



The regeneration characteristics of various red mud granular adsorbents (RMGA) for phosphate removal using different desorption reagents

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ABSTRACT

In this research, various red mud granular adsorbents (RMGA), which were made from red mud – a kind of waste residue from the alumina industry, were manufactured under different sintering temperatures (ST). For the purpose of investigating the regeneration characteristics of them for phosphate removal, systematic experiments were carried out, including adsorption, desorption (using different desorption reagents) and resorption tests. When RMGA were desorbed by HCl solutions, the desorption efficiencies were relatively higher due to acid erosion, but the corresponding resorption capacities became small owing to extraction of effective components. Although RMGA rarely released phosphate in desorption process when being desorbed by deionised water, it performed well on resorption of phosphate afterwards. It was assumed that the lower pH in resorption process, which was caused by the reductive release of CaO into solution, contributed to a weaker competition of OH⁻ on phosphate resorption. When NaOH solution was employed as the desorption reagent, resorption capacities of RMGA were relatively larger and increased with the increase of NaOH concentration, because OH⁻ might ameliorate the chemical composition on the surface of RMGA potentially. In addition, several RMGA manufactured under lower ST obtained larger resorption capacities than their original adsorption capacities, because of the comparatively unstable crystal structure which led to a stronger amelioration on them.

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1. Introduction

Red mud (RM), as the main raw materials for manufacturing red mud granular adsorbents (RMGA) in this study, is a kind of solid waste generated in alkaline processes when alumina is extracted from bauxite [1]. Taking China as an example, 23.8 million tons of alumina was produced approximately during 2009, with an addition of 3.3% compared with that of 2008 [2]. Nowadays, more and more alumina plants have sprung up all over the world to meet the increasing industrial demand. Since RM commonly exists in the form of slurry with 15–30% solids [3] and it is generated at the range of 1–1.5 tons for each ton of alumina production generally [4], large quantities of RM are accumulated. Moreover, RM is highly alkaline (pH 10–12.5) owing to its large calcium and sodium hydroxide content [5]. Therefore, the conventional storage of RM in a dam not only takes up large areas of farmland but also causes serious pollution to surrounding environment [6]. In the past years, a small part of RM produced from alumina plants has been utilized for field compost [7], casting production [8], building material additive [9] and metal recovery [10]. With the development of technology, various

attempts on the reapplication of RM have been done for the purpose of treating waste with waste, including soil remediation [11], gas cleaning [12], wastewater treatment (such as manufacturing coagulant and adsorbent) [13,14] and catalyst production [15,16].

Because of the capability of removing several contaminants, making adsorbents from modified RM has attracted much attention of the researchers. Currently, powdered RM was applied as adsorbents mostly in this area, but it has several disadvantages, such as the waste water output during activation of RM and the difficulty of regeneration and recovery after application [17]. In consideration of the fact that RM is a fine-grained mixture of oxides and hydroxides [18], the intention of preparing an unconventional kind of granular adsorbents has been put forward. The RM-based adsorbents, which are convenient for use in columns, have been prepared by several researchers, whereas some extra chemical preparations (such as Na₂SiO₃ and Na₂CO₃) were injected generally in these studies and this would lead to a relatively high production cost [17,19]. Therefore, it is very necessary to develop a cost-effective, easily-made and widely available granular adsorbent without injecting extra chemical preparations.

In our previous study, RMGA were made from simple raw materials, which contained equably-mixed RM, bentonite and starch. As had been proved in our former experiments, RMGA were available for the removal of phosphate, which is implicated in

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Table 1
The composition of raw materials (wt.%).

Raw materials	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Na ₂ O	TiO ₂	MgO	K ₂ O	SO ₃
RM	31.12	18.63	14.42	13.72	13.35	4.83	2.80	0.22	0.91
Bentonite	3.87	66.18	4.39	16.94	2.59	0.31	3.94	1.78	–

eutrophication of rivers and lakes [20]. The parameters for producing RMGA (such as mass ratio of three materials, preheating time, preheating temperature, sintering time and sintering temperature (ST)) had been investigated in our previous research [21], in which ST was considered as a very important parameter that influenced the characteristics of RMGA for phosphate removal sensitively. In this research, for the purposes of recycling the phosphate-adsorbed RMGA and accumulating empirical data for further column technique, the regeneration characteristics of various RMGA manufactured under different ST were mainly discussed. The investigations were based on systematic experiments, which involved adsorption, desorption and resorption tests. In the desorption process, HCl, NaOH solutions of different concentration and deionised water were applied as the desorption reagents, respectively. Desorption efficiencies and resorption capacities were chosen to evaluate the influences of different desorption reagents on RMGA.

2. Experimental

2.1. Raw materials

RM, which was obtained from Shandong Aluminium Industry Corporation in Zibo, Shandong Province of China, was applied as the main raw materials for manufacturing RMGA. Bentonite and starch were injected as admicular materials in the name of cementing agent and aperture producer, respectively, which was based on the fact that bentonite can play the roles as a kind of quality clay in ceramic industry [22] and starch is aerogenous when being sintered.

The energy dispersive X-ray analysis (EDAX) was conducted to determine the chemical composition of dewatered RM and bentonite, by using a PV9100 X-ray energy spectrometer that was connected with an S-520 scanning electron microscope. The results are shown in Table 1, from which it can be seen that RM is composed mainly of Ca, Si, Fe, Al and Na oxides while bentonite is composed mainly of Si and Al oxides.

2.2. Preparation of RMGA

In this research, RMGA were made with powdered RM, bentonite and starch at the mass ratio of 90:5:5 to achieve the maximum application of RM, and they were manufactured similarly according to the process in our previous research as follows [21]: before granulation, the three raw materials above were comminuted and air dried, and then they were sieved through a 100 mesh screen, thus grain size of less than 0.149 mm was obtained, which would help them to be mixed evenly in the next step. After the powder was evenly blended, an appropriate amount of pure water was injected and the mixture was churned continuously until pasting. Then, an aperture board was used to squeeze the paste before shreds with diameter of 1.5 mm was drawn out, and cylinder granulation of 1.5-mm-long was obtained by dicing the shred to particles. After the raw granules were naturally dried in the open air for 24 h, they were preheated in a muffle furnace at 400 °C for 20 min, and then they were sintered in a tubular furnace for 10 min at the relevant temperatures. The ST of each kind of RMGA differed from one to another, and the range of it was from 950 to 1150 °C

in this research, progressively increased by 10 °C. Finally, various kinds of RMGA were obtained when the sintered granules were cooled down to room temperature naturally.

2.3. Analytical methods

The X-ray diffraction (XRD) patterns of some RMGA samples, which were pretreated by grinding and sieving through a 100 mesh screen, were determined by a D/max-ra X-ray diffractometer with Cu K α radiation at 40 kV and 40 mA over the 2 θ range of 20–70°.

Phosphate solution was prepared by potassium dihydrogen phosphate (KH₂PO₄) of guaranteed grade in this research, and the concentration calculated as elemental P, was measured by the ascorbic acid method that was published in *Monitoring and Analysis Methods of Water and Wastewater* [23], using a 722E visible range spectrophotometer. The relevant chemicals required in the standard analytical method, including sulphuric acid (H₂SO₄), ascorbic acid (C₆H₈O₆), ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) and potassium antimonyl tartrate (K(SbO)C₄H₄O₆·(1/2)H₂O), were of analytical grade. The desorption reagents were prepared by hydrochloric acid (HCl) and sodium hydroxide (NaOH) of guaranteed grade, and deionised water was used as solvent for all the solutions.

2.4. Systematic studies

The systematic studies contained three steps: the adsorption, desorption and resorption process. RMGA that have been used in adsorption test were air dried, then they were applied in the following desorption test. After that, they were treated again as mentioned above for application in the resorption test.

Using a stable temperature horizontal shaking bath, the adsorption and resorption tests were conducted by shaking 25 mL of 50 mg L⁻¹ phosphate solution with 0.1 ± 0.001 g RMGA in the covered conical flasks (the adsorbent dosage was 4 g L⁻¹), and the operation parameters were selected as aquatic temperature of 27 ± 1 °C, stirring speed of 100 rpm and reaction time of 4 h. While, the desorption test was carried out under the same conditions, except for the reaction time which was chosen as 1 h and the solution which was substituted by desorption reagent solution (also 25 mL), using HCl or NaOH solution of different concentration or deionised water in the relevant experiment, respectively. After shaking operation, the solutions were filtered through a 0.45 μ m microporous membrane in order to prevent the chippings from falling off. The final pH (pH_f) in solution was surveyed by a PHS-25C acidometer and the concentration of phosphate was measured according to the ascorbic acid method.

Both the adsorption capacity and resorption capacity (X) were evaluated by Eq. (1):

$$X = \frac{(C_i - C_f)V}{m} \quad (1)$$

where X indicates the mass of phosphorus adsorbed (or resorbed) by per unit mass of RMGA (mg g⁻¹); C_i and C_f are the initial and final concentrations of elemental P in solution (mg L⁻¹), respectively; V is the volume of phosphate solution (L) and m is the weight of dry RMGA (g).

The desorption capacity (Y) and the desorption efficiency (y) were calculated by Eqs. (2) and (3), respectively:

$$Y = \frac{C_p V}{m} \quad (2)$$

$$y = 100\% \cdot \frac{Y}{\bar{X}} \quad (3)$$

where Y is the amount of phosphorus desorbed from per unit mass of RMGA that have been applied in the adsorption process (mg g^{-1}); y signifies the efficiency of phosphorus desorbed from RMGA comparing with that adsorbed on it before (%); C_p is the final concentration of elemental P in desorption solution (mg L^{-1}) and V is the volume of desorption solution (L).

The value of pH altered during the desorption process (ΔpH) was calculated by Eq. (4):

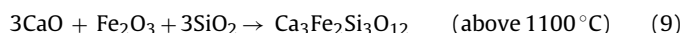
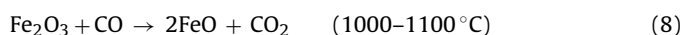
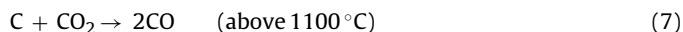
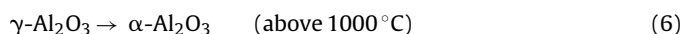
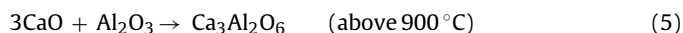
$$\Delta\text{pH} = \text{pH}_f - \text{pH}_s \quad (4)$$

where pH_f is the final pH in solution and pH_s is the original pH of desorption solution.

3. Results and discussion

3.1. Characterization and adsorption capacities of RMGA

Fig. 1 illustrates the crystalline phases of several RMGA samples characterized by XRD analysis. It was found out that the intensity of XRD patterns tended larger with the increase of ST, which implied that stable crystal structures existed in RMGA manufactured under higher temperatures. In addition, some important reactions might occur progressively when ST ranged from 950 to 1150 °C as shown in Eqs. (5)–(9) [24], and it was determined that the strength of RMGA was enhanced by the formation of $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$.



Various RMGA with ST ranging between 950 and 1150 °C were employed to remove phosphate from aqueous solutions in the adsorption process, and the original adsorption capacities are shown in Fig. 2. As can be seen, the adsorption capacity decreased approximately with the increase of ST. Since $\gamma\text{-Al}_2\text{O}_3$ and Fe_2O_3 were effective components for phosphate removal [20,25], the phenomenon above was caused by the reduction of them, due to reactions of transformation and combination in RMGA (represented in Eqs. (6), (8) and (9)).

3.2. Desorption test

3.2.1. Desorption of deionised water

Fig. 2 also illustrates desorption efficiencies for RMGA that had been used in adsorption test, which were obtained by using deionised water as the desorption solution. As shown in the graph, the desorption efficiency was even less than 1% for RMGA sintered between 950 and 1100 °C, while for RMGA sintered above 1100 °C, it rose significantly. Since physical adsorption was comparatively liable to be desorbed [26], the results indicated that the rate of physical adsorption in the total phosphate removal increased gradually with the increase of ST for various RMGA.

For RMGA sintered above 1100 °C, the amount of phosphate adsorbed was excessively small and it tended to be desorbed eas-

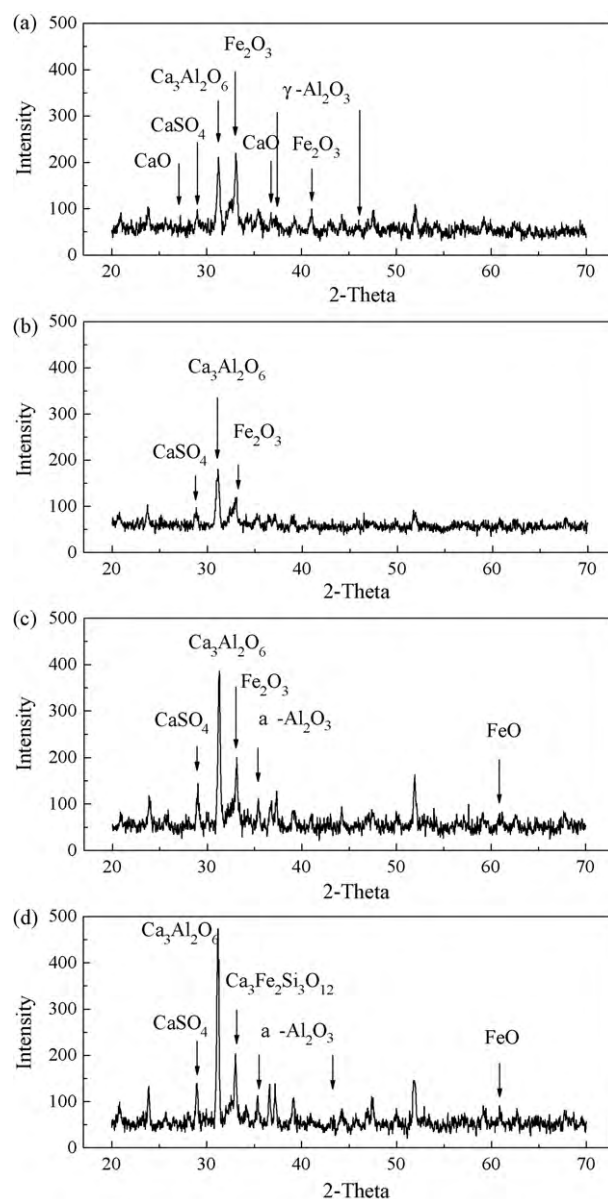


Fig. 1. XRD patterns of RMGA sintered at 950 °C (a), 1000 °C (b), 1050 °C (c) and 1100 °C (d).

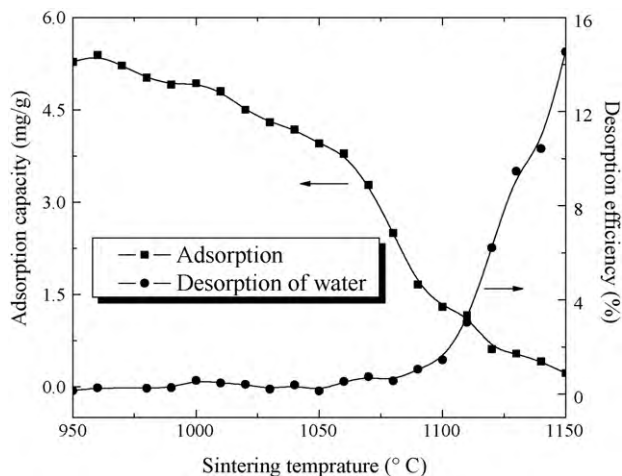


Fig. 2. The adsorption capacity of phosphate and the desorption efficiency of deionised water for various RMGA sintered at different temperatures.

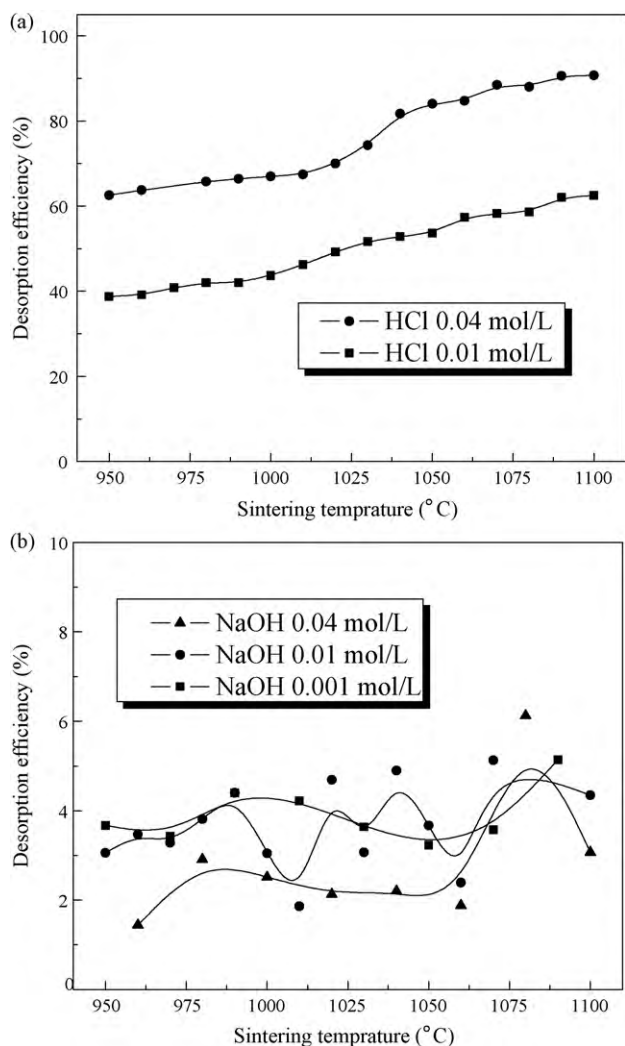


Fig. 3. The desorption efficiency of HCl solution (a) and NaOH solution (b) for various RMGA sintered at different temperatures.

ily even by water, thus they were inappropriate for application in practice and were not investigated in the research afterwards.

3.2.2. Desorption of HCl solution

HCl solutions of 0.01 and 0.04 mol L⁻¹ were applied to treat the phosphate-adsorbed RMGA and desorption efficiencies of them are shown in Fig. 3(a). It was observed that the phosphate adsorbed on RMGA could be desorbed by HCl obviously, and the desorption efficiencies increased with the increase of ST. Moreover, HCl solution of high concentration desorbed phosphate from RMGA much susceptibly, and this could be described as follows: on one hand, part of the adsorbed phosphate could be replaced by Cl⁻, due to the potential competition of concentrated acid ions with phosphate for active sites on adsorbents [27]. On the other hand, HCl solution of high concentration might also result in decomposition on the structures of RMGA, as the remaining weight of RMGA desorbed

by HCl of 0.04 mol L⁻¹ (ranged from 55% to 81% by weight with the increasing ST) was much lighter than that of the corresponding one desorbed by HCl of 0.01 mol L⁻¹ (ranged from 90% to 96% with the increasing ST).

To investigate the influence of HCl on RMGA, several parameters were measured for some RMGA samples after being desorbed by 0.01 mol L⁻¹ HCl solution. As γ -Al₂O₃ and Fe₂O₃ were the effective components for phosphate adsorption, the remaining concentrations of Al³⁺ and Fe³⁺ in the solutions after desorption are presented in Table 2, as well as some other items like mass loss and pH_f. Herein, according to GB/T 5750.6-2006, China (*Standard Examination Methods for Drinking Water – Metal Parameters*) [28], Al³⁺ was determined by the chromazurine-S method using a 722E visible range spectrophotometer and Fe³⁺ was measured by the atomic absorption spectrometry using a TAS-990 atomic absorption spectrophotometer.

As shown in Table 2, the variation of three items, including the mass loss of RMGA and the concentrations of P and Al³⁺ in solution, accompanied similarly with each other. This phenomenon indicated that desorption of phosphate by HCl solution was mainly caused by the decomposition of RMGA. Because γ -Al₂O₃ was well dissolved in acid solution, the structure of RMGA might be destroyed by HCl and the phosphate adsorbed by Al₂O₃ was released simultaneously. In addition, the data of the three items changed very little between the two RMGA samples sintered at 950 and 1000 °C, respectively. It was considered that due to the similar compositions of RMGA samples sintered between 950 and 1000 °C, HCl played a similar role on them. While, the data of the three items dropped simultaneously when ST rose above 1000 °C. It implied that the resistance of RMGA against HCl, which related to the stability of crystal structures in RMGA, enhanced significantly with the increasing ST.

However, the concentration of Fe³⁺ in solution performed differently compared with the three items above, because Fe³⁺ dissolved well barely in strong acid, especially when phosphate coexisted in solution. As can be seen from Table 2, concentration of Fe³⁺ was much lower than that of Al³⁺, and it increased unanimously with the decrease of pH_f in solution, which decreased with the increase of ST of RMGA samples. So it could be learnt that the dissolving of Fe₂O₃ did not display such a close relationship with phosphate desorption as that of Al₂O₃ did. Furthermore, it was also implied that the phosphate adsorbed by Al₂O₃ was more likely to be desorbed by HCl solution because Al³⁺ was more dissolvable, which contributed much to the mass loss of RMGA, while the phosphate adsorbed by Fe₂O₃ was considered to be combined on RMGA more stably.

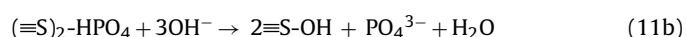
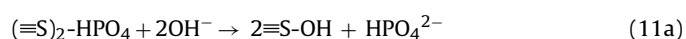
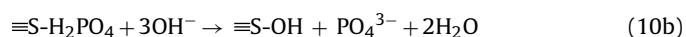
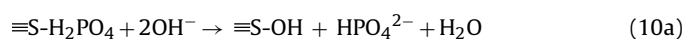
3.2.3. Desorption of NaOH solution

The corresponding desorption efficiencies of NaOH solutions, which were investigated under the same conditions as the other desorption reagents for RMGA, are illustrated in Fig. 3(b). As can be seen, the desorption efficiencies of each kind of NaOH solution fluctuated irregularly for various RMGA with the increasing ST. Thus, the ST was considered as an unimportant parameter affecting desorption of phosphate weakly in this situation.

Table 2
Mass loss (wt.%) of RMGA after the desorption of 0.01 mol L⁻¹ HCl solution and the relevant remaining P, Al³⁺ and Fe³⁺ concentrations (mg L⁻¹) in solution.

ST of RMGA	Mass loss (wt.%)	P concentration (mg L ⁻¹)	Al ³⁺ concentration (mg L ⁻¹)	Fe ³⁺ concentration (mg L ⁻¹)	pH _f in solution
950	9.73	8.53	6.342	0.474	2.94
1000	9.86	8.70	6.563	0.533	2.76
1050	7.72	8.40	5.962	0.815	2.53
1100	3.90	3.28	4.822	1.761	2.17

In addition, the desorption efficiency of NaOH solutions was much lower than that of HCl solutions shown in Fig. 3(a), as there was no obvious mass loss during this process. However, it was a little higher than that of deionised water shown in Fig. 2. Except for the fundamental desorption of less than 1% that was caused by deionised water (related to physical adsorption), the addition was speculated to be created by the reverse reactions of phosphate adsorption, which released hydroxide ion in the initial adsorption process [29]. The reverse reactions were estimated as Eqs. (10a), (10b) and (11a), (11b). The adsorbed phosphate forms were determined mainly as H_2PO_4^- and HPO_4^{2-} according to the pH values during adsorption process (between 5.0 and 9.5), and the desorbed phosphate forms were considered as HPO_4^{2-} and PO_4^{3-} according to the pH_f of desorption process in NaOH solutions (between 10.3 and 12.6).



where $\equiv\text{S}$ represents the effective site on the surface of RMGA. These reactions would lead to a drop of pH in solution, and this phenomenon was similar to the regeneration of exhausted RM column for arsenic adsorption with dilute NaOH by Genç-Fuhrman et al. [30]. However, since the relatively low and irregular desorption efficiencies represented in Fig. 3(b), it was considered that the reaction of ligand exchange between OH^- and H_2PO_4^- (or HPO_4^{2-}) was very weak under this condition, and the diversity of different NaOH concentration for phosphate desorption from RMGA could be ignored to some extent.

3.2.4. The variation of pH during the desorption process

According to our previous study [21], pH in solution increased after adsorption, for the potential hydrolysis of CaO occurred on RMGA: $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{OH}^-$. To discuss the total release or consumption of OH^- from the used RMGA during desorption process, pH_f in solution was surveyed and ΔpH was calculated. Fig. 4 shows the ΔpH for various RMGA treated by the desorption solutions applied above. It was found out that the pH in solutions rose during the desorption of deionised water and HCl solutions, due to the release of hydroxide ion by CaO dissolution; and the ΔpH decreased with the increase of ST, on account of the reduction of CaO and the more stable crystal structures in RMGA samples. While, the pH dropped after desorbed by NaOH solutions, owing to the expense of hydroxide on exchanging phosphate (see Eqs. (10) and (11)); and a slight hydrolyzation of CaO might accompanied in NaOH solution of 0.001 mol L^{-1} , because the tendency of ΔpH with the increase of ST in it was similar to that of deionised water.

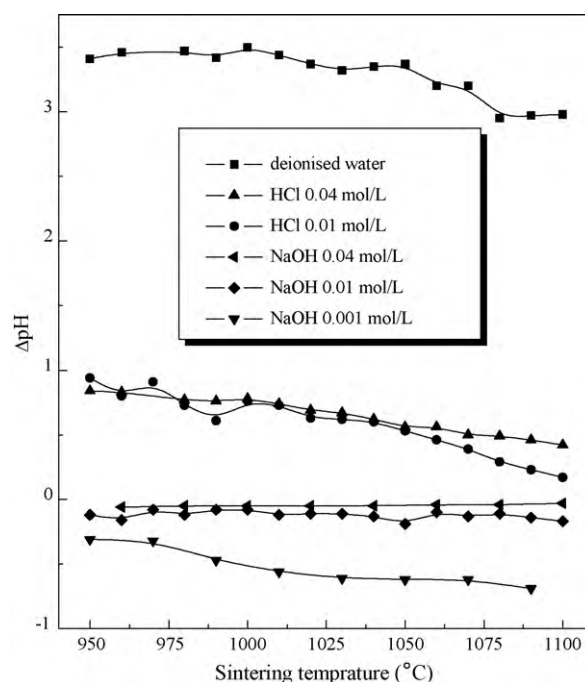


Fig. 4. The ΔpH during desorption process for various RMGA treated by different desorption solutions.

3.2.5. The chemical composition of the surface layer of RMGA after desorption process

For the purpose of investigating changes in chemical composition of RMGA after desorption process, RMGA samples sintered at 1000°C were chosen to be determined by EDAX. The compositions on the surface of RMGA after being treated by deionised water, HCl and NaOH solutions (0.01 mol L^{-1}), compared with that of the original RMGA, were presented in Table 3. As can be seen, mass ratios of most oxides did not change too much after desorption of deionised water and NaOH solution. While for RMGA treated by HCl solution, it could be learnt that the rates of $\text{CaO}:\text{SiO}_2$, $\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$ and $\text{Na}_2\text{O}:\text{TiO}_2$ were all lower than those of the original one. This implied that CaO, Al_2O_3 and Na_2O in RMGA were much easy to be dissolved by HCl solution, while SiO_2 , Fe_2O_3 and TiO_2 might combine on RMGA more stably. As little chloride was observed on RMGA after HCl treatment for desorption, it was considered that the replacement of Cl^- was not dominant in phosphate desorption, but the decomposition on the structure of RMGA caused by acid erosion contributed much.

3.3. Resorption test

Various RMGA, which had adsorbed phosphate and then been desorbed by different desorption solutions shown in the desorp-

Table 3

The composition of the surface layer of RMGA after being treated by different solutions (deionised water, HCl and NaOH solutions) for desorption (wt.%).

Composition	Deionised water	HCl solution	NaOH solution	The original RMGA
CaO	25.35	21.99	23.76	25.82
SiO_2	22.60	27.05	21.98	24.72
Al_2O_3	19.39	18.47	19.20	18.50
Fe_2O_3	16.37	18.98	17.35	16.77
Na_2O	5.58	4.92	6.27	5.49
TiO_2	4.76	5.37	5.09	4.73
MgO	2.71	2.03	2.75	3.22
K_2O	0.24	0.39	0.54	0.41
SO_3	0.24	0.26	0.10	0.35
P_2O_5	2.77	0.51	2.95	–
Cl	–	0.03	–	–

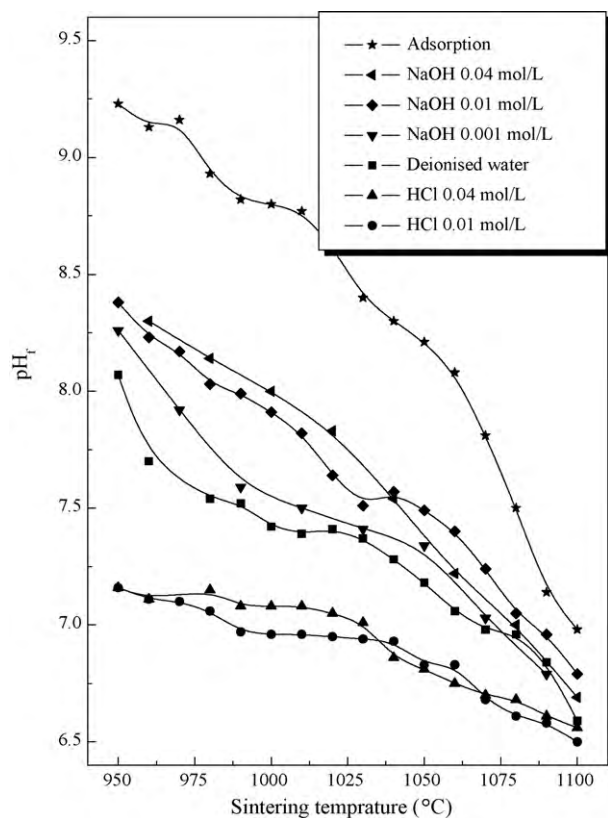


Fig. 5. The pH_f in resorption process for various RMGA treated by different desorption solutions.

tion test, were applied again for phosphate removal in this process, to investigate the disparate influences of desorption reagents on the reuse efficacy of RMGA. The pH_f in solutions after resorption process and the resorption capacities of phosphate are displayed in Figs. 5 and 6, respectively, and pH_f after adsorption process as well as adsorption capacities are presented as contrasts in the corresponding graph. As can be seen, for RMGA treated by each kind of desorption solution, both the pH_f and the resorption capacities in resorption process decreased with the increase of ST, and a larger resorption capacity was related to a higher pH_f .

3.3.1. Resorption of RMGA treated by deionised water

As described in Fig. 5, pH_f in resorption process for RMGA treated by deionised water was lower than that in the original adsorption process. Because CaO was leached out continuously in the previous adsorption and desorption processes, less CaO could be released into solution, corresponding to the smaller pH rising during resorption process.

It was found out from Fig. 6 that phosphate could still be resorbed on RMGA, though the original phosphate adsorbed on RMGA had rarely been desorbed by deionised water in the desorption process (see Fig. 2). According to Yang et al. [31], it was the competition adsorption of OH^- that prevented the further adsorption of phosphate under higher pH. Thus, a lower pH in solution led to a weaker effect of competition between OH^- and phosphate, and that was why RMGA owned certain capacity for resorption. It also indicated that the active sites had not been saturated in the original adsorption process, especially for RMGA sintered under lower temperatures. Although they contained a certain amount of CaO (XRD patterns shown in Fig. 1) and caused a higher pH_f consequently, the resorption capacities of them were still higher.

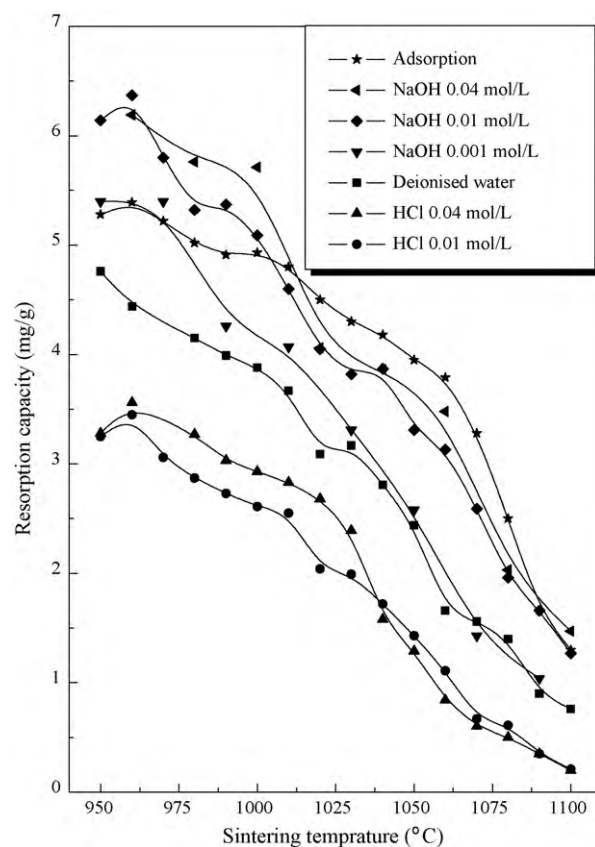


Fig. 6. The resorption capacity of phosphate for various RMGA treated by different desorption solutions.

3.3.2. Resorption of RMGA treated by HCl solution

As shown in Fig. 5, for RMGA desorbed by HCl solutions, pH_f after resorption process were fairly low, due to the numerous lixiviation of CaO by acid solutions in former process.

It can be learnt from Fig. 6 that the resorption capacities for RMGA desorbed by HCl solutions performed much disappointing than those treated by the other desorption solutions. This phenomenon implied that the ligand exchange of Cl^- was not the dominating mechanism for phosphate desorption in this research (Section 3.2.2), as otherwise concentrated phosphate could be resorbed on active sites equally due to the competition effect. As presented in Table 2, large quantities of mass loss and high concentrations of Al^{3+} existed in the solutions after desorption. Therefore, it was considered that the excess extraction of effective components during desorption mainly resulted in the poor performances for RMGA on phosphate resorption.

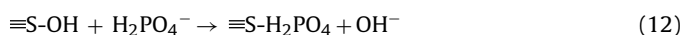
In addition, for RMGA sintered between 950 and 1030°C, the resorption capabilities of those treated by HCl solution of 0.04 mol/L were a little larger than the corresponding ones treated by HCl solution of 0.01 mol/L. According to the lighter remaining weights of RMGA that desorbed by HCl solution of 0.04 mol/L, it was speculated that some active sites inside RMGA might be exposed, owing to the erosion by concentrated acid in desorption process. However, for RMGA sintered above 1030°C, the result was opposite. The amount of effective components for phosphate adsorption reduced rapidly with the increase of ST, and they were relatively easy to be extracted from RMGA by more concentrated acid in desorption process. Thus, when ST was above 1030°C, the resorption capabilities of RMGA were considered to be influenced more significantly by the negative effect of extraction than by the positive effect of erosion.

3.3.3. Resorption of RMGA treated by NaOH solution

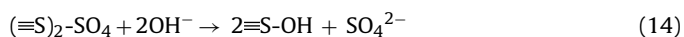
Fig. 5 illustrates that the pH_f after resorption of RMGA treated by NaOH solutions was relatively higher than those of RMGA treated by HCl solutions and deionised water. This was mainly caused by the moderate dissolution of CaO in desorption processes, because the amount of CaO leached out from RMGA by NaOH solutions was less than those by the other desorption solutions. Herein, a certain amount of CaO still released into solutions, but lower than that of the original adsorption obviously.

Although a stronger competition adsorption between OH⁻ and phosphate might existed in solutions due to the higher pH, it can be observed clearly from Fig. 6 that RMGA treated by NaOH solutions performed relatively better on phosphate resorption than those treated by other reagents. It was partly brought about by the less extraction of effective components for phosphate adsorption in desorption processes by NaOH solutions. Moreover, the resorption capacities of RMGA increased progressively with the increase of NaOH concentration, though the variation of desorption efficiencies for RMGA treated by different NaOH concentration was not obvious (see Fig. 3(b)). Therefore, it was speculated that RMGA might be ameliorated to some extent by NaOH solutions during desorption process.

In consideration of pH values which ranged between 5.0 and 9.5 in this research, the phosphate forms were determined mainly as H₂PO₄⁻ and HPO₄²⁻. According to the mechanism of phosphate adsorption explained by Huang et al. [25] and Li et al. [29], the adsorption reactions on RMGA were described in Eqs. (12) and (13):



where ≡S represents the effective site on the surface of RMGA. Hence, ≡S-OH was considered active for phosphate adsorption. While some other functional groups might exist in RM such as gypsum (CaSO₄·2H₂O) [32], the dehydrated form (CaSO₄) of which was thermally stable between 950 and 1050 °C as shown in Fig. 1. It was speculated that a ligand exchange mechanism might take place on the surface of RMGA in desorption process as Eq. (14), which provided more active sites for phosphate adsorption. According to Table 3, the decrease of SO₃ on the surface of RMGA after being treated by NaOH solution might contribute to prove this speculation. In addition, this potential ameliorating effect was promoted with the increase of NaOH concentration, and that was why RMGA desorbed by more concentrated NaOH solution performed much better on phosphate resorption.



However, as shown in Fig. 6, the resorption capacities for RMGA treated by 0.04 mol L⁻¹ NaOH solution were close to those treated by 0.01 mol L⁻¹ NaOH solution. In other words, when NaOH concentration increased from 0.001 to 0.01 mol L⁻¹ in desorption process, the resorption capacity of RMGA increased significantly. While the increasing amount of resorption capacity was not so obvious when NaOH concentration increased from 0.01 to 0.04 mol L⁻¹. It might imply that the scant amount of (≡S)₂-SO₄ limited a further amelioration under this condition, and the ligand exchange between (≡S)₂-SO₄ and OH⁻ became balanced. Thus, NaOH solution of 0.01 mol L⁻¹ was considered as a relatively optimal desorption solution for RMGA in this research, which was also cost-effective.

In addition, it can be perceived from Fig. 6 that significantly larger resorption capacities were obtained for RMGA sintered under lower temperatures when treated by NaOH solutions. For example, the resorption capabilities for RMGA sintered below 1000 °C were even larger than their relevant original adsorption capabilities when NaOH solutions of 0.01 and 0.04 mol L⁻¹ were used before. This phenomenon could be explained as follows: as shown

in Fig. 1, the characteristic diffraction peak of CaSO₄ in RMGA was more sharpened under higher ST. The results of XRD patterns indicated that the crystal structure of RMGA tended unstable when ST dropped. Therefore, the potential ameliorating action (Eq. (14)) in desorption process was superior for RMGA sintered under lower ST, and that was the reason for the better resorption performances of these RMGA.

4. Conclusions

RMGA manufactured under various ST were employed to remove phosphate from aqueous solutions, and the regeneration characteristics of them were investigated by using different desorption reagents, such as HCl, NaOH solutions and deionised water, on the basis of systematic experiments (including adsorption, desorption and resorption processes). It was concluded that the competition between OH⁻ and phosphate prevented more phosphate from being adsorbed on RMGA. Therefore, the lower pH obtained for RMGA in resorption process, which was caused by the reductive release of CaO into solution, was considered as a positive effect for phosphate resorption. The desorption efficiencies of phosphate for RMGA treated by HCl solutions were higher, due to the acid erosion on RMGA; and the corresponding resorption capacities were relatively smaller, owing to the extraction of effective components from RMGA. Although RMGA treated by NaOH solution desorbed little phosphate in desorption process, they performed relatively better on phosphate resorption. This could be explained that the chemical composition on the surface of RMGA might be ameliorated by a potential ligand exchange, which occurred in desorption process. In addition, this effect was even superior for RMGA sintered under lower ST because of the comparatively unstable crystal structure in them. Based on the overall analyses, the phosphate-adsorbed RMGA were considered optimal to be treated by 0.01 mol L⁻¹ NaOH solution, because it obtained better reuse efficacy for RMGA and was also cost-effective.

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