

Study on phosphorus release from medium- and low-grade phosphate ore powders by mechanical activation and low molecular weight organic acid activation

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Abstract: Phosphate ore is an essential resource for producing phosphate fertilizer. International phosphate ore is overmined, and phosphorus resources are becoming depleted; improving the utilization efficiency of medium- and low-grade phosphate ore powder (PR) through activation is the key to the sustainable and efficient use of phosphorus resources. However, the traditional activation method is inefficient and has some limitations on the grade of phosphate ore. In this study, a combination of mechanical activation and low molecular weight organic acid activation was used to activate medium- and low-grade phosphate ore powders, and the activation effects of different mechanical activation conditions, such as mechanical grinding time, the addition of different types and proportions of active minerals (zeolite, bentonite, and kaolin), and different types of low molecular weight organic acids (oxalic acid, tartaric acid, malic acid, and citric acid), on phosphate ore powder were compared. The results show that mechanical activation had a synergistic effect with low molecular weight organic acid activation. Mechanical activation can reduce the particle size of phosphate ore powder and increase the release of effective phosphorus from phosphate ore powder. Mechanical activation for 60 min reduced phosphate ore powder's median diameter (D50) from 41.67 μm to 10.59 μm and increased the effective phosphorus leaching rate from 1.19% to 8.27%. The phosphorus release effect of low molecular weight organic acids was oxalic acid > tartaric acid > malic acid > citric acid, with the optimal concentrations of 0.1 mol/L, 0.3 mol/L, 0.5 mol/L, 0.2 mol/L, and the optimal activation cultivation times were all 6 days. This study optimizes the activation method of phosphorite powder, which can not only alleviate the current global shortage of phosphorite resources but also reduce environmental pollution while maximizing the use of phosphorite resources.

Keywords: phosphate ore powder, active mineral, effective phosphorus, phosphorus release

1. Introduction

Phosphorus is the main element that maintains plant growth and development. To increase crop yield and improve crop quality, applying phosphorus fertilizer has become a routine measure in agricultural production management (Mardamootoo et al., 2021). Phosphate ore is the raw material for producing phosphate fertilizer; over 80% of the world's phosphate ore is used to produce phosphate fertilizer (Zhao et al., 2009). However, phosphate ore is a nonrenewable resource; international phosphate ore resources are expected to be depleted in the next 50-100 years in the face of the uncontrolled exploitation of phosphate ore worldwide (Cooper et al., 2011). China has abundant phosphate resources, but these resources are mainly medium- and low-grade phosphate ore, and high-grade phosphate ore accounts for less than 10% (Wang et al., 2012). How to fully use medium- and low-grade phosphate ore is one of the significant challenges facing agriculture in the world today (Aarab et al., 2022; Raiymbekov et al., 2022).

In recent years, some countries with abundant phosphate ore resources, such as Morocco, China, and the United States, have experimented with directly applying 100 mesh phosphate ore powder to

agricultural soils (Chien et al., 2010; Fang et al., 2022). However, due to the extremely low solubility and reactivity of phosphate ore powder, it is not easily absorbed by plants, and its effect on promoting plant growth and development is not apparent (Somavilla et al., 2021). In addition, traditional phosphate ore processing methods such as inorganic acid leaching (sulfuric acid, hydrochloric acid, nitric acid) and electrothermal phosphorus sublimation have strict requirements for the grade of the phosphorus ore used. In acid leaching, the phosphate ore must contain $\geq 28\%$ P_2O_5 ; in electrothermal processing, $\geq 23\%$ P_2O_5 is required (Kubekova et al., 2022). At the same time, the large amount of tailings produced by industrial flotation of phosphate ores can cause environmental pollution (Gu et al., 2022). In existing studies, mechanical activation and low molecular organic acid activation can not only alleviate the current global shortage of phosphate resources but also reduce environmental pollution while maximizing the use of phosphate resources (Wang et al., 2018; De Oliveira Mendes et al., 2020). Mechanical activation can improve the effective phosphorus content in phosphate ore powder and increase the practicality of phosphorus in phosphate ore powder (Fang et al., 2019; Shan et al., 2020). The mechanism of mechanical activation of phosphate ore powder may be caused by a series of mechanical forces such as friction, impact and shear to cause the accumulation of mechanical energy in the minerals, leading to changes in the internal structure of apatite or phase transformations, prompting the enhancement of its reactivity, thus increasing the complex process of chemical reaction speed between minerals (Boldyrev et al., 1996; Wang et al., 2018; Ibrahim et al., 2010). However, the internal structural changes and chemical reaction mechanisms are still unclear and need further exploration. Acid activation is also a commonly used activation method (Huang et al., 2019; Arroug et al., 2021). Existing studies have shown that the selection of low molecular weight organic acids, such as oxalic acid, tartaric acid, and malic acid, can help to activate medium- and low-grade phosphate ore powder (Basak, 2019; Xie et al., 2019). Low molecular weight organic acids containing hydroxyl and carboxyl groups and other active functional groups can chelate with calcium, iron, aluminum and other insoluble or low-soluble phosphorus compounds in the phosphorus powder, thus releasing soluble phosphorus (Amarasinghe et al., 2022; Jalali and Jalali, 2022). Additionally, zeolite, bentonite, and other active minerals can improve the effectiveness of phosphorus in natural apatite (Huang et al., 2014). The active minerals with high phosphate adsorption capacity and high cation exchange capacity are mixed into the phosphate powder, and when the cations in the phosphate powder are dissolved, they can be adsorbed and combined by the anions in the minerals, thus favoring the further release of phosphate ions. However, the current research on the activation of phosphate ore powder is mainly focused on a particular activation method. In contrast, a single activation method is often not as effective as a combination of activation methods; a variety of activation methods is currently a practical path to improve the activation of phosphate ore powder (Wang et al., 2012).

Therefore, taking fluorine phosphate ore as the research object, an experimental study of the combination of mechanical activation and low molecular weight organic acid was carried out, and the factors of improving the effectiveness of phosphate ore powder and reduced energy consumption were also considered to investigate its phosphorus release characteristics and optimal conditions to provide an experimental reference for the efficient utilization of phosphate ore powder

2. Materials and methods

2.1. Tested phosphate ore

Phosphate ore powder (PR) was purchased from Shandong Chuangyi Chemical Co., Ltd, and the sizes were all around 42 μm . Analysed by X-ray fluorescence (XRF) spectroscopy.

XRF analysis (Table 1) shows that the main components are CaO and P_2O_5 with trace amounts of SrO, TiO_2 , and MgO. Scanning electron microscope (SEM) analysis (Fig. 1) showed that the unactivated phosphate ore powder was mainly in the form of lumps of different sizes and irregular shapes, with dense structure, prominent angles, relatively good crystallinity, extremely easy to break, and good mechanical activation properties (Zhang et al., 2019; Laonapakul et al., 2021).

2.2. Instrument and equipment

Phosphate ore powder was mechanically ground with a planetary ball mill (Boyuntong Instrument XGB2, Nanjing, China), and the particle size was determined by a laser particle sizer (RISE-2006). The surface morphology was analysed by SEM (TESCAN MIRA LMS). Fourier infrared analysis (Thermo

Scientific Nicolet iS20) was performed by the potassium bromide (KBr) compression method with a scan range of 400-4000 cm^{-1} . X-ray diffraction (XRD) patterns of the phosphate ore powders were obtained using an X-ray diffractometer from Bruker D8 Advance. The diffraction angle 2θ was 20° - 90° .

Table 1. Basic composition of phosphate ore powder

Samples	CaO (%)	P ₂ O ₅ (%)	SiO ₂ (%)	Fe ₂ O ₃ (%)	BaO (%)	SO ₃ (%)	Al ₂ O ₃ (%)	F (%)	SrO (%)	TiO ₂ (%)	MgO (%)
PR	70.92	20.22	2.18	1.38	1.34	1.11	0.72	0.57	0.52	0.37	0.33

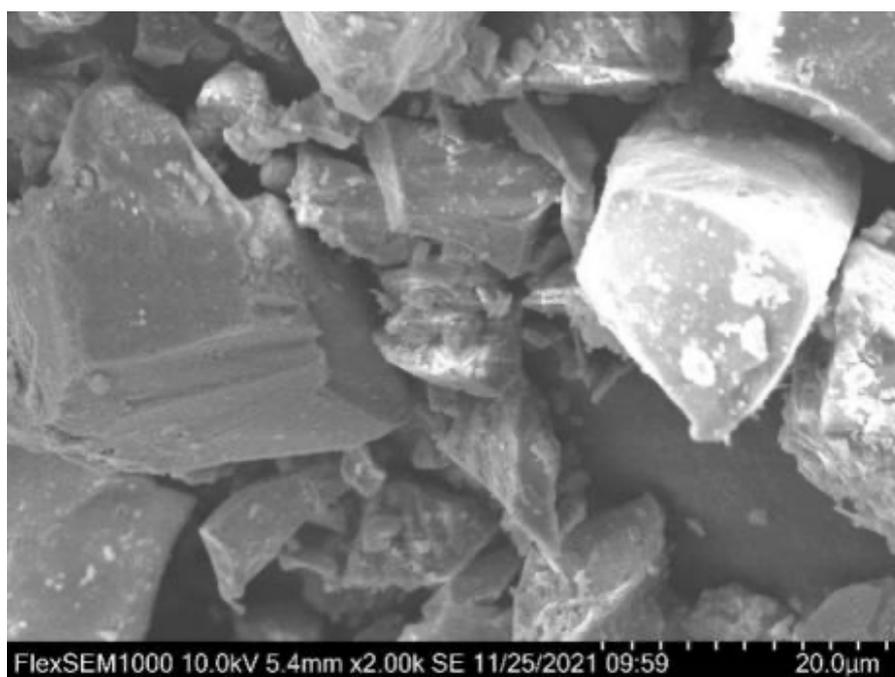


Fig. 1. SEM images of unactivated phosphate ore powder

2.3. Test method

2.3.1. Experimental flow

In order to explore the optimal activation conditions for the combination of mechanical activation and low molecular weight organic acid activation, firstly, the optimal mechanical activation conditions were explored, and secondly, the activation effects of different types of low molecular weight organic acids and their optimal activation concentrations were explored, which in turn served as a reference for the selection of the subsequent experimental parameters, so as to determine the optimal experimental conditions for the combination of the subsequent mechanical activation and low molecular weight organic acid activation. The experimental flow is shown in Fig. 2.

2.3.2. Mechanically activated phosphate ore powder

For the mechanically activated phosphate ore powder (MPR), 20 g of phosphate ore powder was added to a planetary ball mill, and the processing parameters were set to 500 revolutions per minute (rpm), with a steel ball diameter of 20 mm, a ball material ratio of 2:1, and mechanical grinding times as follows: 0, 5, 10, 20, 30, and 60 minutes (min).

For the mechanical activation of phosphate ore powder with an active mineral (AMPR), based on the above processing parameters, three active minerals, zeolite, kaolin and bentonite, were selected and mixed thoroughly according to the mass ratio of active mineral: phosphate ore powder 1:1, 1:2, 1:3, 1:4,1:5. Weigh 20 g of phosphate ore powder at different mass ratios and ground for 60 minutes.

After mechanical activation, phosphate ore powder was extracted with 2% citric acid and its effective phosphorus content was determined by the vanadium-molybdenum yellow method, and its solubility in citric acid was calculated. Citric acid solubility is one of the most important indicators for evaluating

whether phosphate ore can be used as a phosphate fertilizer (Václavková et al., 2018; Amarasinghe et al., 2022), and is expressed as the percentage of P_2O_5 dissolved in 2% citric acid to the percentage of P_2O_5 in the ore before dissolution. Each set of experiments was repeated three times and averaged.

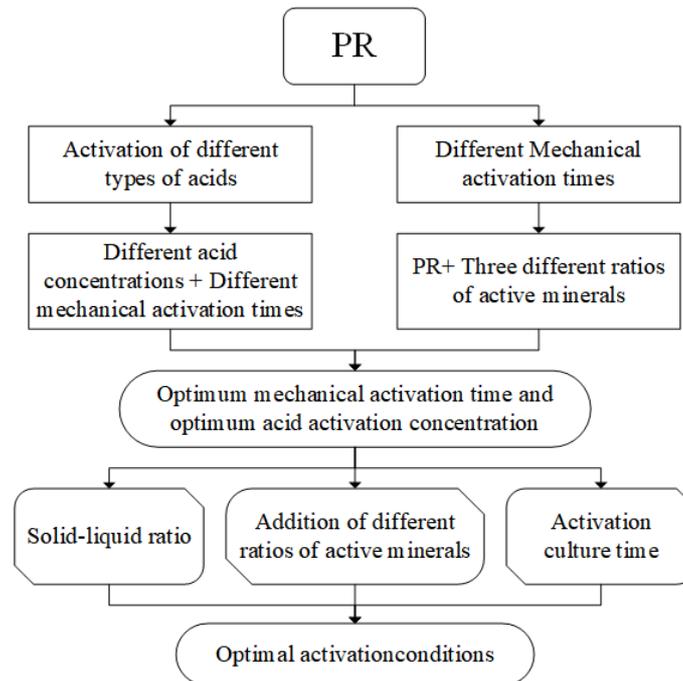


Fig. 2. Experimental flow chart

2.3.3. Low molecular weight organic acid-activated phosphate ore powder

The activation of phosphate ore powder by different kinds of organic acids was as follows: first, 0.5 g of raw phosphate ore powder was weighed, and 10 mL of oxalic acid, tartaric acid, malic acid, citric acid, formic acid, and acetic acid with concentration gradients of 0, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 mol/L, respectively, were added, and the mixture was shaken at room temperature for 6 days (Basak, 2019; De Oliveira Mendes et al., 2020).

The optimization of process parameters for activating phosphate ore powder by organic acid was as follows (Explore the optimal conditions for the current experimental factors when other activation conditions are at their optimal values, based on the experiments that have been carried out): first, 0.5 g of MPR and AMPR were weighed, the organic acid with the better activation effect was selected, and the process optimization of organic acid activation of phosphate ore powder was carried out by the above experimental method from key factors, such as the active mineral to phosphate ore powder mass ratio, activation culture time, and solid–liquid ratio.

After culture activation, the culture solution was centrifuged at 4000 rpm for 15 min and filtered. The P_2O_5 content of the filtrate was determined by the vanadium-molybdenum yellow colorimetric method and expressed as $P_2O_5\%$. All acid reagents used in the experiments were of analytical grade with purity >99.5% and were supplied by Aladdin Reagents Co, Shanghai, China. Each set of experiments was repeated three times and averaged.

3. Results and discussion

3.1. Effect of mechanical activation on phosphate ore powder

3.1.1. Particle sizes of phosphate ore powder and effective phosphorus

The median diameter (D_{50}) of phosphate ore powder decreased significantly with increasing grinding time (Fig. 3). At 5 min of milling, D_{50} decreased from 41.67 μm to 11.83 μm , which was the fastest decrease, indicating that the phosphate ore powder had the most apparent effect at the early stage of mechanical activation. With the extension of grinding time, the decrease in D_{50} decreased significantly, and the grinding efficiency was reduced. When the mechanical activation was 20 min, D_{50} slightly

increased, indicating that when crushed to a certain fineness, the particles agglomerated (Qian et al., 2018). Some of the fine particles of phosphate ore powder at this time regrouped together, increasing in particle size, along with subsequent grinding and disappearance. The D50 was reduced from 41.67 μm to 10.59 μm within 60 min. The particle size stabilised at 60 min, indicating that when the phosphate ore powder is ground to a certain extent, continuing to extend the grinding time does not significantly reduce the phosphate ore powder particle size; thus, 60 min of grinding is both a reasonable and efficient activation time.

In the process of mechanical activation, the particle size of phosphate ore powder decreased, and the effective phosphorus content increased accordingly. In the early stage of mechanical activation, the particle size decreased rapidly, and the effective phosphorus content increased quickly. With increasing grinding time, the particle size decrease slowed, and the increase in effective phosphorus also slowed. The effective phosphorus content increased from 1.19% to 8.27% within 60 min of grinding time, and the effective phosphorus content increased at the fastest rate in the first 5 min. At 20 min of mechanical activation, the particle size of phosphate ore powder increased slightly, and the effective phosphorus content still increased, which was because the small particles formed by the crushing of large particles in turn adhered to the large particles, resulting in small fluctuations in the particle size of the phosphate ore powder, but then disappeared with the subsequent grinding (Zhang et al., 2019). At the same time, the increase of effective phosphorus content in phosphorite powder indicates that the effect of mechanical activation on the reactivity of phosphate ore powder depends not only on the reduction of particle size but also on the change of its internal crystal structure (Chaikina and Aman, 2005; Yaneva et al., 2005). Phosphate ore powder particles collide and rupture during the grinding process, and the internal crystal structure is destroyed, which is conducive to the chemical reaction between minerals and promotes the release of effective phosphorus in phosphate ore powder, which can effectively improve the resource utilization rate of phosphate ore (Qian et al., 2018).

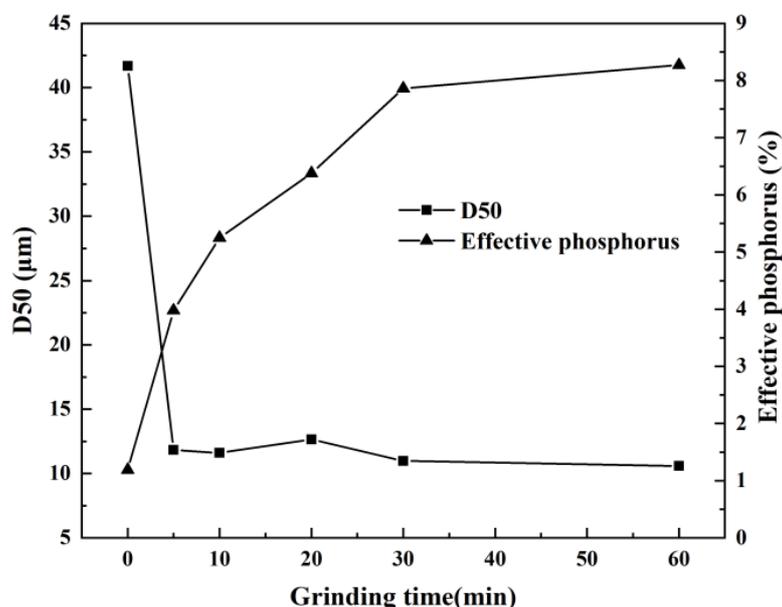


Fig. 3. Relationship curve between median diameter (D50) and effective phosphorus at different grinding times

3.1.2. Citric acid solubility change

Citric acid solubility is one of the essential indicators to evaluate whether phosphate ore powder can be used as a phosphate fertilizer. Under the condition that the total phosphorus content is known, the higher the citric acid solubility is, the better (Braithwaite et al., 1990). Within 60 min of mechanical activation, the citric acid solubility of the phosphate ore powder increased with increasing grinding time (Fig. 4). Studies related to phosphate fertilizer standards in China and Brazil consider that phosphate ore powder can be applied when its citric acid solubility is greater than 30% (Fang et al., 2019; Guo et al., 2011). From 0 to 30 min of mechanical activation, the citric acid solubility increased rapidly. At 10 min of milling, the citric acid solubility reached more than 35%, and with continued milling until 30 min, the citric acid solubility reached 52.40%. The citric acid solubility increased slowly

from 30 to 60 min, and the citric acid solubility reached 55.13% at 60 min of milling, which was 47.20% higher than the citric acid solubility of 7.93% for the nonmechanically activated phosphate ore powder.

An exponential equation for citric acid solubility (y) versus grinding time (x) was obtained by fitting the data to describe the variation of citric acid solubility with grinding time. The obtained equations generally agree with those provided by previous authors (Fang et al., 2019; Petkova et al., 2015), as shown in Fig. 4.

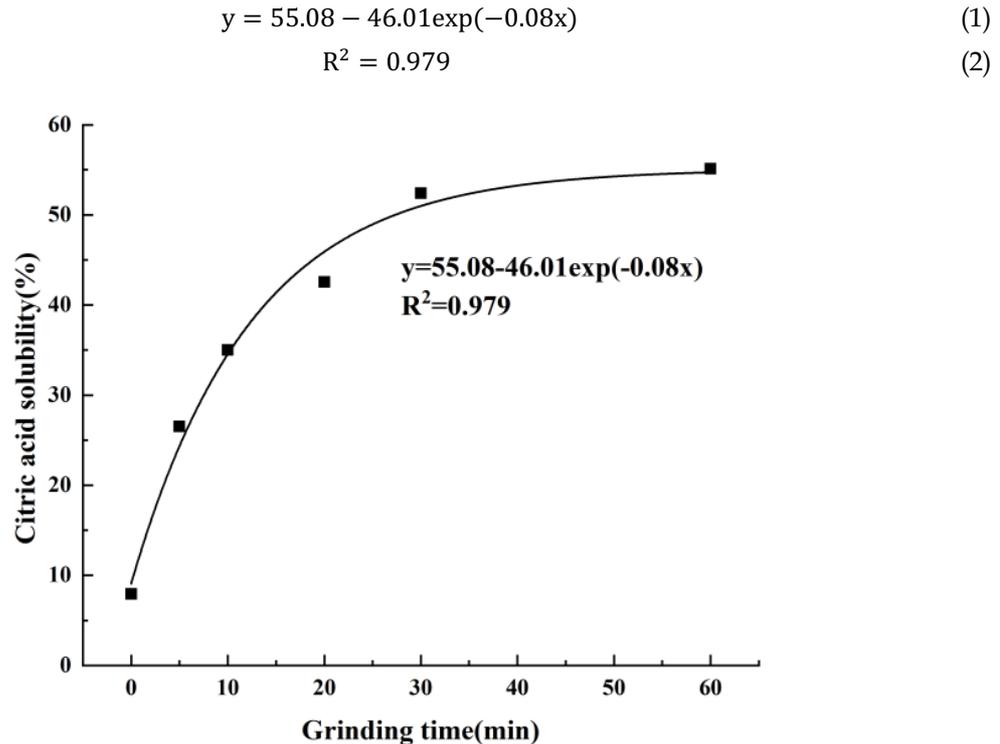


Fig. 4. Fitted curve of citric acid solubility and mechanical grinding time of phosphate ore powder

3.1.3. Citric acid solubility at different active mineral ratios

The addition of an active mineral to the mechanical activation process can promote the transformation of the mineral crystal structure and achieve the release of phosphorus from phosphate ore powder (Laonapakul et al., 2021). The three active minerals (zeolite, kaolin, and bentonite) that were added in this study are based on silica-aluminate, which has a large specific surface area, high void ratio, and negative charge; it can be balanced by metal cations; and has a good adsorption capacity and ion exchange capacity (Feng et al., 2023; Annan et al., 2021). Fig. 5 shows that the citric acid solubility of phosphate ore powder was enhanced by adding three active minerals, but the activation effect differed. The citric acid solubility of phosphate ore powder with zeolite was approximately 17.59%, and the activation effect tended to decrease as the mass ratio decreased. At a mass ratio of zeolite to phosphate ore powder of 1:1, the citric acid solubility reached the maximum value (19.59%), 11.66% higher than that of unactivated phosphate ore powder. The citric acid solubility of phosphate ore powder with the addition of kaolin was approximately 16.13%. With the decrease in mass ratio, the activation effect of kaolin on phosphate ore powder was significantly weakened. At a mass ratio of 1:1, the citric acid solubility reached a maximum (20.04%), 12.11% higher than that of unactivated phosphate ore powder. The citric acid solubility of phosphate ore powder with the addition of bentonite did not vary significantly with the mass ratio, and the citric acid solubility was approximately 18.59%, which was 10.66% higher than that of unactivated phosphate ore powder. The phosphate ore powder with the addition of three active minerals, under the mechanical activation effect, reduces the particle size of the active mineral and phosphate ore powder, increasing its specific surface area, which is conducive to opening the inner pores of mineral particles and forming a new active surface (Qian et al., 2018; Brigatti et al., 2013), making the anionic reactive groups in the active mineral combine with metal cations in phosphate ore powder through complexation, thus releasing phosphate ions and increasing the effective phosphorus of phosphate ore powder (Mabagala, 2022; Bacelo et al., 2020).

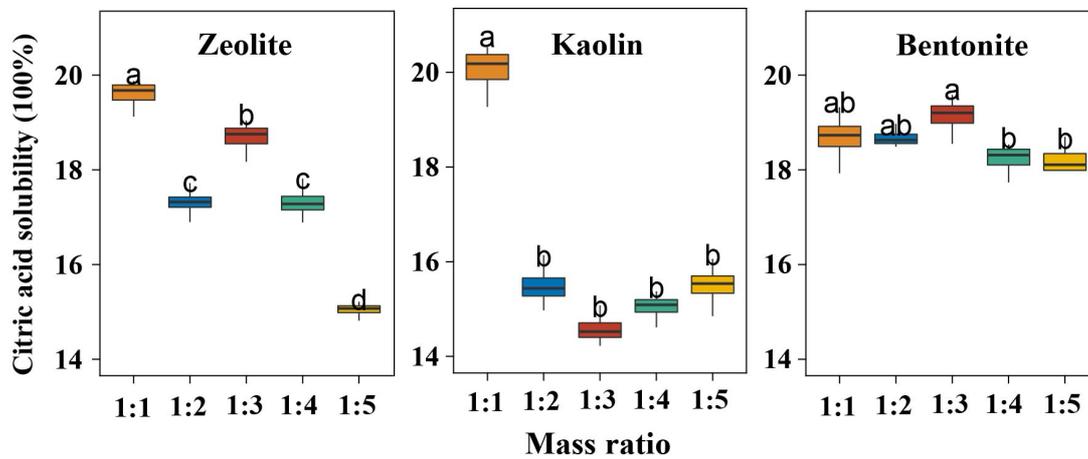


Fig. 5. Effect of different ratios of active mineral on the solubility of citric acid of phosphate ore powder (1:1, 1:2, 1:3, 1:4, 1:5 is the mass ratio of active mineral: phosphate ore powder). Where there is an identically labelled letter, the difference between the five mass ratios is not significant; where there are differently labelled letters, the difference between the five mass ratios is significant ($P < 0.05$; multiple comparisons with Kruskal-Wallis)

3.2. Structural characterization of mechanically activated

3.2.1. Surface morphological changes

Fig. 6 shows the scanning electron microscope images of phosphate ore powder magnified 2000 times under different mechanical activation conditions. The surface morphology of the phosphate ore powder changed greatly under the mechanical grinding effect. Before mechanical activation, the phosphate ore powder particles were of different sizes, irregularly lumpy, well crystallized, had prominent angles, and were extremely easy to break (Fig. 6A). After mechanical grinding for 5-10 min (Fig. 6B, C), the particles were gradually crushed into fine particles, and the angles slowly disappeared. After 20 min of mechanical grinding (Fig. 6D), the surface boundaries of the particles became blurred, and fusion between the particles began to occur. After 60 min of mechanical grinding (Fig. 6F), the laminated phosphate ore powder particles basically disappeared. Some of the large particles are made of tiny particles mingled into a flocculent shape, showing agglomeration (Yaneva et al., 2009; Plotegher and Ribeiro, 2016), making it more difficult to crush and reach the crushing limit. In other words, through the mechanical activation of phosphate ore powder particles and grinding media or particles rubbing against each other, grinding off the edges of the flaky particles, forming irregular flocculent, the particle size distribution tends to be uniform, and the degree of amorphousness increases, which is conducive to improving the release of phosphorus from the phosphate ore powder and is also conducive to the further activation of the phosphate ore powder by other activation methods (Shao et al., 2021).

Based on the scanning electron microscope images of phosphate ore powder with an AMPR mass ratio of 1:1 and mechanical activation 60 min (Fig. 6G, H, I), the surface morphology of the phosphate ore powder particles with the addition of zeolite (Fig. 6G) and bentonite (Fig. 6I) was rough, irregularly shaped and had more angles, while for the phosphate ore powder with the addition of kaolin (Fig. 6H), the phosphate ore powder particles were fine and rounded into a loose flocculent shape with blurred surface boundaries and disappearing angles. This shows that mechanical activation can promote more full contact between the active mineral and phosphate ore powder, which is conducive to improving the activation effect of the active mineral on phosphate ore powder (Zhang et al., 2019).

3.2.2. Infrared spectral analysis

Fourier transform infrared spectroscopy (FTIR) showed (Fig. 7) that PO_4^{3-} , CO_3^{2-} , and OH^- plasma groups were present in the structure of phosphate ore powder. The absorption bands of the functional groups in the samples changed significantly with increasing activation time (Guo et al., 2021). In the FTIR spectrum of raw phosphate ore powder (0 min), the O-Si-O and Si-O-Si absorption bands were located near 470 cm^{-1} and 745 cm^{-1} , respectively. The two split absorption bands located near $572\text{-}604 \text{ cm}^{-1}$ and $1050\text{-}1100 \text{ cm}^{-1}$ are both typical of PO_4^{3-} in the crystalline apatite structure (Koleva and Petkova, 2012), and the broadening of the absorption bands and the weakening of the peaks with the prolon-

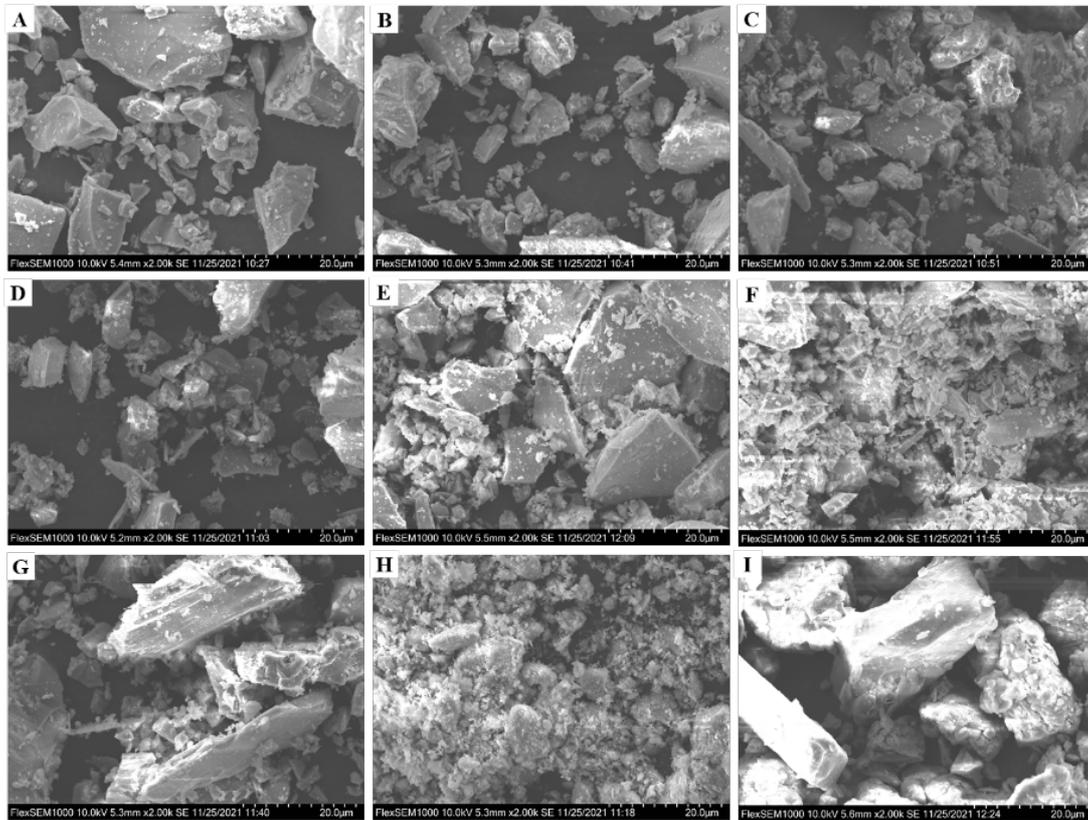


Fig. 6. SEM images of phosphate ore powder under different mechanical activation conditions (A) 0 min, (B) 5 min, (C) 10 min, (D) 20 min, (E) 30 min, (F) 60 min, (G) zeolite, (H) kaolin, (I) bentonite

gation of the mechanical activation time indicates the disruption of the crystal structure of apatite. The presence of calcite and apatite is further indicated by the CO_3^{2-} absorption bands at 729 cm^{-1} and $1425\text{--}1459\text{ cm}^{-1}$. The weakening of the absorption peak at 729 cm^{-1} with the prolongation of the mechanical activation indicates the disruption of the crystal structure of the associated mineral calcite. The absorption peak of the CO_3^{2-} ion band at $1425\text{--}1459\text{ cm}^{-1}$ gradually broadens, decreases in intensity, and even disappears at 30 min of mechanical activation, which is partly due to the combination of apatite with CO_2 in the air during the mechanical activation process, and even more so because of the replacement of PO_4^{3-} by CO_3^{2-} (Fang et al., 2019). And this isomorphous rearrangement process leads to defects in the crystal structure and the release of PO_4^{3-} , which further explains why mechanical activation promotes the increase of phosphorus solubility. The OH^- ion absorption band from $3533\text{--}3538\text{ cm}^{-1}$ belongs to the adsorbed water in the structure, which basically disappears during 10 min of mechanical activation, which may be due to the disappearance of adsorbed water in the apatite structure. As the mechanical activation time increases, the OH^- ion absorption band gradually enhances again, which indicates the presence of hydroxyl groups rather than just the absorption of water vapor in the air (Fang et al., 2019). Therefore, it can be seen that part of the hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) was formed during the mechanical activation process (Jin et al., 2013), and the hydroxyapatite possesses excellent ion-exchange capacity, which is more conducive to the subsequent release of phosphorus. In addition, from the Fourier transform spectrum (Fig. 7) of the phosphate ore powder with AMPR mass ratio of 1:1 and mechanically activated for 60 min, it can be seen that the above absorption peaks belonging to the unique structure of phosphate ore powder basically disappeared after the addition of three kinds of active minerals, which further explains that the phosphate ore powder with the addition of three kinds of active minerals is more conducive to the mechanical activation.

3.2.3. XRD physical phase and structural analysis

The X-ray diffraction pattern of phosphate ore powder (Fig. 8) shows the mineral compositions of the samples with different milling times. The diffraction peaks in the raw ore XRD analysis pattern were mainly caused by fluorapatite ($\text{Ca}_5\text{F}(\text{PO}_4)_3$) and some impurities, such as small amounts of quartz and

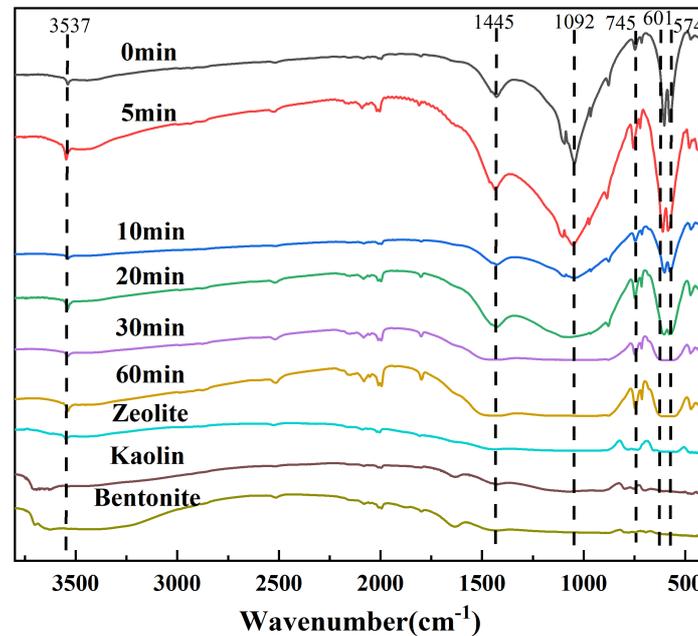


Fig. 7. FTIR diagram of phosphate ore powder under different mechanical activation conditions

CaCO₃. Its peak pattern was sharp, indicating the high crystallinity of the minerals in the phosphate ore powder (Andrić et al., 2015). The diffraction peaks of apatite gradually decrease with increasing mechanical activation time, indicating decreased crystallinity, increased disorder, and increased amorphization, which is consistent with SEM observations. It can be seen that after mechanical activation, the crystal structure of phosphorus minerals in the phosphate ore powder is destroyed or changed, which in turn improves the phosphorus release characteristics of the phosphorite powder (Tõnsuaadu et al., 2011). At 5 min of mechanical activation, the diffraction peaks decreased to a minimum, and the diffraction peaks increased again after prolonging the mechanical activation time, probably due to the appearance of secondary particles. The weak agglomeration was broken at 20 min of mechanical activation, at which time the diffraction peak was reduced, followed by a cyclic phase of weak agglomerate formation and breaking (Wang et al., 2012). Continuing to grind, the XRD pattern no longer changed, indicating that the physical phase of apatite basically no longer changed by continuing to grind, and only the internal microstructure changed. This further explains the insignificant increase in both effective phosphorus and citric acid solubility of phosphate ore powder at 30-60 min of mechanical activation.

The XRD patterns of phosphate ore powders with an AMPR mass ratio of 1:1 and mechanically activated for 60 min showed that the apatite diffraction peaks were significantly weakened. The peak shapes were broadened in the phosphate ore powders with the addition of three activated minerals and mechanical activation for 60 min. Diffraction peaks specific to the three minerals were also detected. The XRD pattern of phosphate ore powder with added zeolite contained sodium feldspar and plagioclase, while the XRD pattern with added kaolinite and bentonite showed mainly quartz, as well as kaolinite and montmorillonite. At the same time, the diffraction peaks of apatite in phosphate ore powder were significantly weakened, and the peak shapes were broadened, which further indicated that the addition of three activating minerals could effectively reduce the crystallinity of phosphate ore powder, destroy the crystal structure of apatite and promote the conversion of bound phosphorus to dissolved phosphorus in phosphate ore powder. However, the accurate identification of the type of homogeneous substitution of phosphate ore powder during mechanical activation still needs further research.

3.3. Effect of low molecular weight organic acids on phosphate ore powder

3.3.1. Effect on phosphate ore powder before mechanical activation

The activation effects of different types of low molecular weight organic acids on phosphate ore powder were different (Fig. 9). The activation effects of oxalic acid, tartaric acid, and citric acid showed a trend

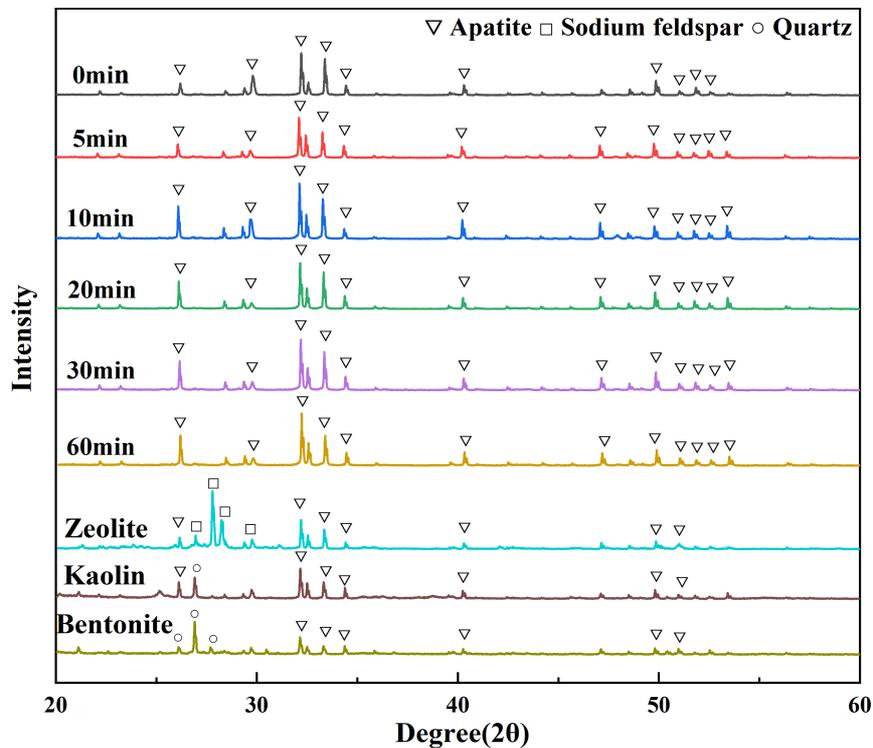


Fig. 8. XRD diagram of phosphate ore powder under different mechanical activation conditions

powder P_2O_5 of 25.72%, 8.94%, and 2.50%. The activation effect of malic acid, formic acid, and acetic acid increased and then decreased with increasing acid concentration, and the best activation effects were achieved at 0.1, 0.3, and 0.2 mol/L, respectively, to obtain maximum contents of phosphate ore acid increased with increasing acid concentration, and all of them had the best activation effect at 0.5 mol/L. The P_2O_5 contents increased from 0.30%, 0.06%, and 0.06% to 8.01%, 1.17%, and 0.18%, respectively. Therefore, the overall activation effects were as follows: oxalic acid > tartaric acid > malic acid > citric acid > formic acid > acetic acid. Oxalic acid activation showed the most significant performance, while formic acid and acetic acid had the worst activation effects. The optimal activation concentration of oxalic acid was only 0.1 mol/L, which was the least concentration relative to other organic acids in the experiment, thus achieving the result of conservation and environmental protection.

Table 2 shows the pKa values of the six low molecular weight organic acids. The smaller pKa value represented the more robust acidity, and the acidic strength of low molecular weight organic acids had a certain similar trend with the activation effect of phosphate ore powder (Rybalkina et al., 2022). Among them, formic acid and acetic acid are monobasic weak acids, and the acidity of formic acid is stronger than that of acetic acid, so the activation effect of formic acid is greater than that of acetic acid. The acidic strength of binary acid is oxalic acid > tartaric acid > malic acid, so the activation effect is oxalic acid > tartaric acid > malic acid. Citric acid is a ternary acid, the acidity is between tartaric acid and malic acid, and the activation effect is second only to malic acid. Generally, low molecular weight organic acids mainly affect the activation of minerals through their ionization of H^+ and acid ions (Lin et al., 2023). H^+ can interact with insoluble phosphates present in phosphate ore powder to form phosphate ions and phosphite ions, thus releasing soluble phosphorus. At the same acid concentration, the H^+ concentration depends on the level of dissociation of the acid itself, that is the pKa value, and therefore the activation effects appear somewhat similar. Secondly, the activation effect does not only depend on the concentration level of H^+ , but is also closely related to the type and number of active functional groups possessed by different types of organic acids (Wei et al., 2014; Yang et al., 2019). Low molecular weight organic acids contain a large number of active functional groups, such as carboxyl and hydroxyl, with chelating and coordination ability, can effectively combine with Ca^{2+} , Fe^{3+} , Al^{3+} , and other metal ions in phosphate ore powder, thus promoting the release of phosphate ions and improving the solubility of phosphorus in phosphate ore powder (Kpombekou-a and Tabatabai, 2003). Therefore, according to the activation effect of organic acids, only oxalic acid, tartaric acid, malic acid, and citric acid were selected for subsequent experiments.

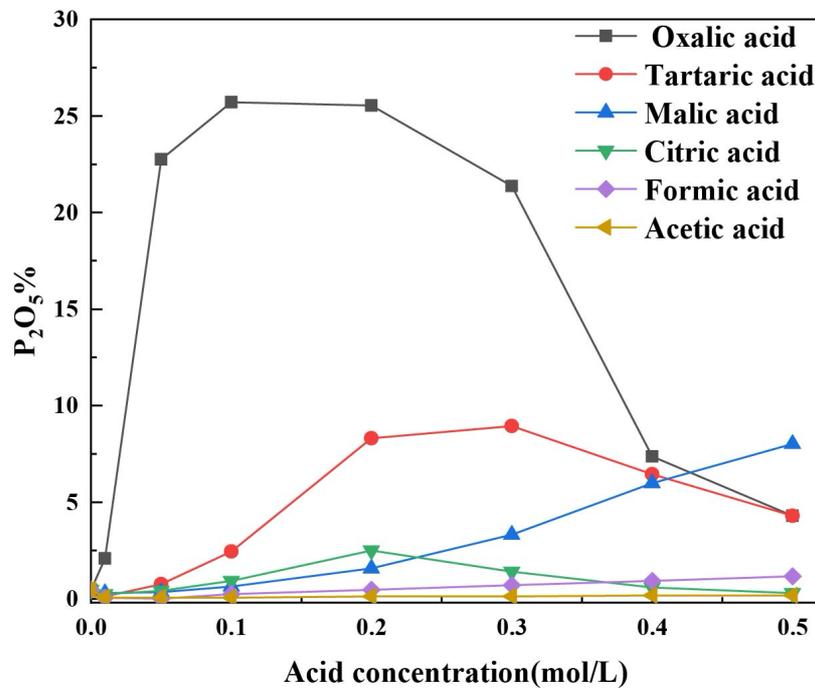


Fig. 9. Activation effect of different types of acids on phosphate ore powder (Concentration gradients of 0, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 mol/L)

Table 2. Different acid pKa values

Acid Name	pKa
oxalic acid	1.22
tartaric acid	3.04
citric acid	3.13
malic acid	3.46
formic acid	3.74
acetic acid	4.74

3.3.2. Effect on phosphate ore powder after mechanical activation

Four low molecular weight organic acids with sound activation effects, oxalic acid, tartaric acid, malic acid, and citric acid were selected for the activation of MPR, as shown in Fig. 10. The phosphate ore powder after mechanical activation does not change the optimal concentration of low molecular weight organic acid for phosphate ore powder activation, and the longer the mechanical grinding time, the better the activation effect of low molecular weight organic acid for phosphate ore powder. When the oxalic acid concentration was 0.1 mol/L, P_2O_5 , the phosphate ore powder reached a maximum release of 27.80%; relative to the unactivated phosphate ore powder, the P_2O_5 content increased by 26.65%, and the activation effect was still the most significant. For the activation of phosphate ore powder by tartaric acid at an optimum concentration of 0.3 mol/L, P_2O_5 reached a maximum release of 12.77%, which was second only to oxalic acid in terms of activation effect. The activation effects of malic acid and tartaric acid on phosphate ore powder at the optimal concentration were not significantly different, where the maximum P_2O_5 content of malic acid-activated phosphate ore powder was 11.68%, and the optimal concentration was 0.5 mol/L. The best activation concentration of citric acid for phosphate ore powder was 0.2 mol/L, and the maximum release of P_2O_5 was 5.87%, which was the worst relative activation effect.

During the activation of phosphate ore powder after mechanical activation by low molecular weight organic acids, it was found that the low molecular weight organic acids were beneficial for exploring the phosphorus release capacity of phosphate ore powder and promoting the amount of phosphorus released from phosphate ore powder. Among them, for tartaric acid, malic acid, and citric acid at a certain acid concentration, the longer the mechanical activation time was, the greater the release of

phosphorus, which is consistent with the results of the change in the effective phosphorus content of phosphate ore powder under different mechanical activation times. However, in the process of the oxalic acid activation of phosphate ore powder, the activation effect of oxalic acid on phosphate ore powder was always at a high level, indicating that the effect of oxalic acid itself on phosphate ore powder activation is much greater than the effect of mechanical activation on phosphate ore powder. Therefore, mechanical activation and low molecular weight organic acid activation are synergistic in the activation process of phosphate ore powder.

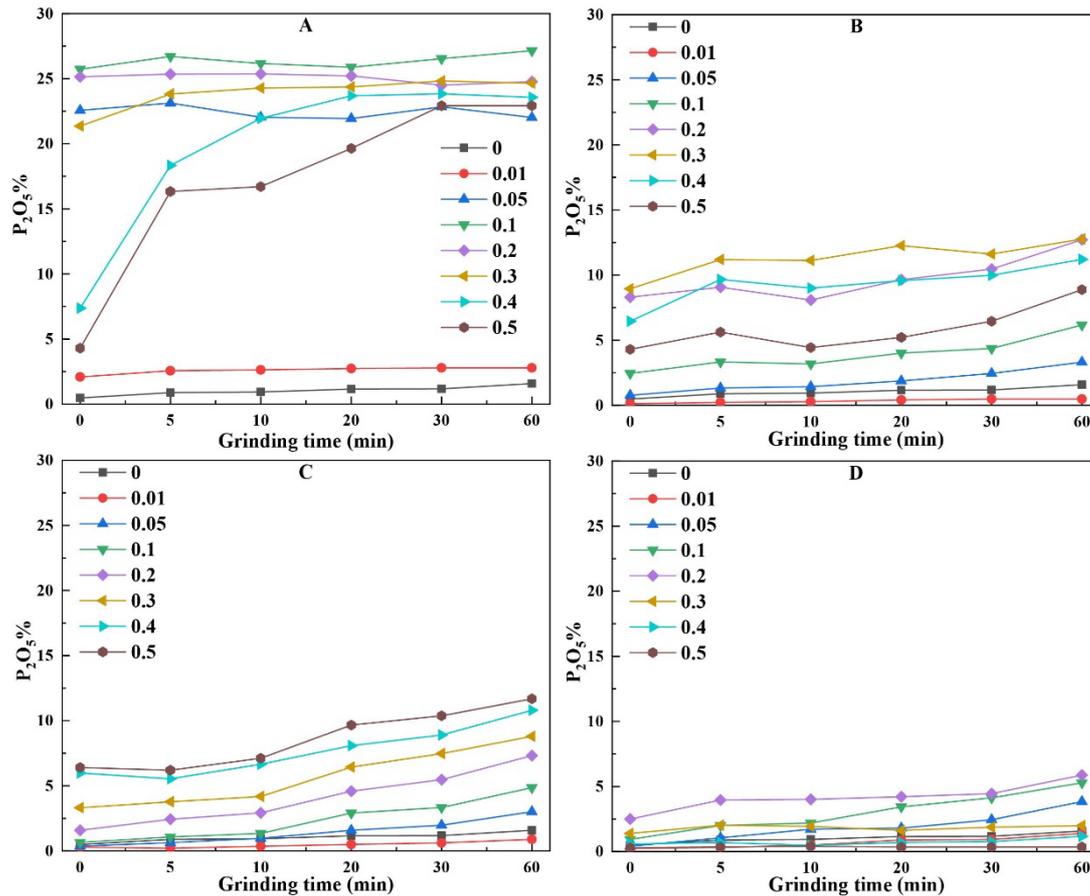


Fig. 10. Activation effect on phosphate ore powder at different acid concentrations (A) oxalic acid, (B) tartaric acid, (C) malic acid, (D) citric acid. (0, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 for organic acid concentration mol/L)

3.4. Activation of low molecular weight organic acids under different conditions

3.4.1. Addition of different proportions of active minerals

Four low molecular weight organic acids activated the AMPR at the optimum concentration (Fig. 11). The activation effect was best under oxalic acid activation conditions. Nevertheless, the mixing ratio of all three active minerals with phosphate ore powder had no significant effect on the activation of phosphate ore powder. The P_2O_5 content was approximately 26.15%, indicating that oxalic acid played a dominant role in the activation process of phosphate ore powder with the addition of active minerals. Under the activation conditions of three low molecular weight organic acids, tartaric acid, malic acid, and citric acid, the P_2O_5 content in phosphate ore powder decreased slowly with the decrease in the mass ratio of the active mineral to phosphate ore powder, which was consistent with the results of the change in the citric acid solubility of phosphate ore powder under mechanical activation conditions. The P_2O_5 content of tartaric acid, malic acid, and citric acid-activated phosphate ore powder reached the maximum value when the mass ratio of active mineral to phosphate ore powder was 1:1, and the values were 13.07%, 11.98%, and 5.34%, respectively. Therefore, the best activation effect on phosphate ore powder was when the mixing ratio of all three active minerals and phosphate ore powder was 1:1. Under the condition of the same mineral ratio, the activation effect of the phosphate ore powder with the addition of acid is better than that of the phosphate ore powder without the addition of acid. The

reason is that phosphate ore powder reacts with acid to decompose the insoluble phosphorus in phosphate ore powder into soluble phosphorus. Combined with three active minerals, all have a high cation exchange capacity and high phosphate adsorption properties, the high cation exchange ability enhances the complexation reaction, and the organic anion reactive groups in the active mineral combine with the metal cations (Ca^{2+} , Fe^{3+} , and Al^{3+}) in the phosphate ore powder, thus releasing more phosphate ions (Na, 2020) and increasing the effectiveness of phosphorus in phosphate ore powder. Therefore, in the acid activation test with the addition of the active mineral, the best mass ratio of active mineral to phosphate ore powder is 1:1. That is, the greater the proportion of active mineral in the phosphate ore powder, the more significant the high cation exchange capacity and high phosphate adsorption properties are, the more acidic the available sites are, the higher the activation of phosphate ore powder is, and the better the phosphorus release effect is. At the same time, the adsorption property of high phosphate may bind the dissolved released phosphorus to its acidic site of the active mineral, which limits the movement of phosphorus in the soil to promote the slow dissolution of phosphate ore powder, thus preventing phosphorus fixation in the soil and providing new ideas for the development of new phosphate fertilizers with slow solubility while promising to improve the efficiency of agricultural phosphate fertilizer utilization (Pickering et al., 2002; Teles et al., 2020).

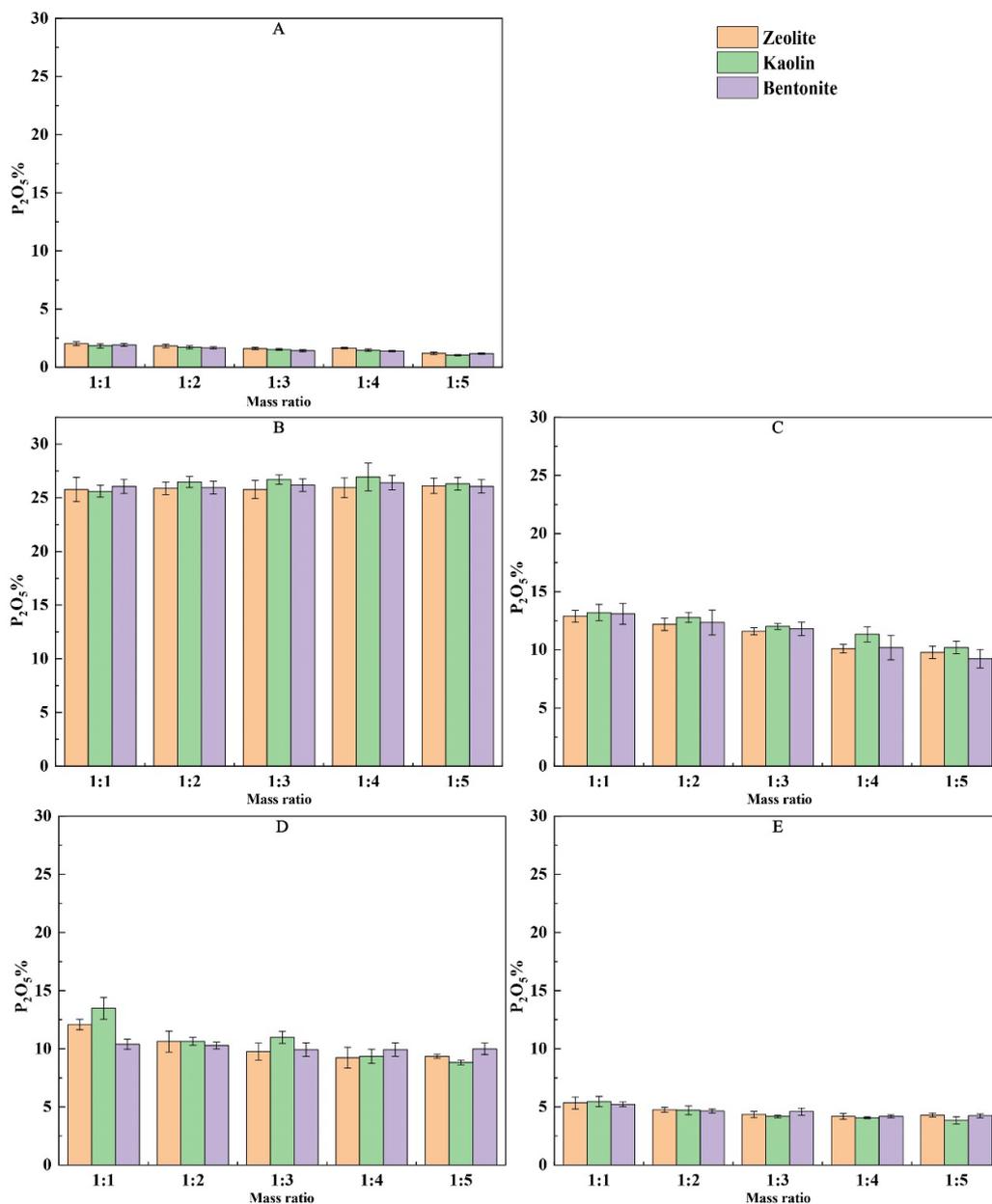


Fig. 11. Activation effect of different acids on the addition of varying mineral phosphate ore powders (A) no acid added, (B) oxalic acid, (C) tartaric acid, (D) malic acid, (E) citric acid

3.4.2. Activation culture time

Four low molecular weight organic acids at optimal concentrations were used to activate the phosphate ore powder with an AMPR mass ratio of 1:1 and MPR mechanical grinding for 60 min. As shown in Fig. 12, the activation culture trends of the four organic acids on phosphate ore powder were basically the same. During the initial cultivation period, the P_2O_5 content in phosphate ore powder increased with the increase in the number of days of cultivation. For the activation culture time of 1-4 days, the P_2O_5 content increased rapidly; for the activation culture time of 4-6 days, the increase in the P_2O_5 content slowed down; and for the activation culture time of 6 days, the P_2O_5 release reached a maximum, continuing to extend the activation time, but the P_2O_5 content in phosphate ore powder decreased. Therefore, the optimal activation cultivation time for all four organic acids was 6 days. Among them, oxalic acid, tartaric acid, malic acid, and citric acid showed maximum P_2O_5 contents of 25.71%, 12.57%, 14.37%, and 6.07%, respectively, after 6 days of activation cultivation.

With increasing cultivation time, H^+ in organic acid was fully released, and the more phosphate in phosphate ore powder was in contact with H^+ , the greater its solubility (Mahawar et al., 2022). At the same time, there may be an exchange of organic anions in the active mineral with phosphate particles in the phosphate ore powder to achieve phosphorus release (Na, 2020), making the P_2O_5 content in the phosphate ore powder gradually increase within 6 days of activation cultivation. However, in the late stage of activation cultivation, the concentration of H^+ in the solution and organic anions in the active mineral decreased, decreasing the phosphorus solubility level of phosphate ore powder. At the same time, metal cations, such as Ca^{2+} , Fe^{3+} , and Al^{3+} , remained in the solution, and some of the phosphate ions might recombine with the metal cations within the phosphate ore powder (Zhang et al., 2018), leading to a significant decrease in the effective phosphorus content.

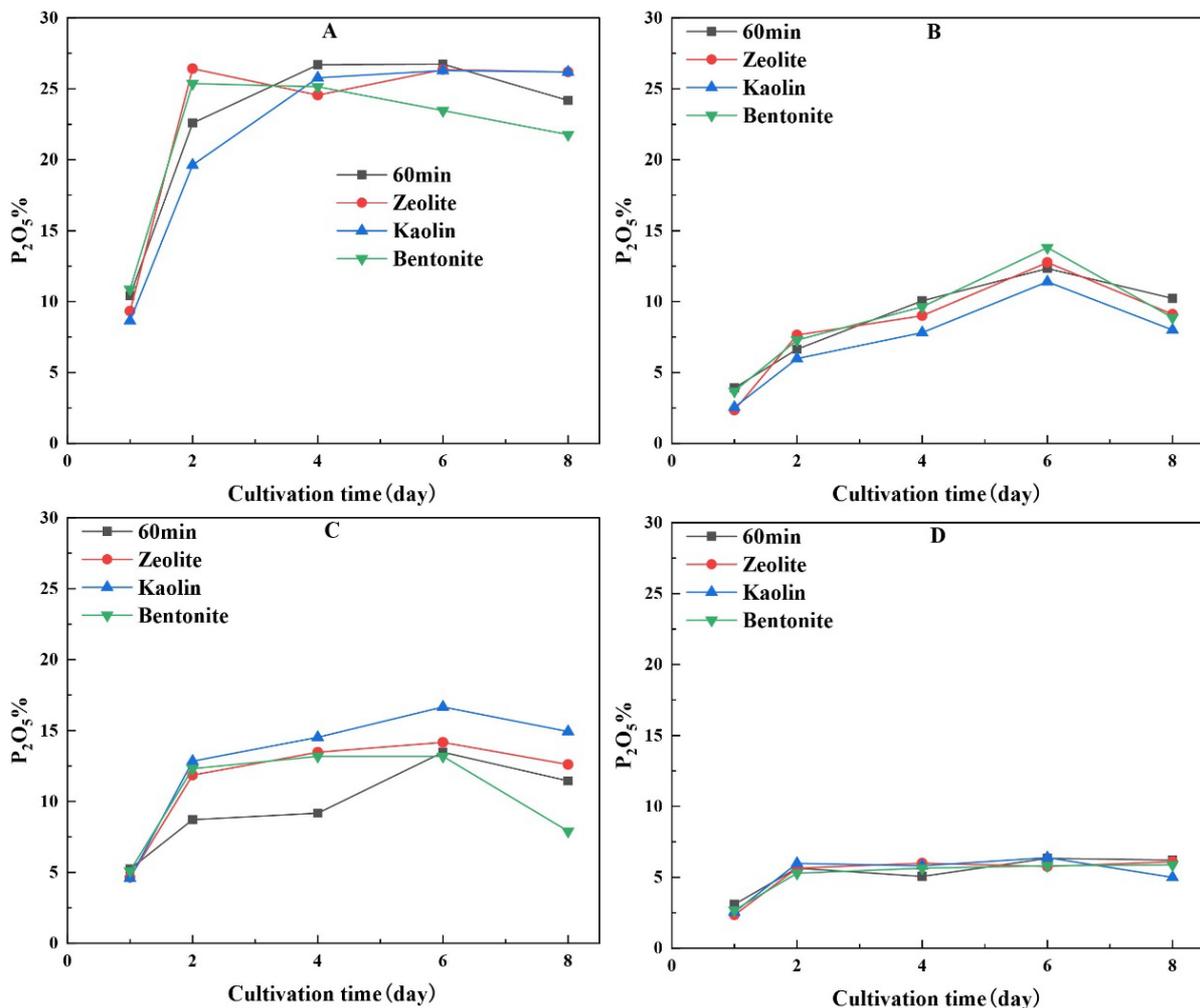


Fig. 12. Effect of different cultivation times on activation of phosphate ore powder (A) oxalic acid, (B) tartaric acid, (C) malic acid, (D) citric acid

3.4.3. Solid–liquid ratio

Four organic acids at optimum concentrations were used to activate MPR under different solid–liquid ratio conditions, as shown in Fig. 13. At the same solid–liquid ratio, the P_2O_5 content of phosphate ore powder increased after mechanical activation. At the same mechanical activation time, with the decrease in the solid–liquid ratio, the activation of oxalic acid on phosphate ore powder showed a trend of first weakening and then enhancing, where the activation effect was best at the solid–liquid ratio of 1:1 with a P_2O_5 content of approximately 25.54%. The activation effect of tartaric acid did not change significantly with the decrease in the solid–liquid ratio, and the P_2O_5 content was always maintained at approximately 11.96%. The activation effects of malic acid and citric acid on phosphate ore powder were enhanced and then weakened with a decreasing solid–liquid ratio, in which the best activation effect was achieved at a solid–liquid ratio of 1:10 with the release of P_2O_5 at approximately 12.99% and 4.86%, respectively.

In general, as the solid–liquid ratio decreases, the greater the number of ions and H^+ available for coordination in low molecular weight organic acids, the more mechanical activation time increases, the higher the surface activity of phosphate ore powder is, and the more favourable the dissolution of insoluble phosphorus in phosphate ore powder is (Wang et al., 2004). Therefore, tartaric, malic, and citric acids with a solid–liquid ratio of 1:10 and a mechanical activation time of 60 min had a good activation effect. Nevertheless, with a solid–liquid ratio of 1:20, the activation effect was not ideal, indicating that when the H^+ content was too high, it was not conducive to the activation of phosphate ore powder. In contrast, the activation effect of oxalic acid was better at a solid–liquid ratio of 1:1 and a mechanical activation time of 60 min, and the optimal concentration at this time was only 0.1 mol/L, which was the least amount of acid and could achieve the maximum resource savings.

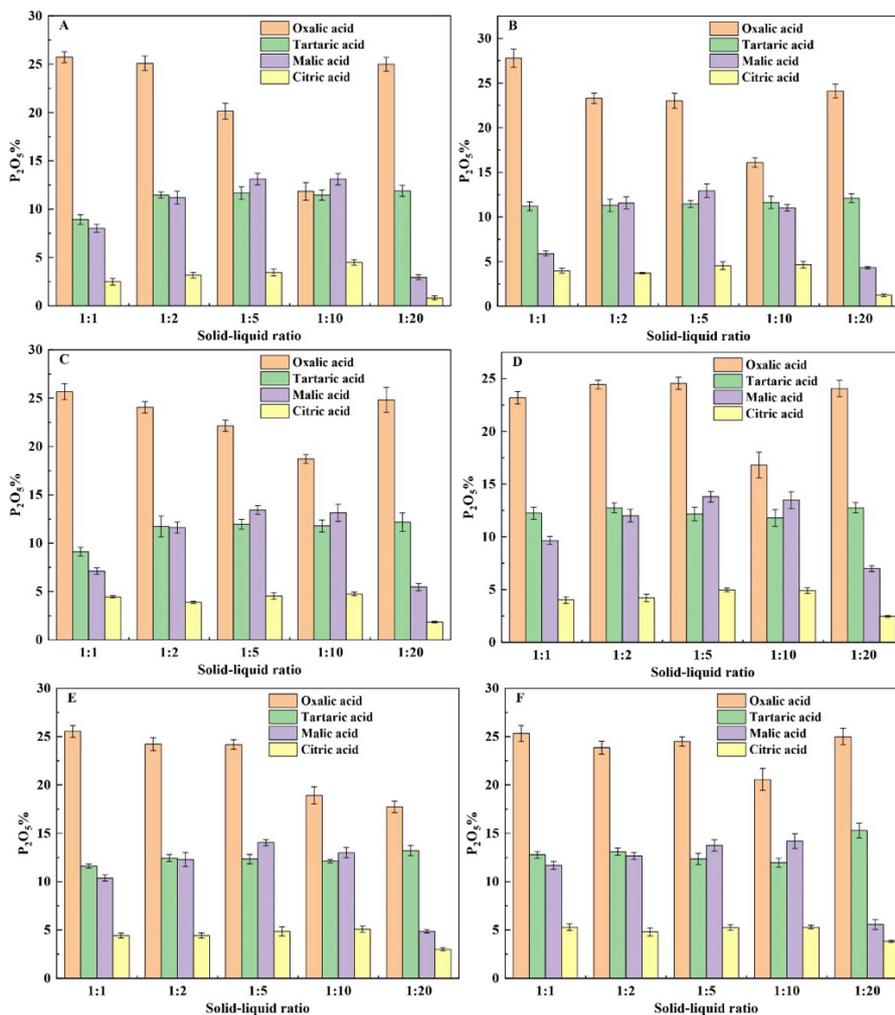


Fig. 13. Effect of different solid–liquid ratios on activation of phosphate ore powder (A) 0 min, (B) 5 min, (C) 10 min, (D) 20 min, (E) 30 min, (F) 60 min

4. Conclusions

The phosphorus release characteristics of phosphorus ore powder under different conditions of mechanical activation and low molecular weight organic acid activation were studied with medium- and low-grade phosphate ore powders as the research object. The main conclusions are as follows:

- (1) Mechanical activation can significantly reduce the particle size of phosphate ore powder. Within 60 min of mechanical grinding, the D50 of phosphate ore powder decreased from 41.67 μm to 10.59 μm , and the effective phosphorus content and citric acid solubility increased significantly with the prolongation of mechanical activation time from 1.19% and 7.93% to 8.27% and 55.13%, respectively.
- (2) As the mechanical activation time increased, the surface of phosphate ore powder became loosely flocculated; the boundaries blurred; the angles gradually disappeared; the intensity of the absorption band of the group structure had an obvious tendency to decrease; some fluorapatite was transformed; a new phase, such as hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), was formed; and the degree of crystallinity was decreased, which further indicated that the mechanical activation promoted the release of phosphorus in phosphate ore powder.
- (3) Low molecular weight organic acid activation promotes the release of phosphorus from phosphate ore powder. The overall phosphorus release effect was oxalic acid > tartaric acid > malic acid > citric acid, with the best concentrations of 0.1 mol/L, 0.3 mol/L, 0.5 mol/L, and 0.2 mol/L, respectively, and the best activation cultivation time of 6 days.
- (4) Mechanical activation and low molecular weight organic acid activation are synergistic. Mechanical activation for 60 min at optimum concentrations of oxalic, tartaric, malic, and citric acids increased the P_2O_5 content of phosphate ore powder from 25.72%, 8.94%, 6.40%, and 2.50% to 27.80%, 12.77%, 11.68%, and 5.87%, respectively.

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