



Frontier research and prospect of phosphate adsorption in wastewater by red mud: a review

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ABSTRACT

Red mud is a red-coloured, mud-like solid waste discharged from the industrial aluminium production process, which has a high output and is a pollutant. It exhibits a small particle size and a large specific surface area and contains active oxides. In this study, “red mud” and “phosphate” were used as keywords to retrieve research hotspots and progress for the red mud as a phosphate adsorbent in the past 10 y. CiteSpace and VOSviewer visual literature analysis software were used to cluster countries, institutions, authors, and keywords. Related patents showed that research on the phosphate adsorption performance of red mud has considerably increased since 2013 and that China has made a significant contribution. This paper summarises the main chemical composition and modification methods of red mud and collects from literature the relevant mechanism research and data on phosphate adsorption/desorption using red mud as an adsorbent. Summarising data on the microstructure of red mud adsorbent, it is found that there are few reports on red mud as adsorbent based on density functional theory. This study suggests that the problem of the steric hindrance of the red mud adsorbent in the phosphate adsorption process needs further research.

Keywords: Red mud sorbent; Modifying methods; Mechanism research; Phosphate adsorption; DFT

1. Introduction

In order to explore the dynamic and evolution track of the overall development of red mud adsorption phosphate in the past 10 y, this paper studies the journal literature, mainly from the aspects of literature, country, institution, author, and keyword for information integration and data mining. This paper summarizes the development characteristics of related research and deeply understanding the dynamic and focus issues in the field, which have important reference significance for researchers to perform relevant theoretical research.

Al_2O_3 is a necessary raw material for petroleum refining, automobile exhaust treatment, nitrogen oxide removal, hydrogenation catalyst, reforming reaction, photocatalysis,

and other industries. Its increasing demand has led to an increasing scale of red mud production, with about 70 million tons of red mud being produced worldwide each year. China is the world's fourth largest Al_2O_3 industrial country, which emits up to 30 million tonnes of red mud per year, but its utilization rate is less than 10%. Red mud particles have a diameter of 0.088–0.25 mm, a specific gravity of 2.7–2.9, a bulk density of 0.8–1.0, a melting point of 1,200°C–1,250°C and contain various trace elements. Red mud has internal and external illumination indices that are greater than 2.0. It exhibits a certain radioactivity and is categorised as a dangerous solid waste [1,2]. Red mud has a pH value of 10.29–11.83 and fluoride content of 4.89–8.6 mg/L. The pH value of a red mud solution is greater than 12.5. The comprehensive sewage discharge is divided into excessive

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wastewater. Thus, red mud (containing liquid) belongs to harmful waste residue. The primary red mud pollutants are alkali, fluoride, sodium and aluminium, which are present in considerable amounts. When these pollutants reach the groundwater and subsequently into the food chain and the human body, the pollution ions will gradually accumulate in the human body and cause harm to it. Particularly, the effect of alkali on some parts of the human body is considerably serious. Highly alkaline sewage penetrating into groundwater or surface water, which increases the pH of the water and effects the toxicity of compounds in water. Due to the small amount of radioactive substances and their fine particle size, long-term storage pollutes the atmosphere. Excessive fluoride content in red mud can cause problems such as skeletal fluorosis and dental fluorosis. The harm of aluminium to the human body is mainly reflected in reducing digestive function, affecting liver function, and also having adverse effects on human brain nerves. In addition, when the red mud filter water enters the groundwater body, in addition to bringing in its own pollutants, it also brings a large amount of SO_4^{2-} and Ca^{2+} into the groundwater body through the action of the solution, resulting in secondary pollution. Red mud stacking occupies a large area of land and is easy to pollute the soil.

Red mud has a complex mineral composition. Its chemical composition forms a unique cemented porous overhead structure with a large porosity, a large specific surface, and a low tightness. It has good compression resistance and overall strength. The cementing and crystal connection components in red mud make it have a strong water-stable connection strength [3], which can be used for environmental pollution control. Several scholars have confirmed that red mud has an effective removal performance for various water pollutants. It has been used to prepare porous ceramsite filter material for water treatment, which is used as a wastewater decolourisation and clarification agent and an adsorption material for the adsorption and removal of heavy metal ions (such as Cu^{2+} , Pb^{2+} , Zn^{2+} , Ni^{2+} , Cr^{6+} , and Cd^{2+}) and anionic pollutants (such as F, As(V), and P(V)) in wastewater [4]. The red mud has fine particles and a large specific surface area, which can effectively fix sulfur components (Fe_2O_3 , Al_2O_3 , CaO , MgO , and Na_2O). It has strong adsorption capacity and reactivity for H_2S , SO_2 , NO_x , and other polluting gases, so it can replace lime/lime milk to treat waste gas. Because red mud still has some soluble alkali, its waste gas evolution effect is better. The methods of red mud treatment of waste gas are divided into dry method and wet method. The dry method is to use the activity of minerals on the surface of red mud to directly adsorb waste gas. The wet method is to use the alkali and acid components in red mud to react.

In recent years, a large amount of domestic sewage and agricultural wastewater rich in nitrogen, phosphorus, and other nutrients has entered the water. Industrial phosphorus-containing wastewater has a large discharge capacity, high phosphorus content, complex composition, difficult reuse, and high treatment costs. Phosphorus is the main limiting factor, causing serious eutrophication. The commonly used phosphorus removal methods mainly include the chemical [5,6], biological [7], crystallization [8], ion exchange [9], and adsorption methods. Although a lot of

basic research work has been done on the adsorption of phosphorus in wastewater by red mud as an adsorbent, there are still some limitations. Firstly, the problem between the cost and environmental benefits of red mud treatment and modification technology in the preparation of phosphorus adsorbents. It is not cheap to treat and modify red mud into phosphorus adsorbents, and most of the time it is energy-intensive. The need for toxic reagents has had some negative effects on environmental protection. Secondly, the impact of red mud treatment and modification technology on the environment and public health. In the process of red mud treatment and modification, a large amount of harmful gases and wastewater will be produced. In addition, if not handled properly, it may also lead to the release of harmful substances such as heavy metals, threatening public health. In addition, if not handled properly, this may cause the release of harmful substances such as heavy metals, threatening a public health. Therefore, in the process of promoting red mud treatment and modification technology, its environmental risks should be fully accessed. Furthermore, from a technical and economic point of view, the comprehensive utilization of red mud project, red mud treatment, and modification technology in the practical application of phosphorus removal has no obvious economic benefits. Because of its large investment and high cost, the project investment in comprehensive utilization of less than 1 million tons of red mud is more than 100 million yuan, and the added value of the products produced is generally not high, the market competitiveness is poor, and the economic benefits of the project are poor. Due to the lack of support for national standards or industry standards, it can only refer to other similar product standards with low market recognition and limited product application, which is difficult to promote on a large scale. Most of the technologies are still in the laboratory stage or individual pilot stage. At this time, costs should be reduced and environmental protection achieved better. The life cycle assessment of red mud is as follows:

- In the process of red mud production, blast furnace steel-making is the main environmental impact factor, including CO_2 , SO_2 , NO_x , and other gas emissions, as well as dust, noise, and other pollution.
- In the treatment process of red mud, both wet treatment and dry treatment have certain environmental impacts, but compared with the storage and idle of red mud, the environmental impact in the treatment process is small.
- In the process of comprehensive utilization of red mud, the production of building materials such as cement and bricks has a high resource utilization rate, but the resource utilization rate of agricultural products such as fertilizers and soil conditioners is low.

2. Literature novelty analysis

2.1. Data sources

All the literature data analysed in this paper are obtained from the core collection of the Web of Science. The journal time span is set from 2012-01-01 to 2023-01-01, and the advanced search conditions are as follows: TS = (red mud) and TS = (phosphorus). A total of 167 records were retrieved.

The literature data from 2013 to 2022 was selected for the visual analysis.

2.2. Literature type

Through the analysis of the type of literature, the main form of the results of the research on the adsorption of phosphate by red mud adsorbent is obtained. According to the classification of literature types, the number of journal articles in more than 160 articles was the largest (147), accounting for 85.5% of the total number of documents. Followed by conference proceedings papers (13), accounting for 7.6% of the total number of documents. According to the analysis, red mud adsorbed phosphate accounted for the largest proportion in the water treatment, about 38%. Others are mineral and metal processing, about 20.5%. Other neighborhoods such as soil science (9%), pollution and phytoremediation (8.4%), bioengineering (6%), concrete science (3%), catalysts (2.4%), marine biology (2.4%), and energy and fuel (1.8%).

Fig. 1 presents the results for “red mud” and “phosphorus” obtained by searching the IPRDB patent query network for 2013–2022. China possesses the most patents, with 116 inventions published and eight invention authorisations, followed by the USA (23), Japan (16), WIPO (16), EU (11), and Republic of Korea (8). Among the applicants, Guizhou University has the largest number of applications, with eight applications, followed by Dow Global Technologies LLC and Anhui New COSCO Chemical Technology Co., Ltd. with five published applications. The applicant types are divided into four categories—enterprises (114), others (44), schools (35), and research institutes (4). The applicants are mainly from China (136) and USA (21). The patent mainly improves the phosphorus status in the soil by compounding red mud and solid waste materials and uses red mud as the basic raw material to prepare a modified red mud adsorbent. It elaborates on the adsorption performance of

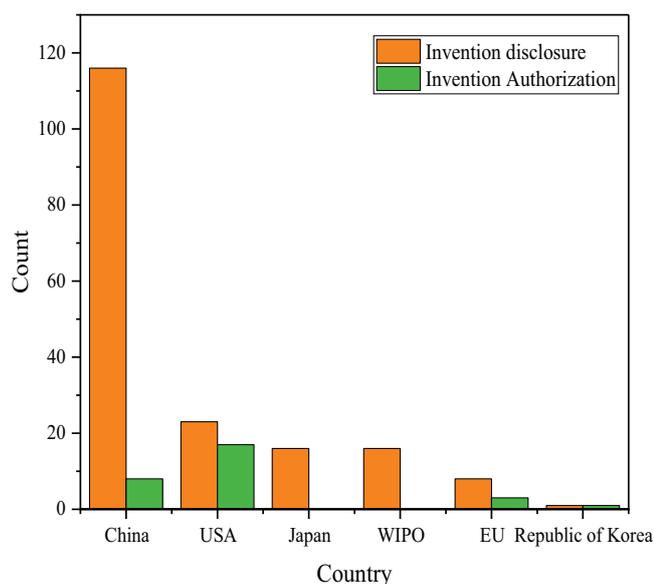


Fig. 1. Patent search.

phosphorus in domestic sewage, the preparation of porous red mud pavement materials for improving the purification of phosphorus-containing pollutants in road rainwater runoff and the addition of ordinary clay to red mud as a filler for improving the adsorption efficiency of phosphorus. The patent invention has high economic, social, and environmental benefits. Chen Xiaohu, an inventor from Guizhou University in China, published the most patents with nine articles. He primarily studies the manufacture of flame retardants and compound fertilisers from phosphogypsum and red mud to improve the utilisation rate of phosphogypsum and red mud waste residue for achieving the effect of “treating waste with waste”.

2.3. Active countries, institutions, and authors

Understanding the number of relevant articles published in different countries is conducive to the research and analysis of countries that have considerably contributed to the red mud phosphate adsorption. A visual co-occurrence analysis was performed in 16 of these countries (Fig. 2a). Each node represents a country, and the connection between two nodes represents a connection between the two countries and node size represents the number of documents issued by the country. From the perspective of the paper output, the People’s Republic of China (77 (38%)), Australia (19 (8%)), and the USA (10 (5%)) published the most number of articles in the research field of phosphate adsorption on red mud. Among them, the People’s Republic of China cooperates with Taiwan, Japan, and Egypt. The thickness of the connections between the nodes in Fig. 2 shows the cooperative relationship between the countries, reflecting that China’s research on this aspect has been greatly developed and deepened in the past decade and has played an important role.

Fig. 2b shows that the publication of various institutions enabled the obtainment of important research institutions and potential collaborators and allowed the effective use of the literature resources of various institutions. It also provided an opportunity for well-known scholars between institutions to communicate and study with each other. A total of 302 institutions participated in the study of sphalerite flotation, and Fig. 2 presents the research institutions with more than three publications. Each node represents the number of articles published by each institution. The connection between the nodes indicates the cooperative relationship among these institutions. The Chinese Academy of Sciences closely cooperates with other institutions. Since the publication in 2013, the number of articles published in 2016 has increased to three, accounting for 3.31% of the total number. Guizhou University began publishing papers in 2019 and will have published seven papers by 2022, but it does not have close cooperation with other institutions. They mainly perform independent research using their internal resources. The Centre National de la Recherche Scientifique has published five papers from 2014 to 2022, accounting for 2.32% of the total number of publications. Meanwhile, Qingdao University of Technology has published five papers from 2020 to 2022, indicating that its research on phosphate adsorption by red mud adsorbent has increased and rapidly developed and has strong independence.

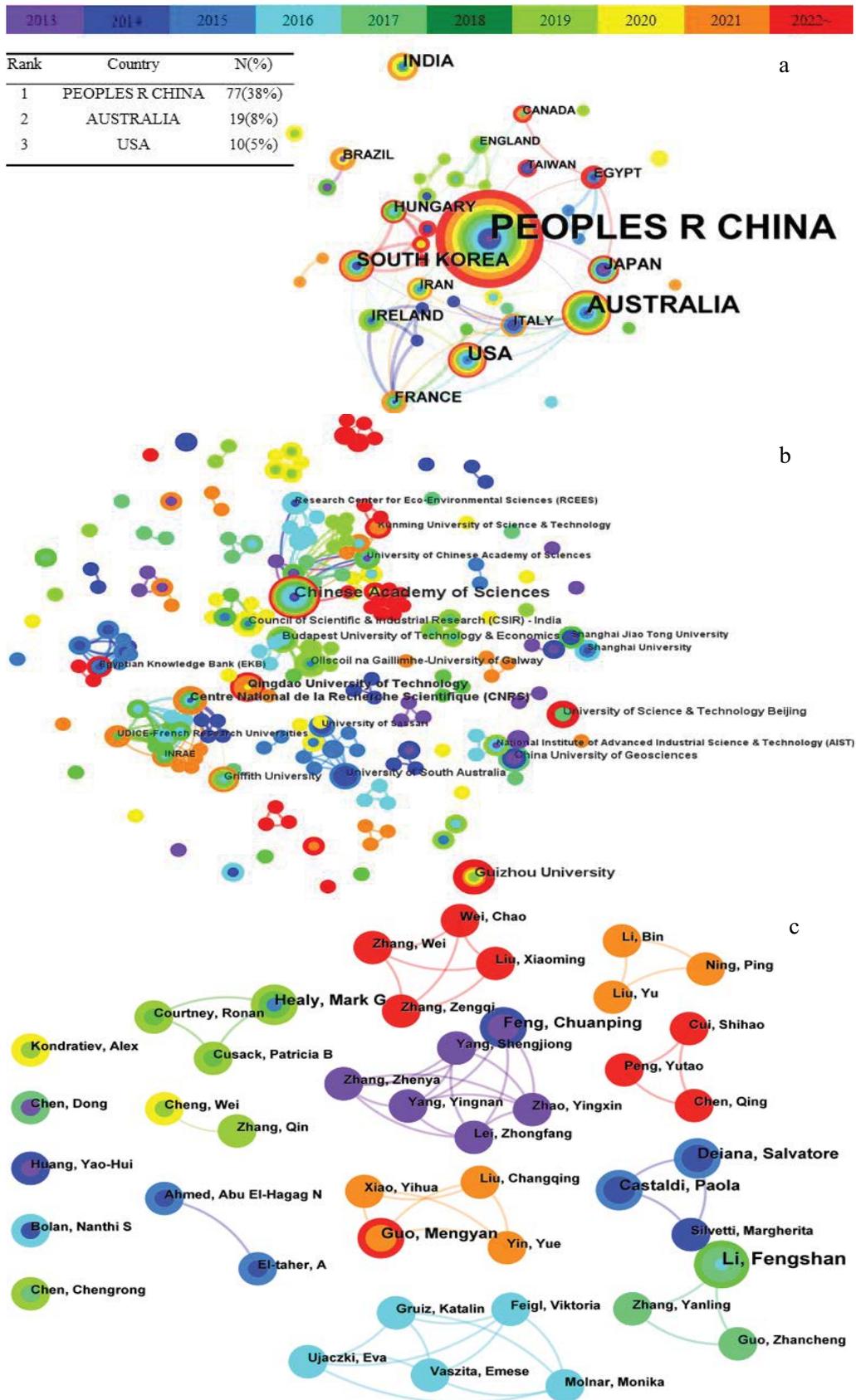


Fig. 2. Co-occurrence analysis of visual knowledge graph (a) the country, (b) the institution and (c) the author.

The node size shown in Fig. 2c represents the number of papers published by the author, and the connection between the nodes represents the cooperative relationship between the authors. Research on phosphate adsorption on red mud is primarily divided into four teams, represented by Wei Zhang, Chuanping Feng, Mengyan Guo and Gruiz, Katalin, and other individual studies. Zhang studied the adsorption method combined with photocatalytic reduction and bio-modified red mud to remove phosphorus from domestic sewage. Feng investigated phosphorus removal from water using ceramic biomaterials synthesised in scallop shells. Guo investigated the adsorption of organic and inorganic phosphorus in aqueous solution using a polypyrrole-modified red mud adsorbent. Meanwhile, Gruiz studied the effect of red mud as a chemical stabiliser on soil pollution. Li studied the dephosphorization of red mud-based flux in steelmaking process. Deiana used various water treatment residues to adsorb phosphate anions from an aqueous solution. Healy treated red mud with gypsum and seawater to study the phosphorus adsorption in aqueous solution.

2.4. Research keywords

To better refine research hotspots, VOSviewer software was used to classify keywords related to phosphate adsorption by red mud adsorbents into five categories, as shown in Fig. 3. Nodes with the same colour in the graph represent the same cluster. Cluster 1 illustrates the mechanism and performance of the adsorption of wastewater by adding fly ash, concrete, and steel slag to red mud raw materials. Cluster 2 shows that the main study of red mud adsorption to remove phosphate. The keywords focus on “adsorption”, “wastewater”, “adsorption removal”, “phosphorus removal”, and “phosphate adsorption”. Cluster 3 shows that red mud can bind slag and biochar to adsorb aqueous solution. The keywords are “adsorbent”, “slag”, “biochar”, and “removal”. Cluster 4 shows that red mud can be used as an adsorbent to recover heavy metals in aqueous solution. The keywords focuses on “phosphorus”, “aluminium”, “bauxite residue”, “water”, “arsenic”, “metals”, “vanadium”, and “recovery”.

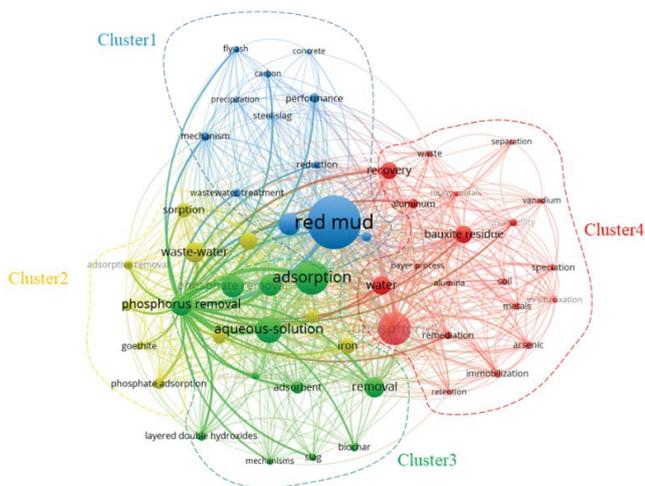


Fig. 3. Studies the co-occurrence analysis of hot words.

Fig. 4 depicts a map of the emergent words generated by the sample literature, drawing 13 emergent words from 2013 to 2022. From the prominent words, it can be seen that the duration of its hot spots shows a trend from long to short. “Year” represents the year in which the keyword appears for the first time, “Begin” and “End” represent the starting and ending years of the keyword as the frontier, respectively, and “Strength” represents the burst strength. The highest burst strength is recovery, yielding a strength value of 3.38, and the initial burst strength was in 2013. The utilization rate of solid waste such as red mud, phosphogypsum and fly ash is still low. It is necessary to promote solid waste source reduction, resource recycling and harmless disposal, and promote the comprehensive utilization of resources to achieve new development. From 2016 to 2022, the average duration of coal fly ash, recovery, phosphate adsorption, vanadium, acid, and alumina is 2 y. From 2018 to 2022, performance, bauxite residue, iron and phosphate highlight the development context and trend of the research field of phosphate adsorption by red mud in the future.

3. Adsorption mechanisms

3.1. Raw material

The chemical composition of the red mud raw material mainly includes SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , Na_2O , TiO_2 , and other substances (Table 1). Red mud is a grey and dark red powder that changes colour depending on the amount of Fe_2O_3 contained in it. The main mineral composition of red mud is calcite, cancrinite, andradite, hematite, and katoite, in which clay minerals mainly refer to montmorillonite, illite, kaolinite, and so on. The layered structure of these clay minerals contains abundant adsorption sites and has a strong adsorption capacity for phosphate. It also includes clay minerals containing iron oxides, which are mainly composed of Fe_2O_3 and $\text{Fe}(\text{OH})_3$. These components form considerable Fe_2O_3 and $\text{Fe}(\text{OH})_3$ crystals on the red mud surface, which have a strong adsorption capacity and can effectively adsorb phosphate. Considerable iron oxide hydrates can be found on the iron oxide surface, which can

Keywords	Year	Strength	Begin	End	2013 - 2022
fly ash	2013	2.82	2013	2015	
waste water	2013	2.79	2013	2014	
sorption	2013	1.85	2013	2015	
coal fly ash	2015	1.24	2015	2017	
recovery	2016	3.38	2016	2020	
phosphate adsorption	2013	1.99	2016	2018	
vanadium	2017	1.82	2017	2019	
performance	2018	1.57	2018	2022	
bauxite residue	2014	1.37	2018	2022	
iron	2013	1.29	2018	2022	
acid	2019	1.6	2019	2020	
alumina	2016	1.43	2019	2020	
phosphate	2017	2.82	2020	2022	

Fig. 4. Top 13 most prominent words.

Table 1
Chemical composition of red mud from different sources (wt.%)

Source of materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	References
China	25.66	18.12	13.50	26.63	4.31	9.55	–	2.22	[10]
China	24.86	15.80	15.44	28.32	2.34	8.70	0.25	4.04	[11]
China	18.63	13.72	14.42	31.12	2.80	13.35	0.22	4.83	[12]
Guinea	5.5	26.6	48.4	1.2	0.9	–	–	2.8	[13]
China	18.25	21.58	12.31	22.12	0.56	8.61	–	3.71	[14]
China	21.3	37.6	29.2	6.3	–	4.2	–	–	[15]
China	19.14	6.93	12.76	46.02	1.15	2.37	1.20	3.43	[16]
Australia	5	15	60	–	–	16	–	5	[17]
China	18.08	8.26	15.30	38.02	1.63	3.55	0.36	4.51	[18]
Hungary	20.00	14.30	37.00	7.70	0.53	4.80	–	3.80	[19]
India	6.58	15.47	58.78	1.49	–	3.63	–	4.39	[20]
India	4.24	16.44	54.6	1.99	–	2.76	–	6.82	[21]
Iraqi commercial markets	8.52	18.94	26.41	21.84	–	4.75	0.068	7.40	[22]
Turkey	13.8	20.9	32.1	12.2	2.7	6.7	–	3.6	[23]
China	19.1	6.93	14.93	36.82	1.15	2.37	1.20	1.08	[24]
China	8.88	22.38	47.39	0.86	–	12.76	0.05	7.33	[25]

form hydrogen or chemical bonds with phosphate ions in phosphate to achieve adsorption. The iron hydroxide surface has a certain positive charge, which can form an electrostatic interaction with the negative charge of a phosphate ion; thereby achieving adsorption. Appropriate amounts of Al³⁺ can considerably improve the phosphate removal rate of the red mud adsorbent, but excessive amounts of Al³⁺ reduce the adsorption performance of the red mud adsorbent. The organic matter in the red mud adsorbent can change its surface properties and form a complex with phosphate to further improve its adsorption performance.

The structural characteristics of the red mud adsorbent primarily include pore structure, chemical properties, and surface electrical properties. The silicon and Al₂O₃ in red mud are sintered at high temperatures to form a tightly arranged crystal structure that forms multiple micropores and mesopores, thereby providing a large surface area for adsorption. The pore structure of the modified red mud adsorbent is more developed, further improving the adsorption performance. The active components, such as silicate and Fe₂O₃ in red mud can be coordinated and adsorbed with phosphate. An acid–base neutralisation reaction occurs during the contact process between phosphate solution and red mud, reducing the H⁺ concentration in the phosphate solution, thereby promoting phosphate adsorption. The main principle of phosphate adsorption on red mud is the surface electrical effect. The surface of red mud particles is negatively charged, while the phosphate ions are positively charged. Due to the attraction of heterogeneous charges, the red mud particles can effectively adsorb phosphate ions. Furthermore, the adsorption performance of the red mud adsorbent is affected by several factors, such as adsorbent content, adsorption reaction time, adsorption reaction temperature, initial phosphorus concentration, pH value, and coexisting ions (Cl[−], SO₄^{2−}, and NO₃[−]).

Red mud can be divided into Bayer [26], sintering [27], and Bayer-sintering [28] red muds according to different

treatment methods. Fig. 5 illustrates the treatment process. The Bayer red mud directly uses the circulating mother liquor containing a large amount of caustic alkali to treat bauxite. Alumina in the bauxite is dissolved to obtain the sodium aluminate solution, and then the aluminium hydroxide (Al(OH)₃) seed crystal is added to the sodium aluminate solution. After long-term stirring and decomposition, the Al(OH)₃ crystal is precipitated, and then it is roasted to obtain alumina. The Bayer red mud has higher Al₂O₃ and Fe₂O₃ contents, followed by CaTiO₃, CaCO₃, and Na₅AlO₄. Its production process is simple, with low energy consumption, low cost, good product quality, and high purity. To form a furnace burden, limestone and soda ash were added to bauxite using the sintering method. The furnace burden was sintered at high temperature to obtain a clinker containing solid sodium aluminate (sodium aluminate, sodium ferrite, calcium orthosilicate, and calcium titanate). Subsequently, the clinker was dissolved in water or a dilute alkali solution to obtain a sodium aluminate solution. After the purification of the sodium aluminate solution, carbon dioxide was introduced to decompose and crystallise Al(OH)₃, which was then calcined to alumina. Meanwhile, the sintering red mud contains higher CaO and SiO₂ contents, followed by Ca₂SiO₄, CaCO₃, CaTiO₃, and Fe₃O₄. However, it has a complex process, large investment, high energy consumption, and slightly poor product quality. The Bayer–sintering combined method utilises the sintering method to partially treat the Bayer red mud. The main advantages of this method are the high total recovery rate of alumina, low alkali consumption, and small production of the sintering method. However, during the sintering part, the alumina content in the red mud furnace charge is low and the clinker conversion ratio is high, and thus the sintering is difficult.

Scholars have performed extensive research on phosphorus adsorption by red mud, mainly studying the effects of phosphorus concentration, pH, temperature, and coexisting ion concentration on the adsorption effect. Most of

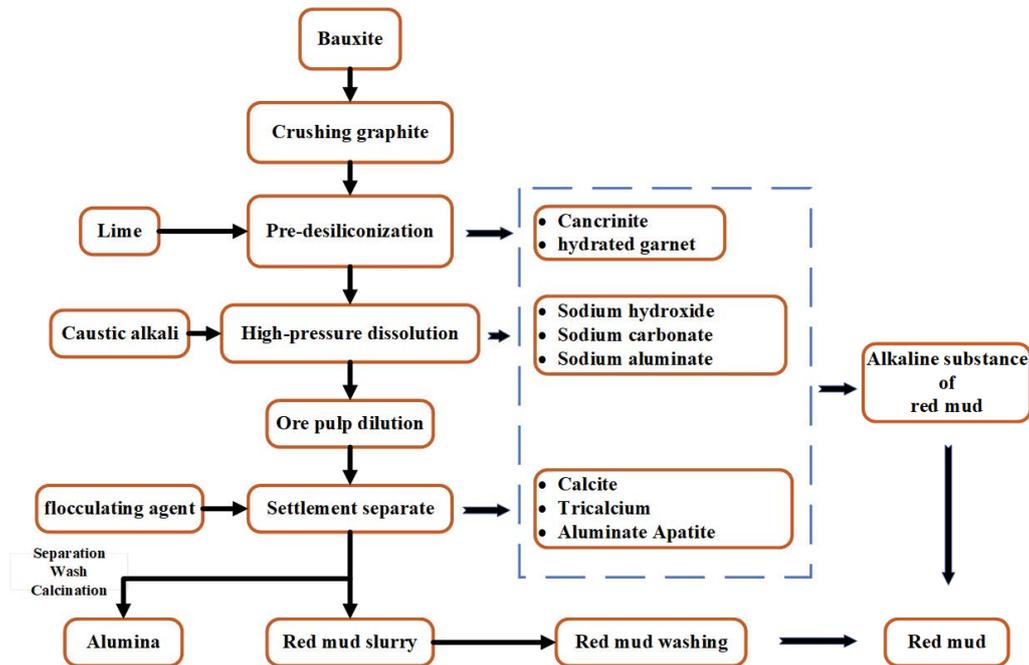


Fig. 5. Red mud treatment process diagram.

the phosphorus-containing wastewater used is simulated wastewater, that is, simulated phosphorus-containing wastewater after dissolving KH_2PO_4 or soluble phosphorus in deionized water. The research theory has certain limitations for industrial wastewater treatment. The Ca^{2+} and SO_4^{2-} concentrations in industrial phosphorus-containing wastewater are relatively high. Furthermore, the concentrations of F and As compounds, chemical oxygen demand, and pH value exceed the standard limit. The concentrations of H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} increase with an increase in pH value in a certain range.

Several methods are available for the determination of phosphate content in water, among which the most commonly used methods are molybdenum–antimony anti-spectrophotometric method, ion chromatography, stannous chloride reduction molybdenum blue method, malachite green spectrophotometric method, and electroanalytical method [30] (Table 2). Molybdenum–antimony anti-spectrophotometry is a traditional method commonly used in the laboratory, but it has the disadvantages of a short stability time, low sensitivity and high detection limit, and cannot detect the presence of trace phosphorus. Ion chromatography has the advantages of high resolution, high sensitivity, and simple operation. It can determine the inorganic and organic phosphates in water and provide an effective means for determining the phosphate content of some complex water bodies. Moreover, it has been widely used to determine the phosphate content in water. The stannous chloride reduction molybdenum blue method has a higher sensitivity in determining the phosphate content in water and can detect lower phosphate concentrations. The traditional molybdenum blue method must be performed under strong acidic conditions. In contrast, the stannous chloride reduction molybdenum blue method has a

narrower acidity range and is safer and more convenient to operate. The method of reducing molybdenum blue using stannous chloride has a stronger anti-interference ability than Fe^{3+} and can effectively eliminate the interference of iron ions. Additionally, the colour development is more stable and can be measured in a wide temperature range, improving the determination accuracy. Meanwhile, malachite green spectrophotometry has high accuracy and sensitivity. The stability time of the ion complex is longer than that in molybdenum–antimony spectrophotometry, making it more conducive to observation and recording. However, malachite green spectrophotometry can be performed on water samples only under specific conditions. Only in the presence of polyvinyl alcohol can the chromogenic agent molybdenum–antimony anti-malachite green be combined with phosphate to form a green complex.

3.2. Red mud modification method

Various red mud modification methods exist, and the ultimate aims of these methods are to optimise and improve its adsorption characteristics. Acid activation, oxidation, thermal activation, metal ion activation, and other techniques are primarily used to improve the adsorption capacity of red mud. Mechanical activation [11] is the simplest modification method. In this method, red mud is broken, ground, sieved, and dried without mineral transformation to increase its specific surface area, improve the uniformity of its particles and remove residual water and impurities. Oxidation, pyrolysis, and reduction reactions were performed via heat treatment approaches such as heating, high-temperature and microwave calcinations, and the hydrothermal method [34–36]. High-temperature pore formation and mass transfer resistance reduction enable $\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$

Table 2
Method for determination of phosphate

Method	Reagent	Principle
Molybdenum antimony spectrophotometry [29]	Sulfuric acid, anti-blood acid solution, silverate solution, turbidity-color compensation liquid, phosphate reserve solution, phosphate standard solution	Under acidic conditions, orthophosphate reacts with ammonium molybdate and potassium antimonate tartrate to form phosphomolybdate heteropoly acid, which is reduced by reducing agent ascorbic acid and becomes a blue complex, commonly known as phosphomolybdate blue. An appropriate amount of water sample filtered or digested by the filter membrane (the phosphorus content does not exceed 30 µg) were added to a 50 mL colorimetric tube and diluted with water to the standard line. The following color development and measurement are performed according to the steps of drawing the calibration curve. Then subtract absorbance of the blank test and check the phosphorus content from the calibration curve.
Malachite green spectrophotometric method [31]	Ammonium molybdate solution, malachite green solution, polyvinyl alcohol solution, phosphate reserve solution, phosphate standard solution, 5% potassium persulfate solution, concentrated sulfuric acid solution	Under neutral conditions, the sample was digested with potassium persulfate, and all the total phosphorus was oxidized to orthophosphate. In acidic medium, orthophosphate reacted with ammonium molybdate. After a series of reactions, the substance reacted with the chromogenic agent. The absorbance was measured by spectrophotometer, and the total phosphorus content was calculated from the standard curve.
Ion chromatography [32]	Potassium hydroxide, potassium dihydrogen phosphate, methanol, phosphate reserve solution, phosphate standard solution for use	Various forms of orthophosphate in in the test sample entered the anion chromatographic column with the strong alkaline eluent. After being separated in the form of phosphate (PO_4^{3-}), it was detected by conductivity detector. According to the retention time, the total phosphorus content was calculated according to the same chromatographic conditions as the calibration curve.
Stannous chloride reduction molybdenum blue method [33]	Sulfuric acid solution, stannous chloride glycerin solution, ammonium molybdate-sulfuric acid mixed reagent, ammonium molybdate solution, phosphate reserve solution, phosphate standard solution for use	Under strong acidic conditions, the active phosphate in the water sample reacts with ammonium molybdate to form a pale-yellow phosphorus molybdenum yellow. Phosphomolybdate yellow is reduced to blue phosphomolybdate blue by stannous chloride. The blue shade is proportional to the content of active phosphate, and has the maximum absorption value at the wavelength of 690 nm. The content of active phosphate in water samples can be measured by colorimetry.

and $\text{CaCO}_3 \rightarrow \text{CaO}$. Table 3 shows that the adsorption capacity of phosphate in wastewater changes after different red mud modifications. The primary modification method is acid modification. After the complexation reaction is obtained by adding organic or inorganic acid, the Ca^{2+} concentration increases. Furthermore, the specific surface area of red mud increased after acid activation [37], consequently changing the point of zero charge. Loading metal ions such as aluminium, lanthanide, cerium, and cobalt activate red mud [38] and increases the adsorption sites and surface-active functional groups of red mud to improve its adsorption capacity. As a catalyst [39,40], red mud can achieve the effects of carbon attachment and phase transformation simultaneously. Adding H_2O_2 , $\text{Na}_2\text{S}_2\text{O}_8$, and other modified red mud [41] enables a redox reaction that converts Fe^{2+} into Fe^{3+} to change the phase valence and increase affinity with pollutants. Moreover, the red mud can be modified by adding concentrated hydrochloric acid + silane and concentrated hydrochloric acid + FeCl_3 + CTAB [18,42], which can increase the affinity with pollutants and improve the

adsorption capacity of a single layer. In addition to the abovementioned modification methods, adding activators and foaming agents is an effective modification method.

3.3. Mechanism research method

Scholars have studied the phosphorus adsorption mechanism of the red mud adsorbent. At the macro level, the adsorption performance of the adsorbent is evaluated and its adsorption mechanism is discussed by combining the adsorption kinetics, adsorption isotherm and, adsorption thermodynamics. At the micro-level, the phosphorus adsorption mechanism of the red mud adsorbent is discussed using various modern instrument analysis techniques. However, the adsorption process of the red mud adsorbent on phosphorus-containing wastewater is a complex system that includes physical and chemical adsorption and synergistic effects (Fig. 6).

Physical adsorption refers to the adsorption of heavy metal ions by the red mud adsorbent through the pore

Table 3
Adsorption capacity of phosphate in wastewater by modified red mud

Raw material	Modifying methods	pH	BET (m ² ·g ⁻¹)	Adsorption quantity (mg·g ⁻¹)	References
Red mud	1,000°C	3–6	–	6.64	[12]
Red mud	HCl	7	19.35	24.67	[13]
Red mud	ZrOCl ₂	8	–	13.64	[19]
Red mud	HCl	2	28.63	205.13	[20]
Red mud	900°C	3.5–11.5	–	149.29	[23]
Bauxite	HCl	8.2–8.6	80.63	55.72	[24]
Carbide slag, red mud	–	7	42.46	16.06	[43]
Red mud, boron mud	NaOH	6–9	–	96.81%	[44]
Red mud	HCl	6–8.5	–	33.56	[45]
Red mud	HCl	7.7	232.634	7.63	[46]
Red mud	HCl	2	28.63	112	[47]
Red mud	HCl	4.5	80.63	492.46	[48]
Red mud	HCl	5.5	28.48	0.58	[17]
Red mud	–	3–7	18.3	17.0	[49]
Red mud	Ca(NO ₃) ₂ NaCl	5.5	–	8.153	[50]
Clay, kaolin, red mud, zeolite and volcanic corrosive soil	NaOH HCl	7	1.049–0.693	420	[51]
Red mud	Polypropylene	6.5–7.5	–	14.47	[52]
Red mud, phosphogypsum	Ca(NO ₃) ₂ NaCl	5.5 ± 0.2	–	94%	[53]
Red mud, fly ash	Na ₂ SiO ₃ ·9H ₂ O RnOCH ₂ COONa	5.64–11.24	25.1871	26.77	[54]
Red mud	Polypyrrole	2–5	102.24	28.57	[55]
Straw, red mud	–	3.0	90.52	11.78	[56]
Red mud	HCl	2.5–3	–	12.9	[57]
Red mud	700°C	2–10	37.1	93.1%	[58]
Red mud	HCl	4.0	–	192.62	[59]
Red mud	HCl	–	113.54	86.69	[60]
Red mud	ZrOCl ₂	3–7	96.97	33.14	[61]
Lime slurry	HCl	7	–	160.7	[62]
Red mud	MgO	3.4	65.72	128.05	[63]

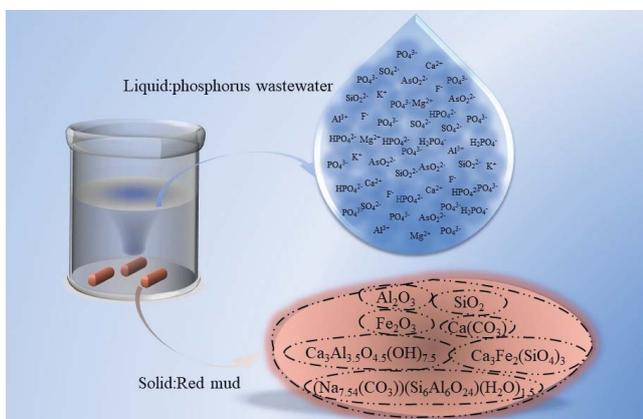
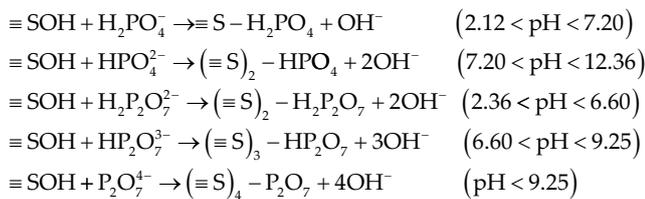


Fig. 6. Simulation process of red mud adsorbing phosphorus-containing wastewater.

structure and specific surface area, which also becomes a van der Waals adsorption. Because the van der Waals force exists between any two molecules, physical adsorption can occur on any solid surface (multi-layer adsorption) and desorption can easily occur due to the small binding force. The larger the pore structure and specific surface area of the red mud adsorbent, the stronger its ability to adsorb heavy metal ions. By changing the pore structure and surface properties of red mud, its physical adsorption capacity can be improved. Chemical adsorption refers to the formation of chemical bonds between adsorbate molecules and atoms or molecules in adsorbents through electron transfer, exchange, and sharing. Common chemical adsorption mechanisms include ion exchange, coordination bonds, and covalent bonds. By modifying red mud, new active components can be introduced that will enhance its chemical adsorption capacity. Chemical adsorption usually occurs on the surface of metal oxides such as alumina and iron oxide. Physical adsorption

and chemical adsorption often occur at the same time in the adsorption process of red mud. These two promote each other and work together to achieve an efficient adsorption effect. The adsorption process of red mud on phosphorus is dominated by physical adsorption and accompanied by chemical adsorption, mainly including ion exchange, precipitation, and surface deposition. Red mud contains a large amount of Fe^{3+} and Al^{3+} , which have a high positive charge that can effectively reduce or eliminate the zeta potential of the suspended particles in water, reduce the electric double layer thickness, and decrease the repulsion between phosphorus particles, such that the physical stability of the particles decreases and they aggregate into flocs, forming a loose fibrous structure, thereby resulting in flocculation precipitation. The chemical action occurring in the adsorption process is primarily the complex exchange mechanism between the phosphate anion and the calcium-containing hydroxyl oxide on the red mud surface. The surface hydroxylation process is the hydration of the phosphate solution and Al_2O_3 and Fe_2O_3 on the red mud surface. The hydroxide complex loses water molecules and directly interacts with the red mud surface to form a metal hydroxide adsorption configuration, which hydroxylates the adsorbent surface.

The main forms of phosphate ions in the solution under low pH conditions are H_2PO_4^- and HPO_4^{2-} . The chemical reaction at different pH values is as follows:



where $\equiv \text{S}$ represents the adsorption site on the red mud surface.

Scholars have performed extensive research work and made multiple control measures to improve the red mud adsorption capacity for phosphate. These approaches include shape and component control, acid and thermal activation, specific surface, and pore control and wettability and zeta potential control. These research works laid a good foundation for the application of red mud adsorption of phosphate ions in phosphorus-containing wastewater. The adsorption of phosphate ions in water by red mud primarily depends on the surface physical or chemical adsorptions of $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$, SiO_2 , CaO , calcite, nepheline, microcline, diaspore, and phosphate ions in red mud [64].

Shape control refers to the shape of the adsorbent formed in the production process, which can be divided into categories such as powder, columnar, granular, and flake. The adsorption effect is better for adsorbents with powder shape. The adsorbents with columnar, granular, and flake shapes have good regeneration, mechanical properties, and water pulverisation rate; furthermore, the acid and alkali resistance is high. However, after powder adsorption, the product can easily form colloids with water, which cannot be easily dehydrated and regenerated. The adsorbents with columnar, granular, and flake shapes can easily form plugging holes on the surface to reduce the adsorption rate.

Component control refers to the addition of other substances to red mud, which increases its useful adsorption components. Commonly used component control additives include calcined gypsum, volcanic ash, diatom mud, blast furnace slag, plant ash, fly ash, vanadium–titanium magnetite tailings, and phosphorus slag having a porous structure, a large specific surface area, and a strong adsorption capacity. However, excessive fly ash addition will cause the adsorbent strength to decrease. Xiao et al. [43] prepared a carbide slag red mud composite (CR-LDH) to adsorb phosphate. The adsorption test results revealed that the optimum adsorbent dosage and phosphate pH were $5 \text{ g}\cdot\text{L}^{-1}$ and 7, respectively. The maximum adsorption capacity obtained using the Langmuir isotherm model at 25°C was $16.06 \text{ mg}\cdot\text{g}^{-1}$. Microscopic analysis and adsorption mechanism studies revealed that phosphate binds to CR-LDH through synergistic effects, such as physical adsorption, ion exchange, anion intercalation, and chemical precipitation. For phosphate adsorption, Hu et al. [44] used a layered double-hydroxide adsorbent prepared using boron and red mud under alkaline conditions, and a phosphate removal rate of 93% was achieved. The results show that phosphate is transferred from the aqueous solution to the site on the adsorbent, and the ion exchange between the interlayer CO_3^{2-} and the phosphate species is adsorbed by the electrostatic attraction of the active site. The adsorption mechanism is shown in Fig. 7. The Freundlich isotherm fitting of phosphate adsorption is better than the Langmuir isotherm, indicating that adsorption is primarily a multi-layer adsorption. Wang et al. [45] studied phosphorus adsorption using three industrial solid wastes, namely, fly ash, red mud and jarosite water treatment residue, and their modified materials. The experiment results revealed that the pH value strongly affects the phosphorus species and the surface charge of the adsorbent. The dissolved organic matter (DOM) in water may promote the phosphate adsorption, which is attributed to the combined effects of humic-related Al and Fe complexes with a higher adsorption capacity, pH buffering function of DOM and competitive adsorption.

Currently, the acid activation method of the red mud particle adsorbent is the dominant activation method. Acid activation refers to the activation of red mud by soaking it in acid before the adsorbent production. The most commonly used acids are hydrochloric, sulfuric, nitric, and citric acids. The corrosion resistance of equipment materials is high due to the strong oxidation and corrosion resistance of sulfuric and nitric acids. Hydrochloric and citric acids are usually used for acid activation. Fig. 8 displays the adsorption mechanism of the acid-modified red mud. The acid activation of red mud at an appropriate concentration can enhance the positive charge on the metal oxide surface in red mud, which is conducive to the phosphate adsorption on the surface of active red mud (ARM). Under acidic conditions, calcium and other acid-soluble salts are partially dissolved. Furthermore, large external pores and new pores will appear during acidification. Ye et al. [48,65] used hydroxypropyl methyl cellulose and powdered straw as the main components of the granular acid-activated neutralisation red mud production for phosphorus removal. Based on the results of the ion exchange, precipitation, and surface deposition mechanism studies, $>60\%$ of

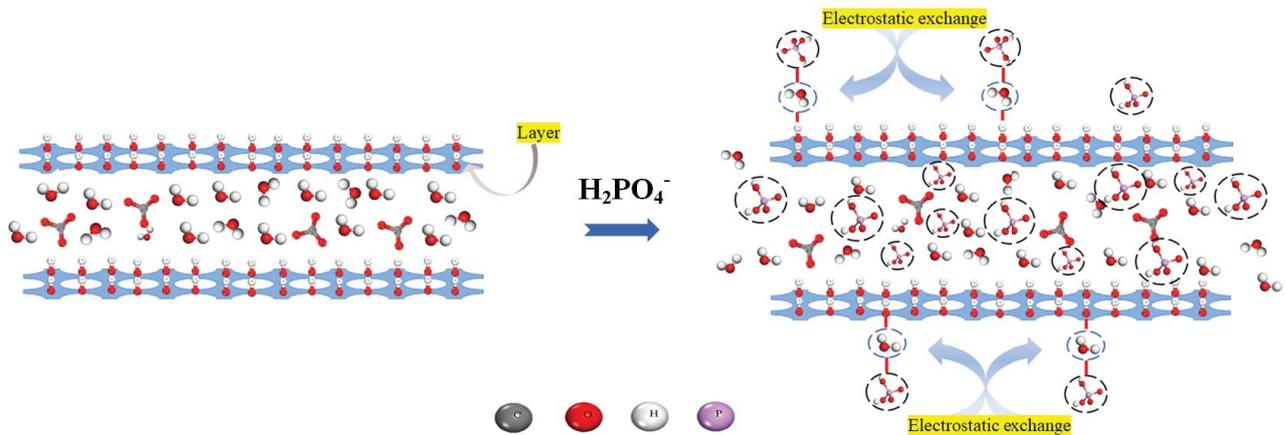


Fig. 7. Adsorption mechanism of layered hydroxide modified red mud.

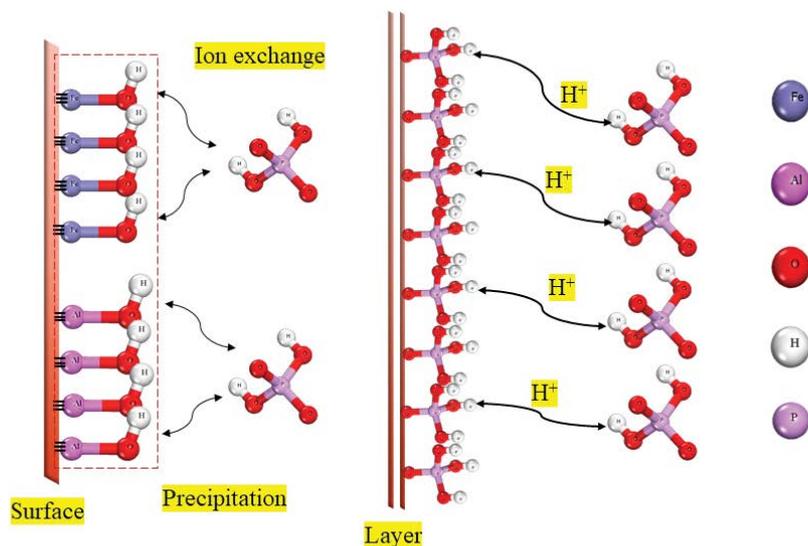


Fig. 8. Adsorption process of acid modified red mud.

phosphate is adsorbed by precipitation and ion exchange mechanisms with strong chemical bonds, while <40% of phosphate is adsorbed by surface deposition mechanisms with weak chemical bonds. Tengfei et al. [46] obtained ARM via acid treatment, and its surface area increased from 10–28 to 220–350 $\text{m}^2\cdot\text{g}^{-1}$. The phosphate adsorptions by the Langmuir and Freundlich constants among the sintered red mud (GZ3), hydrochloric acid-activated high-iron Bayer red mud (AGX), high-iron rock Bayer red mud (GX), and hydrochloric acid-activated sintered red mud (AGZ3) were compared. Tangde et al. [47] used hydrochloric acid to activate red mud and used the Langmuir adsorption isotherm to obtain the maximum adsorption capacity of phosphate (112 $\text{mg}\cdot\text{g}^{-1}$). The adsorption data analysis revealed that the Langmuir isotherm provided a better fit than the Freundlich isotherm. Huang et al. [17] treated raw red mud using acid and acid heat treatments and found that all ARM samples exhibited a higher surface area and total pore volume as well as a higher phosphate removal adsorption capacity. Low pH value solution can enhance phosphate

adsorption and high temperature increases the adsorption capacity.

Refers to an adsorbent synergistic method in which the adsorbent loses bound, crystal, and structural water by high temperature, microwave, or sintering heating and removes organic impurities, thereby increasing the specific surface area, dredging the adsorbent pores and exposing the active sites. The adsorption mechanism of thermally activated red mud is shown in Fig. 9. After thermal activation, the mechanical properties are good, the specific surface area is large, the regeneration performance is strong, the pore distribution is uniform, the phosphorus removal effect of the adsorbent is improved and the strength and pulverisation resistance of the adsorbent are increased. However, the energy consumption in the sintering process is considerably high, easily causing air pollution. Thus, finding an alternative method for activating the adsorbent using the non-thermal activation method is urgent. Tie et al. [67] improved the adsorption capacity of the alum sludge using heat treatment and affected its adsorption performance by changing the

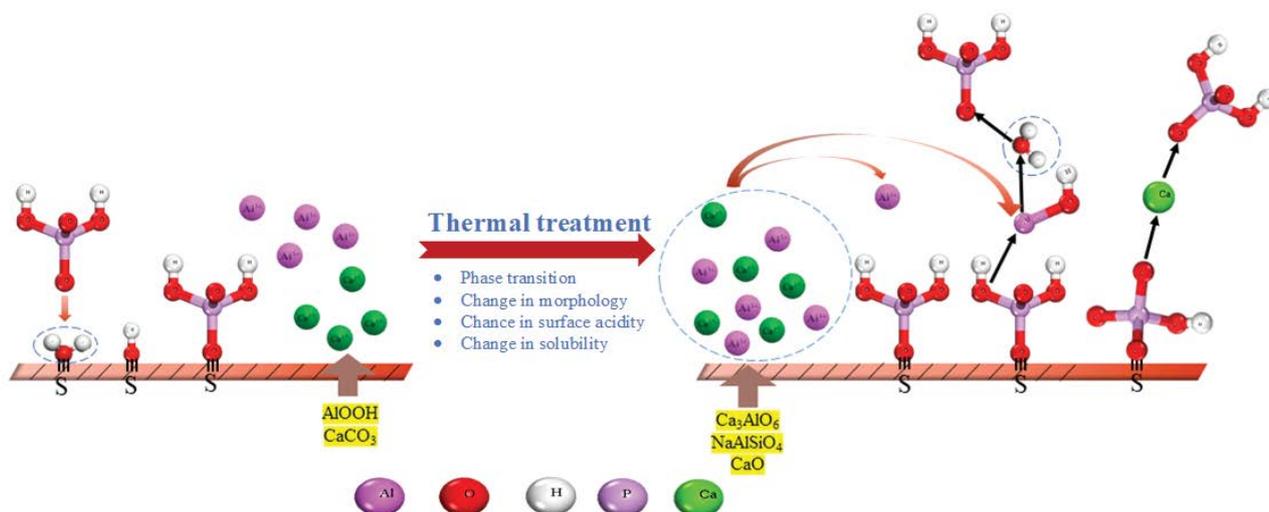


Fig. 9. Adsorption mechanism of thermally activated red mud.

physical and chemical properties of the alum sludge adsorbent. The phosphorus adsorption by the alum sludge adsorbent conforms to the Freundlich isotherm. A higher solution temperature and a lower pH are favourable for phosphorus adsorption. Deng et al. [68] studied the relationship between the phosphate adsorption by the ceramsite prepared from unburned and activated red mud and the dosage, pH value, and reaction time. The phosphate adsorption on red mud during the roasting process conforms to the Langmuir isotherm. The phosphorus removal mechanism in red mud and ARM is the surface complexation mechanism of the metal oxides; it also includes co-precipitation. Lu et al. [58] used carbon-rich, alcohol-based distiller's grains to reduce and roast red mud to prepare the magnetic adsorption materials. The phosphorus removal mechanism includes chemical precipitation, coordination exchange, physical adsorption, and electrostatic attraction, improving the adsorption performance of RM for low-concentration phosphorus in water and promoting adsorbent separation and recovery. Table 4 shows the adsorption isotherm results of activated red mud on phosphate.

The specific surface and pore regulation methods primarily include the sintering and foaming methods. The sintering control method thermally activates the adsorbent before and after granulation for improving the phosphorus removal capacity, while the foaming method mainly adds the foaming agent to the foam during the adsorbent granulation for increasing its specific surface area and active adsorption site. Non-sintered foaming is divided into cold and hot foaming. Cold foaming uses hydrogen peroxide as the foaming agent, manganese dioxide as the catalyst, and silicone amide foam stabiliser for foaming. Thermal foaming is a foaming method that heats the material to ~40°C and adds aluminium and foaming powder.

Wettability adjustment refers to the addition of a wetting agent and a surfactant to the adsorbent. A good correlation exists between wettability and adsorption capacity. The better the wettability of the adsorbent surface, the better the adsorption effect. In the adsorption process, on the surface with a small wetting angle, water is more likely to

immerse into the adsorbent pores and carry considerable target adsorbates into them, thereby reducing the liquid film tension, enhancing the interaction with the adsorbate and producing a better adsorption effect. The wettability regulation method involves the addition of wetting agents (such as GSK-588, Tween, and Span) or anionic surfactants (such as SDBS and sodium dodecyl sulphate) for reduce the surface wetting angle of the adsorbent and regulate the surface wetting activity. Research on the wettability regulation of the red mud adsorbent is in the initial stage.

Zeta potential is an important index for measuring the adsorption system's stability and determining its electrochemical properties. Its value indicates the degree of electrostatic repulsion between the adjacent charged particles in the dispersion. A low zeta potential weakens the electrostatic repulsion between the particles, causing the van der Waals attraction between the particles to exceed the repulsion, thereby resulting in particle coagulation and colloid destruction. At a high zeta potential, the repulsive force between particles is dominant, thus, it resists aggregation and stabilises the dispersion. Therefore, colloids with a high zeta potential are stable, while those with a low zeta potential tend to flocculate. The main factors affecting the zeta potential are pH, ionic strength, and additives. For particles with a negative zeta potential, the particles tend to obtain more negative charges if alkali is added to the suspension. In contrast, the particles will reach the point of charge neutralisation if acid is added to the suspension. The zeta potential can be used to quantitatively represent the charged properties of the particle surface. Based on the phosphorus adsorption of substances with different charges, the variation of zeta potential in the adsorption process and its correlation with the adsorption capacity were discussed. The application of the zeta potential regulation in the RM granular adsorbent is still in the initial research stage.

3.4. Research status of phosphorus removal agents

There are several types of adsorption phosphorus removal agents. Based on the source, they can be divided

Table 4
Adsorption isotherm results of activated red mud on phosphate

Categories	Adsorbents	Adsorbate	Temperature (°C)	Langmuir		Freundlich		References	
				Q_m (mg·g ⁻¹)	b (L·mg ⁻¹)	n	K_f (mg·g ⁻¹)		
Component regulation	Red mud	Phosphate	25	16.06	1.53	8.12	9.45	[43]	
			35	16.59	2.19	8.07	9.97		
	Layered double hydroxide adsorbent Red mud	Phosphate	25	2.615	0.0312	1.270	3.244	[44]	
			–	29.12	0.01	0.75	0.33	[45]	
			–	108.58	0.005	0.10	18.32		
Acid activation	Acid-activated red mud	Phosphate	40	162.687	0.015	0.258	25.329	[57]	
			–	5.4765	0.0827	1.3243	0.4423	[38]	
	Organic modified red mud	Phosphate	–	7.6278	5.7500	3.8344	5.4075		
			–	2.8490	0.0904	1.4355	0.2622		
	Activation neutralization red mud	Phosphate	–	6.6578	0.7284	2.3218	2.4831		
			–	112.36	0.042	3.74	3.82	[39]	
	Thermal activation	Sintered red mud	Phosphate	30	396.355	0.016	0.315	48.580	[40]
				30	0.346	545.24	5.302	0.477	[17]
		Activation of high iron bayer red mud by hydrochloric acid	Phosphate	40	0.462	146.39	4.281	0.623	
				30	0.271	2.73	1.675	0.242	
High-speed rail rock bayer red mud		Phosphate	40	1.106	0.407	1.241	0.325		
			–	12.66	0.049	3.080	2.220	[67]	
Sintered red mud activated by hydrochloric acid	Phosphate	20	16.10	0.066	3.384	3.404			
		35	19.08	0.081	3.192	3.980			
Red mud activated by hydrochloric acid	Phosphate	900	149.29	0.013	–	–	[58]		
		–	17.02	0.025	3.800	3.376	[69]		

into categories such as natural, industrial waste, and synthetic phosphorus removal agents. According to the material properties, it can be divided into inorganic phosphorus removal agents and organic phosphorus removal agents (biomass and carbon-based phosphorus removal agents) (Table 5).

Natural inorganic phosphorus removal agents mainly include zeolite [70], attapulgite, bentonite, montmorillonite, vermiculite, and iron oxide minerals. Factors affecting their adsorption performance include the type and ratio of metal ions, lattice structure, and surface functional groups of the adsorbent. The pore volume and specific surface area of the goethite-kaolinite complex [71], which is an efficient phosphate adsorbent, increase the surface-active sites. The negative effect of bacteria on phosphate adsorption by goethite may be due to the bacteria-induced surface charge modification and competitive adsorption [72]. Phosphate adsorption by La(III)- and Fe(III)-modified montmorillonite [73] depends on the content of La, and the cation determines its adsorption capacity. Dolomite [74] removes phosphate via chemical bonding or chemical adsorption. Kaolinite, montmorillonite, and vermiculite natural clay were modified using Zr [75] to enhance the adsorption sites and form inner surface complexes for phosphate adsorption. Aphanitic magnesite-bentonite nanocomposites [76] adsorb phosphate

in wastewater via monolayer adsorption. The concentration of Ca²⁺ in heat-treated, calcium-rich palygorskite [77] affects its phosphorus removal capacity. Additionally, the types of Ca–P precipitates formed under different phosphorus concentrations may be different.

Renewable resource-based phosphorus removal agents (biomass materials) mainly include straw, peel, eggshell, oyster shell, clam shell, and shrimp skin, which usually need to be modified by loading treatment, chemical grafting modification, calcination, and other modification treatments. Zhang et al. [78] found that straw can produce porous structures, and biochar made by pyrolysis can be used to neutralize acidic wastewater. Biochar (BC) supports layered double hydroxides (LDHs) composites (LDH-BC). Fulazzaky et al. [79] showed that the mass transfer resistance of phosphate adsorption on iron-loaded waste mussel shells depends on porous diffusion and membrane mass transfer through dynamic column experiments. A La(OH)₃ modified canna biochar (CBC-La) [80] was prepared by the co-precipitation method (impregnation method). In the presence of NO₃⁻, HCO₃⁻, and CO₃²⁻, the removal rate can still maintain >99.8%. The main mechanisms of phosphate adsorption by CBC-La are electrostatic adsorption, ion exchange, ligand exchange, and inner layer complexation. In the phosphate adsorption process by the oyster shell-modified tobacco straw

Table 5

Comparison of inorganic phosphorus removal agent and organic phosphorus removal agent

Classification	Organic phosphorus removal agent	Inorganic phosphorus removal agent
Composition	It includes crop waste and organic waste in life, such as wood fiber, corn stalk, straw, sawdust, bark and crop straw.	It is composed of inorganic substances, such as metal oxides, metal salts and so on.
Adsorption property	It usually has high selectivity and can selectively adsorb phosphate without affecting other components. It is suitable for low concentration phosphorus adsorption. Phosphorus release and recycling performance of regeneration can also be achieved.	The selectivity is low, and it may adsorb other ions or substances at the same time. It usually has high adsorption capacity and fast adsorption rate, which is suitable for high concentration phosphorus adsorption.
Adsorption mechanism	It interacts with phosphates through chemical bonds or physical adsorption, such as hydrogen bonds and ionic bonds. It refers to organic compounds with phosphate groups, such as polymers and resins.	It interacts with phosphate by surface adsorption, ion exchange or chemical reaction. Inorganic materials with high specific surface area, such as iron manganese oxides and alumina.
Applications	It is usually used in water treatment, environmental pollution control and other fields, such as removing phosphate from wastewater. It is mainly used in the field of agriculture and can be used as a fertilizer additive or soil amendment to provide phosphorus for plants.	It is widely used in catalysts, adsorbents and separation materials, such as gas separation and catalytic reactions. It can also be applied to wastewater treatment, lake and river restoration and farmland drainage treatment, which can efficiently remove phosphorus pollutants in water.

biochar [81], CaO was converted into Ca(OH)₂ and chemically precipitated by neutralization with H⁺.

Solid waste-based adsorption phosphorus removal agents can be divided into water plant sludge (water supply sludge and sludge ceramsite), industrial waste residue (steel slag, fly ash, and red mud) and other wastes (potassium silicon powder and biogas slurry). The waste is usually modified via granulation–calcination and acid activation. Yu et al. [82] found that CaCO₃ and iron salts in sludge were converted into CaO and Fe₃O₄ through pyrolysis at high temperature. CaO is the active site of chemical precipitation, exhibiting a synergistic effect with iron oxide compounds (Fe₃O₄ and α-Fe₂O₃) to remove phosphate through chemical precipitation, ligand exchange and complexation. The problem of cementation and blockage of slag in water treatment was solved by using bacteria combined with alkaline oxygen furnace slag [83] to strengthen phosphorus removal from wastewater. The adsorption of phosphorus by Cu/Fe modified fly ash [84] is mainly achieved by heterogeneous chemical adsorption and electrostatic interaction.

The synthetic inorganic phosphorus removal primarily includes metal hydroxide, mesoporous silica, hydrotalcite, etc., represented by iron hydroxide, iron oxide, activated alumina, etc. The phosphorus removal capacity depends on the pore structure and can be improved by chelating treatment, grafting modification, doping modification, and coating modification. A new adsorbent, bagasse iron oxide biochar (BIBC) [85], was prepared to remove phosphate from an aqueous solution. It was stable in the pH range of 4.0–10.0 without secondary pollution. The new Al-Ti bimetallic composite adsorbent [86] had the advantages of a large adsorption capacity and easy regeneration. In the adsorption process of lanthanum carbonate hydroxide/magnetite nanoparticles functionalized porous biochar [87], the ligand exchange (inner complexation) and electrostatic attraction between phosphate and carbonate/hydroxyl groups of

La(CO₃)OH play a leading role. MgO in the biochar of MgO nanoparticles [88] promotes the formation of micropores and mesopores, which can distribute the active sites on the outer surface and is conducive to the removal and recovery of phosphate in aqueous solution.

Carbon-based phosphorus removal agents mainly include porous carbon [89], activated carbon fiber [90], expanded graphite [91], carbon nanotubes [92] and graphene [93]. The modification methods are mainly considered based on the pore structure, surface chemical properties of the carbon materials and effective matching with other materials. In recent years, rare earth-based phosphorus removal agents represented by lanthanum oxide and hydrated lanthanum oxide have been studied in depth owing to their excellent phosphorus removal abilities. In addition to the abovementioned adsorbent types, metal–organic framework materials, polymer nanofibers, and biopolymers represented by chitosan can have good adsorption and phosphorus removal performances. Plasticized magnetic starch-based Fe₃O₄ clay polymer nanocomposites [94] can be synthesised to adsorb phosphate in an aqueous solution. They exhibit a heterogeneous porous surface, mainly through multi-layer adsorption such as electrostatic and ion exchange. Diatomite/polyethylene glycol hydrogel nanocomposites [95] adsorb phosphate through hydrogen bonding, electrostatic, and pore filling. Iron-loaded cross-linked chitosan-montmorillonite composite [96] enhances the adsorption capacity of montmorillonite for phosphate by changing the lattice structure.

Adsorption materials can also be divided into adsorption materials containing rare earth elements (REE) and adsorption materials without REE. Adsorption materials without rare earth elements include natural minerals, metal oxides, and carbon materials. Materials containing rare earth elements are usually modified by adding Zr, La, Ce, and other rare earth elements to the adsorbent, so that the rare earth

adsorbent has a high adsorption capacity, fast adsorption rate, strong anti-interference ion ability, good selectivity, and wide pH tolerance range, as shown in Fig. 10.

The red mud contains a large amount of REE (La, Ce, Nd, Sc, Y), which are mainly leached by nitric acid, hydrochloric acid, or sulfuric acid. However, there are some problems in the recovery method, such as the large investment, high energy consumption, and high cost. It is not economical and has not reached industrial application. It is still in the academic research stage. Compared with the adsorption process of phosphorus removal from red mud and other solid wastes, steel slag has a high adsorption efficiency and a wide application range owing to its rich metal oxides. Red mud has potential advantages in the field of phosphate adsorption treatment owing to its abundant resources and low cost. Fly ash has a slow adsorption rate, making it suitable for treating low-concentration phosphate wastewater. In contrast, red mud has a fast adsorption rate, making it suitable for treating high-concentration phosphate wastewater. Sludge often contains particles and organic matter, reducing the adsorption sites for effective phosphorus removal, thereby causing a decrease in the adsorption capacity. The heat energy and chemical agents required in the modification process and the dried sludge increase the adsorption cost. Biomass waste must first be carbonised to make porous material biochar; however, the carbonisation process requires heat energy and the adsorption cost is relatively high. Moreover, the process produces organic tail gas, which must be treated to reduce environmental pollution. Red mud contains a certain amount of heavy metal ions, such as lead and cadmium.

During phosphate adsorption, heavy metal ions may enter the water body and cause secondary environmental pollution. Additionally, the phosphate adsorption capacity of red mud is relatively low and must be used in large quantities, which is not conducive to resource conservation. Therefore, the use of red mud as a phosphorus removal agent to remove phosphate in water is the mainstream trend of ‘treating waste with waste’. However, in practical applications, its cost and environmental problems limit the promotion of this technology.

Therefore, to realize better environmental protection while reducing costs, other economical and eco-friendly technological means should be considered. Simultaneously, new environmental protection technologies should be continuously explored to provide more effective means of environmental protection and sustainable development.

3.5. Status of research on regeneration of adsorbents for desorbed phosphorus

Phosphorus adsorbent regeneration refers to the desorption or removal of phosphate substances adsorbed in the adsorbent from the adsorbent without destroying the original structure of the adsorbent. The adsorption performance of the adsorbent can be restored, so that the adsorbent can be restored to a reusable state. The commonly used regeneration methods include heating method, solvent method, ozonation method and biological method as shown in Table 6.

Adsorbent adsorption of phosphorus includes physical adsorption and chemical adsorption. Physical adsorption

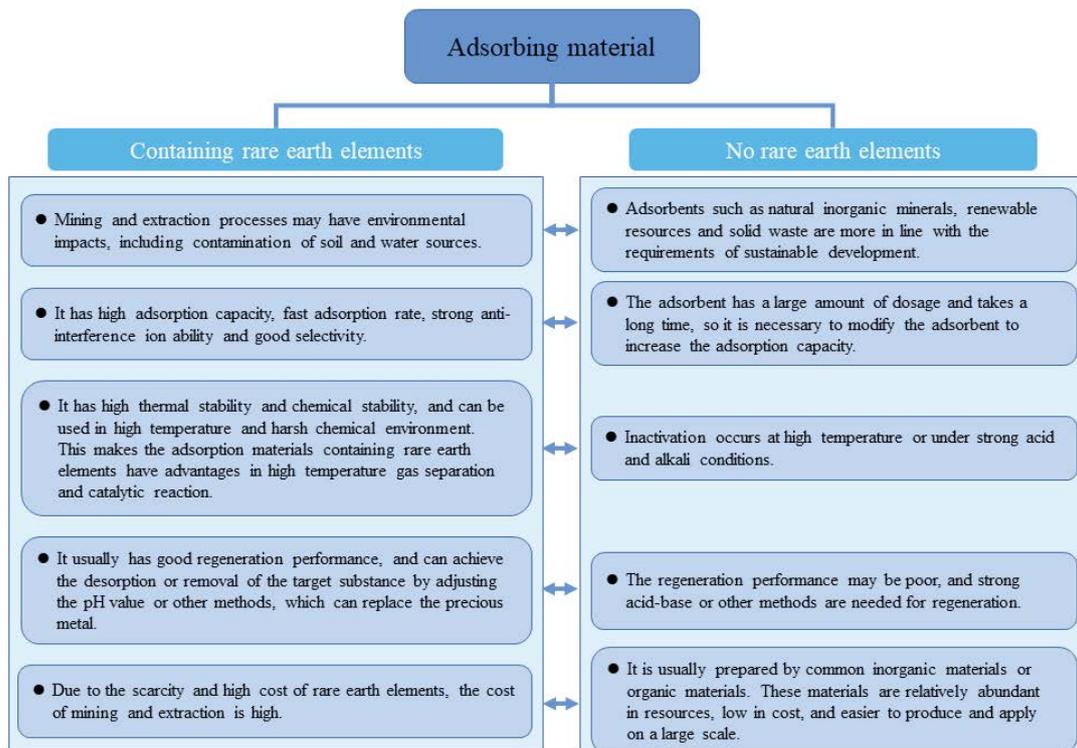


Fig. 10. Distinguish between adsorption materials containing rare earth elements and adsorption materials without rare earth elements.

Table 6
Methods of adsorbent regeneration

Methods	Principle	Feature
Acid/alkali regeneration	It can change the pH and react directly with some adsorbates.	It is only applicable to adsorbents affected by pH. Using the reversible adsorption process, the adsorption capacity of the adsorbent cannot be completely regenerated, but the transfer of pollutants is not completely removed.
Bio-regeneration	The adsorption saturated adsorbent is treated by microorganisms, and the adsorbate adsorbed on the surface of the adsorbent is degraded by microorganisms into CO ₂ and H ₂ O, so as to achieve the purpose of regeneration.	It is suitable for adsorbate of organic matter which is easy to be biodegraded, has adsorption reversibility and easy to desorb. Biofilm aggregation is easy to block the pores of the adsorbent, reducing the adsorption performance, long regeneration time and low efficiency.
Ozone regeneration	The regeneration medium is O ₂ /O ₃ mixed gas.	At present, it is mainly used for the regeneration of saturated activated carbon. Activated carbon cannot be regenerated by ozone method when its adsorption saturation is high.
Microwave regeneration	The organic pollutants on the adsorbent were carbonized by high temperature produced by microwave to restore its adsorption capacity.	With the increase of regeneration times, the porosity of the adsorbent continues to decrease and the average pore size increases. It can be used to adsorb saturated activated carbon and carbon nanotubes. The regeneration time is short, the energy consumption is low, and the regeneration efficiency is high.
Organic solvent regeneration	Organic solvents such as acetone, methanol, dichloromethane and ethyl acetate were used to extract the substances on the saturated adsorbent.	The reversible adsorption process cannot completely release the adsorption capacity of the adsorbent and cannot be completely removed.
Electrochemical regeneration	The regeneration range is narrow, which is mainly suitable for carbon-based adsorption materials with high porosity.	The regeneration efficiency is high and has little effect on the adsorbent. At present, most of the electrode materials are graphite and precious metals, but graphite has large volume, high resistance and high cost of precious metals.

refers to the adsorption of phosphorus on the surface of the adsorbent through van der Waals force and electrostatic interaction. Chemical adsorption refers to the chemical reaction between phosphorus and adsorbent and the formation of chemical bonds. Phosphorus usually exists in water as HPO₄⁻, and the active sites on the adsorbent will react with H⁺ in phosphorus to form P–O chemical bonds, so that phosphorus is firmly adsorbed on the surface of the adsorbent. Pickling is one of the most commonly used regeneration methods in the regeneration process of phosphorus adsorbent. The strong acidity of acid can be used to release phosphorus ions on the adsorbent. The influencing factors in the regeneration process of the adsorbent include the selection, concentration and temperature of the regenerant, and the contact time between the adsorbent and the regenerant. The desorption methods of phosphate mainly include acid desorption, alkali desorption agent and salt desorption agent (Table 7).

Adding an acid desorption agent (HCl) and a phosphorus-containing adsorbent reduces the pH of the whole system and produce a large amount of H⁺, which first dissolves the soluble salt on the adsorbent surface and enters the pores to dissolve the phosphorus adsorbed on the pore surface. The effective adsorption site of the red mud adsorbent is exposed to the surface to achieve desorption (Fig. 11). However, adding HCl makes the desorption solution turbid.

This is because HCl not only dissolves phosphorus substances but also dissolves the active components of phosphorus adsorption (Al₂O₃, Fe₂O₃, and CaCO₃) during the desorption process, resulting in the reduction of adsorption active sites and altering the effect of re-adsorption after desorption. Thus, HCl is used as a desorption agent, and the desorption solution concentration must be controlled under the actions of adsorption and desorption. To a certain extent, the low acid concentration dredges the pores of the particles due to the action of acid and the effective points inside the particles are exposed and re-adsorbed. Thus, the low-concentration HCl solution is an ideal desorption agent.

After NaOH desorption (Fig. 12), the pH value of the desorption solution decreased and the pH value of the granular adsorbent increased. A large amount of OH⁻ dissolved the phosphate ions, hydroxylated the adsorbent surface, formed a ligand exchange reaction and reduced the adsorption capacity of the adsorbent. The surface material of the desorption process undergoes chemical changes. The surface structure is improved, such that the regenerated adsorbent has a higher adsorption activity, and the phosphorus re-adsorption is better than the HCl desorption and re-adsorption.

Salt desorption agents such as NaCl and KCl desorb phosphate through an ion exchange process. However,

Table 7
Phosphate desorption agents

Adsorbent	Desorbing agent	Desorption efficiency	References
Mesoscopic structure of zirconium sulfate surfactant micelle	0.1 M NaOH	90%	[97]
Chitosan/Ca organic modified montmorillonite	0.1 M NaOH	84%	[98]
Magnetic ZrO ₂	0.1 M NaOH + 1 M NaCl	91.2%	[99]
Zirconium iron and iron modified biochar	(NH ₄) ₂ SO ₄ NaOH	(NH ₄) ₂ SO ₄ : 70.43% NaOH: 74%	[100]
A type of La(OH) ₃ loaded magnetic MAPTAC-based cationic hydrogel	3.0 M NaOH + 3.0 M NaCl	76.8%	[101]
HFeO	6% NaCl	97%	[102]
Magnetic polymer	0.5 M NaOH	66.43%	[103]
Graft copolymer	0.1 M Na ₂ CO ₃	99.2%	[104]

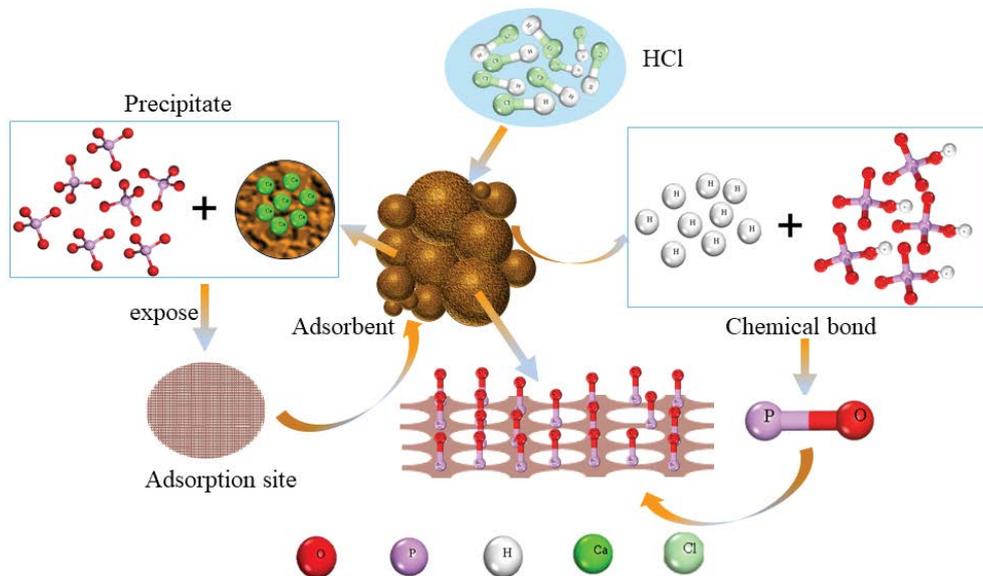


Fig. 11. Desorption regeneration process of acid desorption agent.

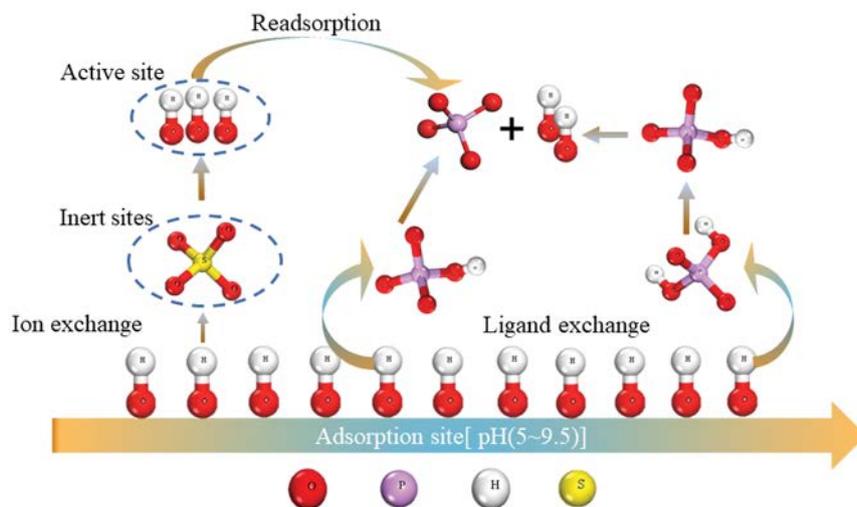


Fig. 12. Desorption regeneration process of alkali desorption agent.

because NaCl is a soluble salt, the addition will increase the Cl⁻ in the solution system, corrode the metal structures, and deteriorate the quality of the comprehensive utilisation of red mud after desorption. High salt concentrations are used for effective desorption, resulting in the phosphate recovery in desorbed solution, which is then used for fertilisation and irrigation of crops due to the high salinity risk. Salts cannot effectively desorb phosphate from strongly phosphate-adsorbed sorbents through specific adsorption mechanisms.

The efficiency and economy of using the red mud adsorbent to remove phosphate from wastewater have been considerably improved; however, less attention has been paid to the recovery of used adsorbents and phosphorus resources. Scholars have studied the use of different desorption agents, but the research is limited. Only a limited adsorption–desorption cycle can be performed. Moreover, only a few studies have focused on the recovery of the phosphate adsorption–desorption resources using the red mud adsorbents, considering the resource utilisation of waste adsorbents.

4. Research progress on test calculation of red mud as an adsorbent

Molecular dynamics simulation can establish a position suitable for biochemical molecular systems, polymers, metals, and non-metals, improving the accuracy of calculating complex system structures. The particle motion simulation has the correct physical basis and can be used to study various surface-related characteristics. The mechanism of the red mud adsorbent on phosphorus adsorption is revealed from a microscopic point of view by establishing an adsorption model of the red mud adsorbent + phosphate + water. Taking the non-thermally activated red mud granular adsorbent (ARMFA) [105] as an example, the effects of the surface and granular adsorbent properties on phosphorus adsorption were studied herein from a microscopic viewpoint. First, the single crystal cell of each mineral was constructed and the structure of the main adsorption components of the adsorbent was optimised. The ARMFA adsorption on the phosphorus-containing wastewater was explored based on two aspects: surface and porous adsorption. The results are shown in Fig. 13. Materials Studio software was used to simulate the periodic repetitive cells of the ARMFA mass components—Fe₂O₃, CaCO₃, Ca₂Fe₂O₇, Ca(Si₆Al₂)O₁₆, Ca₃Al₂O₆, Al₂O₃, and SiO₂—using the amorphous cell module to adsorb the PO₄³⁻, HPO₄²⁻, and H₂PO₄⁻ in wastewater.

The adsorption mechanism is further explained from a microscopic viewpoint. For example, the quantum mechanics density functional method [106,107] is used to reveal the adsorption mechanism of adsorbent components on phosphorus. Liu et al. [108] studied the structure and energetics of benzene adsorbed on the surface of transition metals based on density functional theory (DFT). The collective screening effect leads to strong adsorption of Bz at Pd(111), Pt(111), Rh(111), and Ir(111). Bz molecules are adsorbed on all metal surfaces in a flat arrangement, so that Bz is weakly adsorbed at Cu(111), Ag(111), and Au(111). Hu et al. [109] analyzed that Fe³⁺ doping promoted the N₂ photofixation ability of the honeycomb graphite carbon nitride through experiments and DFT simulations. The Fe³⁺ site was not

only used as an active site for adsorbing and activating N₂ molecules but also promoted the interface charge transfer from the catalyst to the N₂ molecules, thereby considerably improving the photofixation ability of nitrogen. Peng et al. [110] studied the effects of head group type and alkyl chain length on the adsorption of alkylamine cations on montmorillonite (001) surface by using DFT, sedimentation, contact angle, and adsorption capacity measurements. The calculation shows that the cationic form is easily adsorbed on the quartz surface by electrostatic attraction. Zou et al. [111] synthesized a new type of high-efficiency glycerol-modified nanoscale-layered double hydroxide with an excellent adsorption capacity for aqueous U(VI) under various environmental conditions. Furthermore, the DFT calculations demonstrate that the higher adsorption energy is mainly attributed to the stronger hydrogen bonds and electrostatic interactions. Dzade et al. [112] studied the benzene adsorption on the hematite (α -Fe₂O₃) surface using DFT and showed that the adsorption geometry parallel to the surface is more stable in energy than the vertical geometry. Benzene molecules interact with the hematite surface through the π bonds in the parallel adsorption geometry and the weak hydrogen bonds in the vertical geometry. Chen et al. [113] studied the interaction between Ni(II) and graphene oxide by theoretical DFT calculations. The results show that the adsorption of Ni(II) on graphene oxide is mainly attributed to –COH and –COC groups.

Based on the DFT [114–118], the electronic structure of the composite phase was revealed by analyzing the energy band structure, density of states, and Mulliken population of the red mud composite. The microscopic adsorption mechanism of phosphorus by red mud in a complex system was calculated and analyzed by DFT. The quantum theory model of adsorbent surface interaction was established. The DFT was used to study the surface coordination of multi-component mineral pores in a red mud-based granular adsorbent [49] and the influence of the spatial structure on the residual valence bond structure as well as the electronic properties of surface phosphorus-absorbing active atoms. The effects of the surface spatial structure and residual valence bond properties on the molecular structure and phosphorus substance adsorption were studied. The thermodynamic model, reaction microcalorimetry, and adsorption kinetic model of the interaction between the phosphorus substances and the surface atoms of the red mud-based adsorbents were established. The steric hindrance thermal effect and the adsorption entropy change effect of the phosphorus substances in the phosphate ore dressing wastewater on the pore surface of the adsorption materials were investigated. Moreover, the adsorption and desorption mechanisms of the red mud on phosphorus were studied from a macro perspective.

5. Prospect

By summarising research data from the past decade on phosphate adsorption using red mud adsorbent materials in the past decade, red mud adsorbents simultaneously and stably adsorb polymorphic phosphate and have an integrated chemical phosphorus removal capability suitable for pan-concentration of wastewater and removal

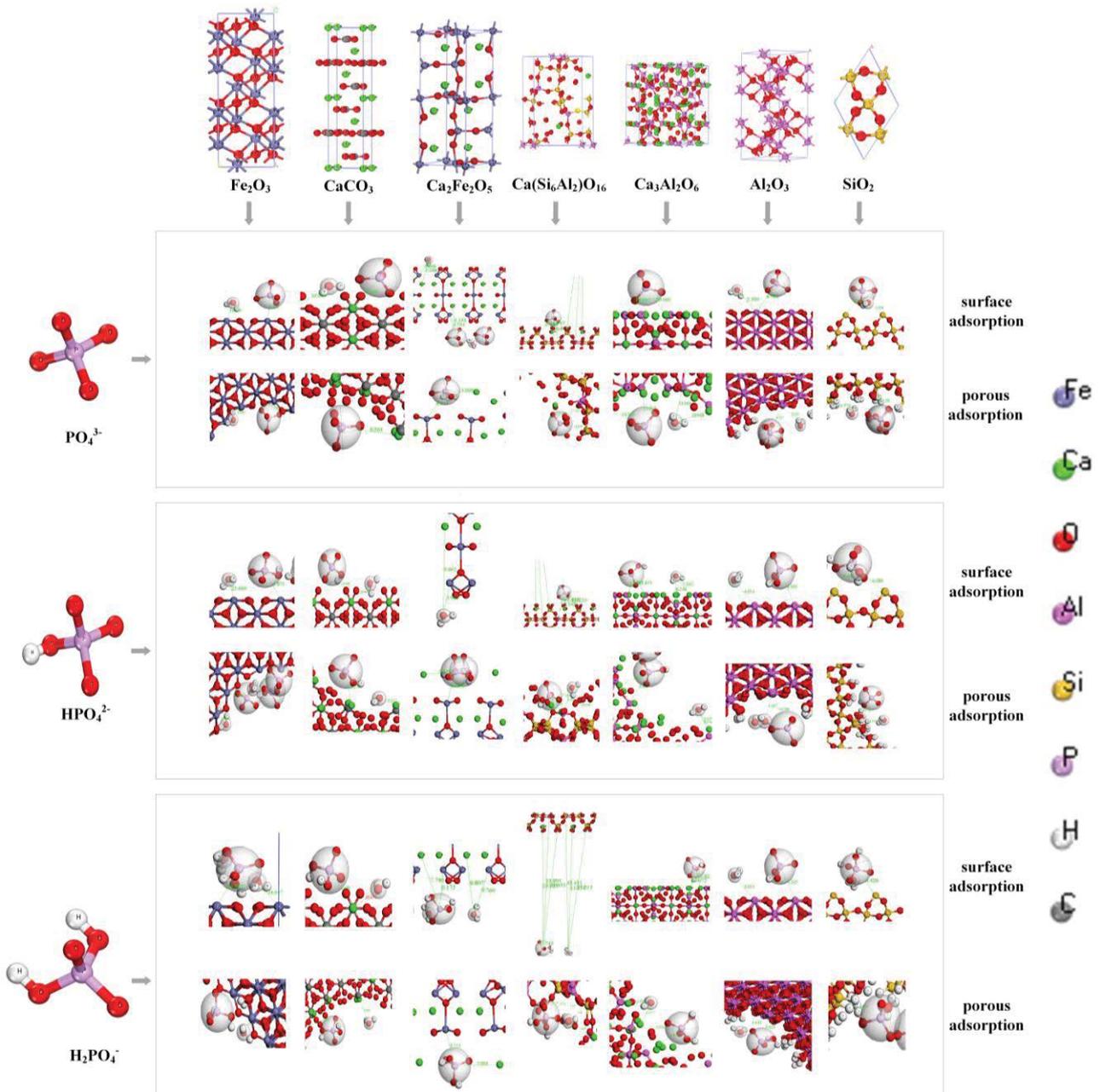


Fig. 13. Adsorption process of non-thermal activated red mud granular adsorbent.

of polymorphic phosphorus. The red mud adsorbent after adsorption saturation can not only be regenerated simply but also be used as a phosphorus-rich compound fertiliser that is returned to the field to improve the acidic soil. Secondary pollution is less, and the resource recycling of red mud is realised in line with the circular economy concept. With increasing research on the comprehensive application of red mud, scope for the development of red mud adsorbent materials still exists. The following conclusions are drawn from this work:

- Combined with the quantum chemistry calculation programme based on the density functional method, the

adsorption energy of the phosphate ions and red mud adsorbents with different structures at different spatial structure positions and the geometric deformation of the structure were studied to determine the steric hindrance effect of the adsorption process, which has broad promotion prospects and application value.

- The microscopic adsorption mechanism of red mud is not sufficiently clear. Due to the relatively complex composition of red mud adsorbent, the current simulation calculation mainly starts with a relatively simple single mineral; however, the typical mineral composition of different regions and production processes needs to be expanded. There are few molecular dynamics

studies on phosphorus adsorption and desorption by the micro-spatial structure of the red mud adsorbent, which is worthy of further study.

- In industrial applications, only a few studies have been performed on the desorption of phosphorus resource recovery after phosphate adsorption by the red mud adsorbent. At present, complete adsorption and desorption equipments are lacking. Furthermore, the regeneration process of the red mud adsorbent for phosphorus desorption remains to be studied.

Credit authorship contribution statement

Yalan Wang: Investigation, Data curation, Writing – original draft. Longjiang Li: Conceptualization, Methodology, Writing – review & editing. Zhicheng Liu: Investigation. Zhiwei Ren: Investigation.

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