhairem mine.

It was found that in the temperature range of 200 - 600°C, crystalline porous cakes were formed (Fig. 1), whereas in the product synthesized at 800°C, the formation of a significant amount of glass phase was observed. The aqueous solubility of the synthesized products was studied (Table 1).

Electron microscopic images of the surface of the synthesized samples (Fig. 2) showed that the sample obtained at 600°C is crystalline, has a free porous space, which is a labyrinth of expansions and contractions of various shapes with sizes from 0.2 to 50 μm (Fig. 2a). Whereas the sample obtained at 800°C is denser, with observed glassy needle-like formations (Fig. 2b), which confirms the formation of a glass phase with an increase in the synthesis temperature.

Using a set of physicochemical methods of analysis, the molecular, material and phase composition of the synthesized products was studied. From the results of the material analysis of the phosphate products (Table 1), it follows that the main components of the products at all synthesis temperatures are calcium, phosphorus and manganese, but their molar ratio changes with increasing temperature. Thus, in the product obtained at 200°C, the phosphate content in terms of phosphorus pentoxide is (73.64 ± 1.33) wt. % (Table 1). In this case, the molar ratio of the main components in terms of oxides is CaO : MnO : P_2O_5 = 1.00 : 0.11 : 1.54.

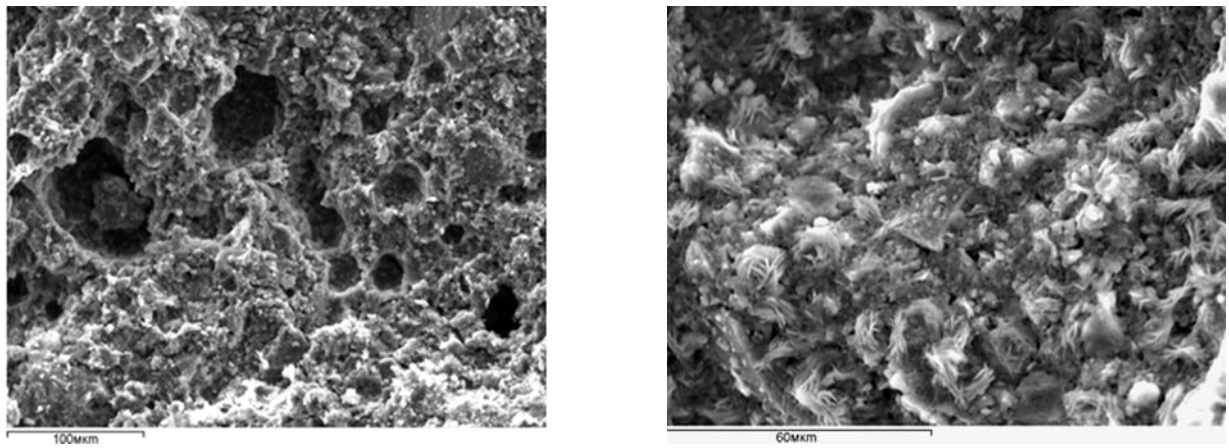

Fig. 2. SEM images of the surface of materials synthesized from Zhairem ore enrichment waste at (a) 600°C and (b) 800°C.

Table 1. Composition of original waste sample and phosphate materials synthesized from Zhairem manganese ore enrichment waste by EPMA.

Temperature of product synthesis,°C	Average content of components, wt. %								
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO	FeO
Original waste sample	0.96m ± 0.28	1.56 ± 0.30	3.50 ± 0.53	24.34 ± 6.30	0.00	0.77 ± 0.21	54.42 ± 6.55	10.12 ± 5.47	2.67 ± 1.34
200°C	0.00	0.25 ± 0.07	0.62 ± 0.26	3.72 ± 0.52	73.64 ± 1.33	0.14 ± 0.11	18.23 ± 0.49	2.56 ± 0.26	0.84 ± 0.24
400°C	0.33 ± 0.11	0.57 ± 0.12	1.24 ± 0.17	6.69 ± 0.79	63.16 ± 1.00	0.22 ± 0.06	22.78 ± 2.15	4.11 ± 0.97	0.89 ± 0.19
800°C	0.33 ± 0.02	0.64 ± 0.14	1.90 ± 0.36	10.14 ± 1.36	51.57 ± 1.44	0.37 ± 0.05	28.84 ± 0.16	5.27 ± 0.46	0.94 ± 0.07

In the product obtained at 400°C, the P_2O_5 content decreases to 63.16 ± 1.00 wt. % with a molar ratio of components $CaO:MnO:P_2O_5$ = 1.00:0.14:1.09, and in the product synthesized at 800°C, the molar ratio $CaO:MnO:P_2O_5$ = 1.00:0.14:0.70, while the P_2O_5 content here is 51.57 ± 1.44 wt. % (Table 1).

A decrease in the content of phosphorus pentoxide in the products with an increase in the synthesis temperature may indirectly indicate the occurrence of a process of dehydration of the primarily formed dihydrogen phosphates with the formation of condensed phosphates, which is accompanied by the loss of both P_2O_5 and structurally bound water into the gas phase:

$$MeO + 2H_3PO_4 \rightarrow Me(H_2PO_4)_2 + H_2O$$

$$Me(H_2PO_4)_2 \xrightarrow{T,\,^oC} Me(PO_3)_2 + 2H_2O$$

The increase in the content of condensed phosphates such as $Ca(HPO_3)_2 \cdot H_2O$, $Ca(PO_3)_2$, and $Mn(PO_3)_3$ in the synthesized products with rising synthesis temperature is supported by X-ray diffraction data (Table 2) and the results of semi-finished product loss measurements (SFPL) into the gas phase presented in Table 3.

Studies of the solubility of the obtained products showed that the dependence of solubility on the synthesis temperature is extreme with a minimum (9.91 rel. %) at 600°C (Table 3). The decrease in the solubility of the synthesized products at 600°C is explained by the deepening of the dehydration process of structurally bound water with an increase in the synthesis temperature and the formation of poorly soluble polymeric phosphates, which is confirmed by the X-ray diffraction results (Table 2). Whereas the increase in the solubility of the products obtained at 800°C can be explained by the presence of a more soluble amorphous glass phase, as well as the presence of fairly soluble silicon diphosphate SiP_2O_7.

The study of the total pore volume of products synthesized at temperatures of 400 - 800°C also showed the extreme nature of the "Total pore volume - synthesis temperature" dependence with a maximum at 600°C.

The sorption properties of the synthesized products were determined in a static mode by adding a certain

Table 2. Results of semi-quantitative X-ray phase analysis of phosphate products synthesized based on manganese ore enrichment tailings from the Zhairem deposit.

Phase name	Chemical formula	Synthesis temperature, °C		
		200	600	800
		Content, wt. %		
Calcium dihydrogen phosphate	$Ca(H_2PO_4)_2$	21.0	0.0	9.0
Calcium dihydrogen diphosphate, monohydrate	$Ca_3H_2(P_2O_7)_2 \cdot H_2O$	16.6	3.6	0.0
Calcium dihydrogen diphosphate	$CaH_2P_2O_7$	14.1	0.0	0.0
Calcium dihydrogen diphosphate, dihydrate	$CaH_2P_2O_7 \cdot 2H_2O$	0.0	3.7	0.0
Calcium polyphosphate, monohydrate	$Ca(HPO_3)_2 \cdot H_2O$	13.8	13.6	0.0
Calcium polyphosphate	$Ca(PO_3)_2$	12.9	32.4	32.5
Ruisite	$Ca_2Mn_2(Si_4O_{11}(OH)_2)(OH)_2(H_2O)_2$	5.6	5.7	0.0
Quartz	SiO_2	4.7	7.7	16.2
Brushite	$CaHPO_4 \cdot 2H_2O$	4.6	3.7	0.0
Mangangordonite	$MnAl_2(PO_4)_2(OH)_2 \cdot 8H_2O$	4.7	0.0	0.0
Manganese (III) phosphate	$Mn_3(PO_4)_2$	2.0	0.0	0.0
Manganese (III) polyphosphate	$Mn(PO_3)_3$	0.0	4.9	0.0
Calcite	$CaCO_3$	0.0	11.7	34.0
Grouthite	MnO(OH)	0.0	8.6	0.0
Aleganit	$Mn_5((OH)_2(SiO_4)_2)$	0.0	4.4	0.0
Brownite	$(Mn_2O_3)_3MnSiO_3$	0.0	0.0	8.3

Table 3. Influence of synthesis temperature on semi-finished product losses (SFPL) to the gas phase and solubility of the synthesized materials.

Temperature, °C			
200	400	600	800
SFPL into the gas phase, rel. %			
22.22	27.97	38.09	28.86
Solubility in water, rel. %			
92.41	29.53	9.91	14.42

volume of a heavy metal salt solution to a known amount of the sorbent and leaving it on a shaker until equilibrium was achieved. Then the sorbent was separated from the solution by filtration, and its static exchange capacity (SEC) was determined. The studies were carried out, as indicated above, using a solution of nickel chloride $NiCl_2$ (Table 5). Also, to remove water-soluble components and improve the sorption properties of the synthesized materials, they were acidically activated in a 0.4 wt. % of hydrochloric acid solution with stirring for 30 min at room temperature, after which the products were washed with distilled water and dried at 105°C for an h. Then their sorption capacity with respect to nickel cations was re-studied (Table 5).

The results show that the maximum sorption capacity of 0.2934 mg-eq Ni^{2+} g^{-1} with respect to nickel cations under static conditions is possessed by the product synthesized based on manganese ore enrichment waste from the Zhairem mine at 600°C (Table 5). It was also established that preliminary acid activation increases the SEC of the product obtained at 600°C by 1.6 times.

Thus, calcium-manganese phosphate product synthesized at 600°C can be recommended as a possible sorption material. However, it is necessary to carry out its acid activation to remove the water-soluble part and reduce the overall solubility.

Table 4. Dependence of the total pore volume of calcium phosphate products synthesized based on manganese ore enrichment waste from the Zhairem mine on the synthesis temperature.

Temperature, °C		
400	600	800
Total pore volume of products before acid activation, $cm^3\ g^{-1}$		
0.157	0.175	0.121
Total pore volume of products after acid activation in 0.4 wt. % of HCl (30 min), $cm^3\ g^{-1}$		
0.207	0.315	0.160

Table 5. Sorption properties of phosphate products synthesized based on manganese ore enrichment waste from Zhairem mine.

Synthesis temperature, °C	Average mass of sorbent from three parallel experiments, g	Initial concentration of nickel ions in solutions, mol L^{-1}	Average residual concentration of nickel ions in solutions, mol L^{-1}	Average static exchange capacity, mg-eq $Ni^{2+}\ g^{-1}$
400	1.02	0.058	0.054	0.1150
600	1.00	0.058	0.048	0.2934
800	1.10	0.058	0.052	0.1601
After acid activation in 0.4 wt. % of HCl (30 min)				
400	1.00	0.055	0.051	0.2348
600	1.01	0.055	0.047	0.4697
800	1.02	0.055	0.052	0.1761

CONCLUSIONS

The calcium - manganese phosphate material obtained at 600°C demonstrated favourable structural and sorption characteristics, highlighting its potential as an efficient sorbent for heavy metal removal from aqueous media. The combination of phosphoric acid modification and thermal treatment enabled the transformation of manganese ore tailings from the Zhairem deposit into functional materials with enhanced sorption performance.

XRD and EPMA analyses identified significant mineralogical changes upon phosphatization and subsequent heating, particularly within the 200 - 600°C range, resulting in the formation of phosphate phases with high affinity for Ni^{2+} ions. The sample treated at 600°C exhibited optimal properties, including a well-developed porous structure (0.175 $cm^3\ g^{-1}$), acceptable solubility (9.91 %), and a notable static exchange capacity (0.2934 mg-eq g^{-1}), which increased to 0.4697 mg-eq g^{-1} following mild acid activation (0.4 wt. % of HCl).

SEM imaging confirmed the formation of a heterogeneous, porous surface at this temperature, while treatment at 800°C caused surface vitrification and decreased sorption performance. Importantly, no hazardous elements such as Pb, Cd, or As were detected in the final products, underscoring their environmental safety.

Overall, the calcium - manganese phosphate synthesized at 600°C represents a cost-effective and eco-friendly material for heavy metal remediation in water treatment applications.

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Authors' contributions

A.K.: Experimental work, Writing, Management and Presentation of the main idea; S.K.: Structural analysis, Review; V.K.: Implementation of the synthesis methodology, Review, Editing, Writing; S.L.: Review, Editing, Writing.

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