XRF and nitrogen adsorption studies of acid-activated palygorskite

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ABSTRACT: The effects of acid activation on the chemical composition, surface area and pore structure of palygorskite from Xuyi (Jiangsu, P.R. China) were investigated systematically using X-ray fluorescence (XRF) and BET techniques. The palygorskite samples were activated with HCl, H_2SO_4 and H_3PO_4 of various concentrations at 80ºC for 4 h. The influences of acid concentration and acid type on the chemical composition, adsorption-desorption isotherms at 77 K, pore-size distribution, surface area and pore volume were studied in detail. The contents of most components of palygorskite decrease with increasing acid concentration except for Si and Ti. HCl shows a greater activation activity and its effect on the dissolution of components of palygorskite is greater than that of H_2SO_4 and H_3PO_4. It was found that 3 mol l^{-1} H_3PO_4 is a more efficient activator for increasing the number of micropores in palygorskite, whereas 12 mol l^{-1} HCl is more suitable for use in enhancing the number of meso- and macropores. The acid concentration and acid type have a great influence on the surface area and pore volume. HCl is the most effective at enhancing the external surface area and mesopore volume of palygorskite, whereas, H_3PO_4 is more suitable for use in improving the micropore surface and volume.

KEYWORDS: palygorskite, micropore, mesopore, macropore, acid activation, X-ray fluorescence, BET, H_2SO_4, H_3PO_4.

Palygorskite is a crystalline hydrated magnesium silicate with a fibrous morphology and a theoretical formula of $Si_8Mg_5O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ which was first proposed by Bradley (1940). It contains a continuous two-dimensional tetrahedral sheet, but differs from other layer silicates in lacking continuous octahedral sheets. The tetrahedral basal oxygen atoms invert their apical direction at regular intervals, coordinating talc-like ribbons. Each talc-like ribbon alternates with channels of 3.7 Å × 6.4 Å along the fibre axis. Natural palygorskite adsorbs many exchangeable cations, evident from the isomorphic substitutions occurring during its forma-tion process. The porous structure and adsorbed cations lead to a large specific surface area, moderate cation exchange capacity, and good adsorptive and rheological properties, which have made it widely used in various applications including animal waste adsorbent, drug carrier, decolourizing agent, catalyst support, heavy metal and dye adsorbent as well as polymer reinforcement (Zhang *et al.*, 2006; Xue *et al.*, 2006; Miao *et al.*, 2007; Chen *et al.*, 2007; Annabi-Bergaya, 2008).

Acid activation is the most frequently employed method for improving physicochemical properties of clay minerals for a number of applications (Suárez-Barrios *et al.*, 1995; Rodríguez *et al.*, 1996). For palygorskite, acid activation can eliminate impurities, change its composition, generate more active OH⁻ groups on its surface,

increase its surface area and pore volume as well as the number of adsorption sites by disaggregation of palygorskite particles (Myriam *et al.*, 1998). This process leads to almost full removal of carbonate minerals and partially diminishes the Mg, Fe and Al content of palygorskite. Moreover, the incorporation of considerable amounts of silanol groups (Si−OH) onto palygorskite surfaces compared to other layer silicates can be obtained by acid activation (Galan, 1996; Myriam *et al.*, 1998). Thus, many physico-chemical properties of palygorskite are improved by acid activation, facilitating the practical applications of palygorskite. For example, water absorbency of superabsorbent composites containing palygorskite was greatly improved by acid activation of palygorskite (Li *et al.*, 2004). The effects of acid activation on the physicochemical properties of palygorskite have been investigated previously from different aspects (Barrios *et al.*, 1995). The specific surface area of palygorskite increased with increasing HCl concentration to 5 M, and then decreased with further increasing HCl concentration to 7 M according to these authors, who believed that the decreased surface area could be attributed to the blocking of the newly generated pores by impurities (Barrios *et al.*, 1995). The greatest increase in specific surface area was obtained for palygorskite by boiling with 9 M HC1 under reflux condition (Myriam *et al.*, 1998). The effect of acid activation has been studied by means of Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmisson electron micro-scopy (TEM), BET, X-ray fluorescence (XRF),

and thermo analysis simultaneously (Dai & Liu, 2005). All aspects of the basic physicochemical properties of palygorskite have been investigated previously but not in systematic detail. Thus, it is important to study the effect of acid activation on the properties of palygorskite using several techniques in detail. In-depth studies of the pore structure and chemical composition of palygorskite after acid activation have not previously been reported. In addition, unlike HCl, H_2SO_4 and H_3PO_4 are not frequently used for the acid activation of palygorskite; these two acids might have different influences on the properties.

The aim of this paper is to investigate the effects of acid activation on the pore structure and chemical composition of palygorskite using the BET and XRF techniques. The influences of acid concentration and acid type were also studied.

EXPERIMENTAL

Materials

Palygorskite (supplied as a grey powder by the Jiuchuan Clay Mineral Tech. Development Co., Ltd, Jiangsu, China) without any purification was milled through a 320-mesh screen and dried at 105ºC for 8 h before use. The XRD pattern (obtained using a PANalytical Co. X'pert PRO instrument) of the untreated palygorskite is shown in Fig. 1. HCl, H_2SO_4 and H_3PO_4 were all of analytical grade and all solutions were prepared with distilled water.
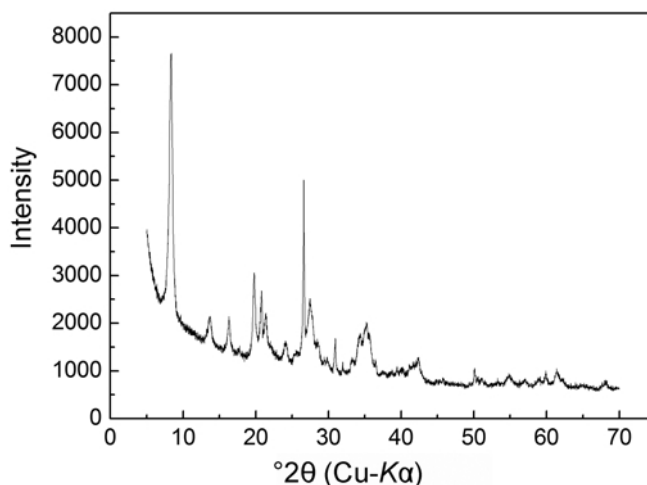

FIG. 1. XRD pattern of natural palygorskite.

Acid activation of palygorskite

Acid-activated palygorskite samples were obtained by the following method. 10.0 g of palygorskite micro-powder was immersed in 100 ml acid solutions of various concentrations and was stirred vigorously at 1000 rpm at 80ºC for 1 h. The concentrations of HCl, H_2SO_4 and H_3PO_4 are as follows:

HCl series: 1, 2, 4, 6, 8 and 12 mol l^{-1};
H_2SO_4 series: 0.1, 0.2, 0.5, 1.6, 2.3 and 3 mol l^{-1};
H_3PO_4 series: 0.2, 0.5, 1.6, 2.3, 3 and 3.6 mol l^{-1}.

After acid treatment, the palygorskite samples were washed with distilled water until pH 6 was achieved, then dried at 105ºC for 8 h and milled through a 320-mesh screen before BET and XRF analysis.

XRF analysis

The effect of acid concentration and acid type on the chemical composition of the palygorskite samples was investigated by XRF. The composition of the samples was measured in boric acid pellets using an X-ray fluorescence spectrometer (PANalytical Co., MiniPal 4). The pellets, comprising 4.0 g of palygorskite and 8.0 g of boric acid, were prepared with a pelletizer at 10 MPa.

BET analysis

The BET surface area (S_{BET}) and pore properties of the palygorskite samples were determined from N_2 adsorption-desorption experiments at 77 K using an Accelerated Surface Area and Porosimetry System (Micromeritics, ASAP 2020). All the samples were outgassed at 90ºC for 10 h to remove any moisture or adsorbed contaminants prior to the surface area measurements. The microporous surface area (S_{micro}), external surface area (S_{ext}) and the micropore volume (V_{micro}) were obtained by the t-plot method. Meanwhile, the mesopore volume (V_{meso}) and pore-size distribution were estimated by the Barrett-Joyner-Halenda (BJH) method (Barret *et al.*, 1951; Passe-Coutrin *et al.*, 2008). The total pore volume (V_{total}) was estimated from the volume of liquid N_2 held at the relative pressure $P/P_0 = 0.95$. V_{meso} was determined when $P/P_0 = {\sim}0.1-0.95$ (Girgis *et al.*, 2002). The relationships between the surface areas and pore volumes are as follows:

$$S_{BET} = S_{micro} + S_{ext} \qquad (1)$$
$$V_{total} = V_{micro} + V_{meso} \qquad (2)$$

RESULTS AND DISCUSSION

XRF analysis

The effects of acid concentration and acid type on the chemical composition of palygorskite were investigated by XRF and the results are shown in Fig. 2. As can be seen, the contents of Al_2O_3, Fe_2O_3, MgO, CaO and K_2O decrease with increasing acid concentration, while the content of SiO_2 increases gradually. The Al_2O_3, Fe_2O_3, MgO and SiO_2 contents of natural palygorskite were 13.2, 8.2, 8.9 and 67.2 wt.%, respectively. After activation by 12 mol l^{-1} HCl these changed to 6.8, 1.9, 3.2 and 87.2 wt.%, respectively. Mg, Al and Fe are the main constituents of the octahedral sheets of palygorskite. Acid activation could result in a progressive dissolution of the octahedral sheets from both ends of the palygorskite rod-like crystals (Chen *et al.*, 2004). Similar observations have also been reported by Myriam *et al.* (1998). Silicon is the dominant constituent in the tetrahedral sheets and is relatively resistant to acid attack. The relative content of SiO_2 obtained by XRF increases with the dissolution of Mg, Al and Fe, etc. Moreover, the contents of Fe_2O_3 and MgO decrease sharply with increasing acid concentration, whereas Al_2O_3 is difficult to remove compared with Fe_2O_3 and MgO. This is attributed to the fact that Al occupies the centre and Mg exclusively the edges of the octahedral ribbons of palygorskite. This result is in accordance with Güven's observations concerning the coordination of Al ions in the palygorskite structure (Güven *et al.*, 1992). In addition, it is well known that Mg salts are more soluble in acidic media than Al salts, which is another reason for the rapid decrease in Mg content. It can also be seen from Fig. 2 that HCl, H_2SO_4 and H_3PO_4 have different influences on the dissolution of the octahedral sheets, although a similar tendency was observed. The effect of acid activation by H_2SO_4 and H_3PO_4 is greater than HCl. The dissolution of the octahedral sheets is obviously accelerated and relatively low concentrations of H_2SO_4 and H_3PO_4 have the same acid activation effect as HCl. Moreover, H_2SO_4 and H_3PO_4 almost have the same effect on the dissolution of Al_2O_3 and Fe_2O_3. The effect of
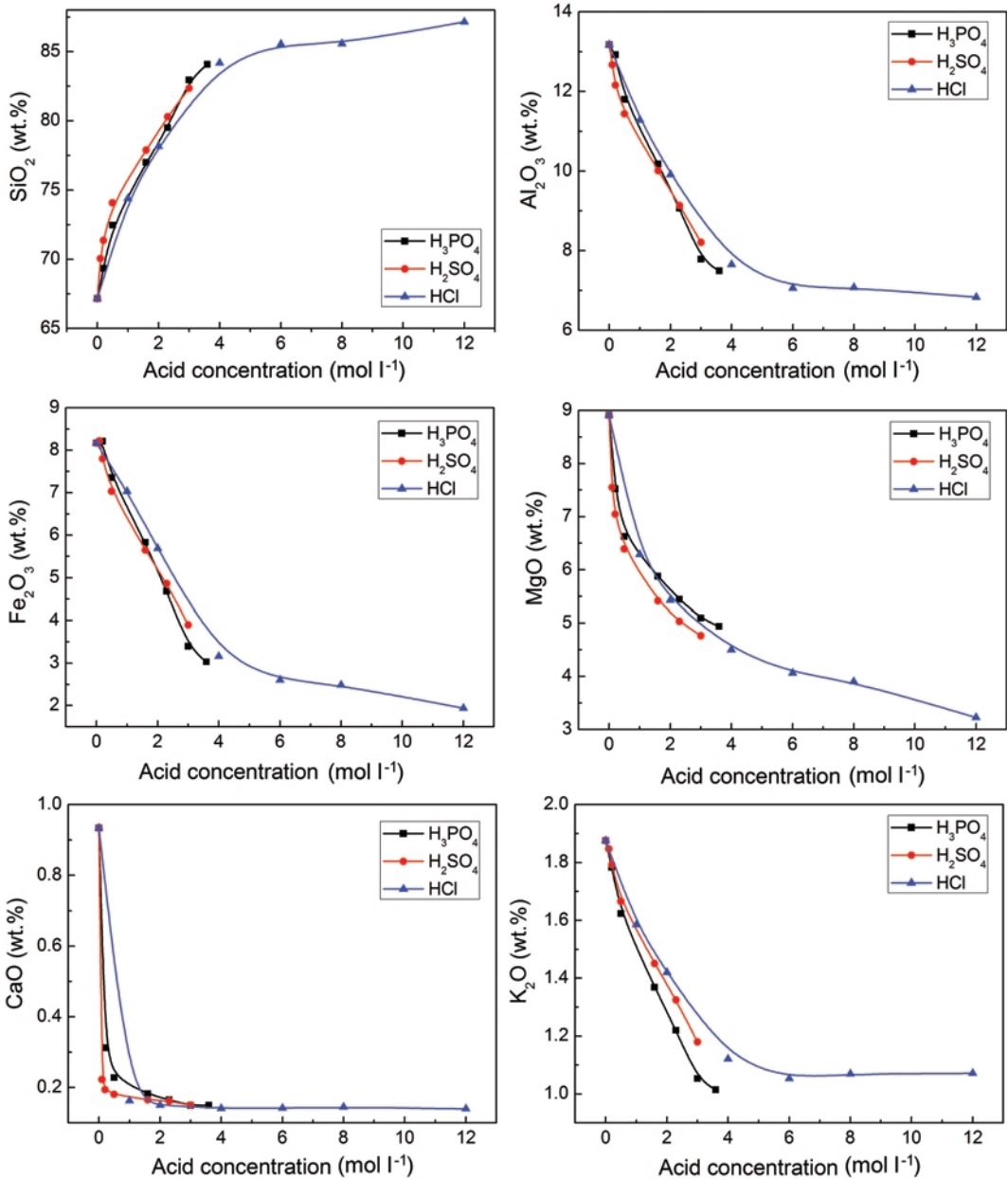
FIG. 2. Chemical composition of the natural and acid-activated palygorskite after treatment with HCl, H_2SO_4 and H_3PO_4 of various concentrations.

H_2SO_4 and H_3PO_4 on the dissolution of MgO and K_2O is in the order $H_2SO_4 > H_3PO_4$ and $H_2SO_4 < H_3PO_4$, respectively. Calcium is mainly in the form of carbonate, which can be decomposed easily in acidic media. Thus, the content of CaO decreased markedly after acid of low concentration was added and the acid type has no obvious influence on its decomposition rate.

Palygorskite is used in many fields, including as a catalyst carrier, in which the microcomponents of

palygorskite may play important roles and influence physicochemical properties. However, the effect of acid activation on microcomponents of palygorskite has seldom been investigated. Thus, the effects of acid concentration and acid type on microcomponents of palygorskite were also investigated by XRF in this work. It is apparent (Fig. 3) that there are many microcomponents in palygorskite, including Cr (~300 ppm), Mn (~800 ppm), Ni (~110 ppm), Cu (~60 ppm), Zn (~140 ppm), P (~1200 ppm) and Ti (8000 ppm), etc. These microcomponents may exist between layers of palygorskite as exchangeable cations or as part of the octahedral ribbons of palygorskite. In addition, impurities in palygorskite
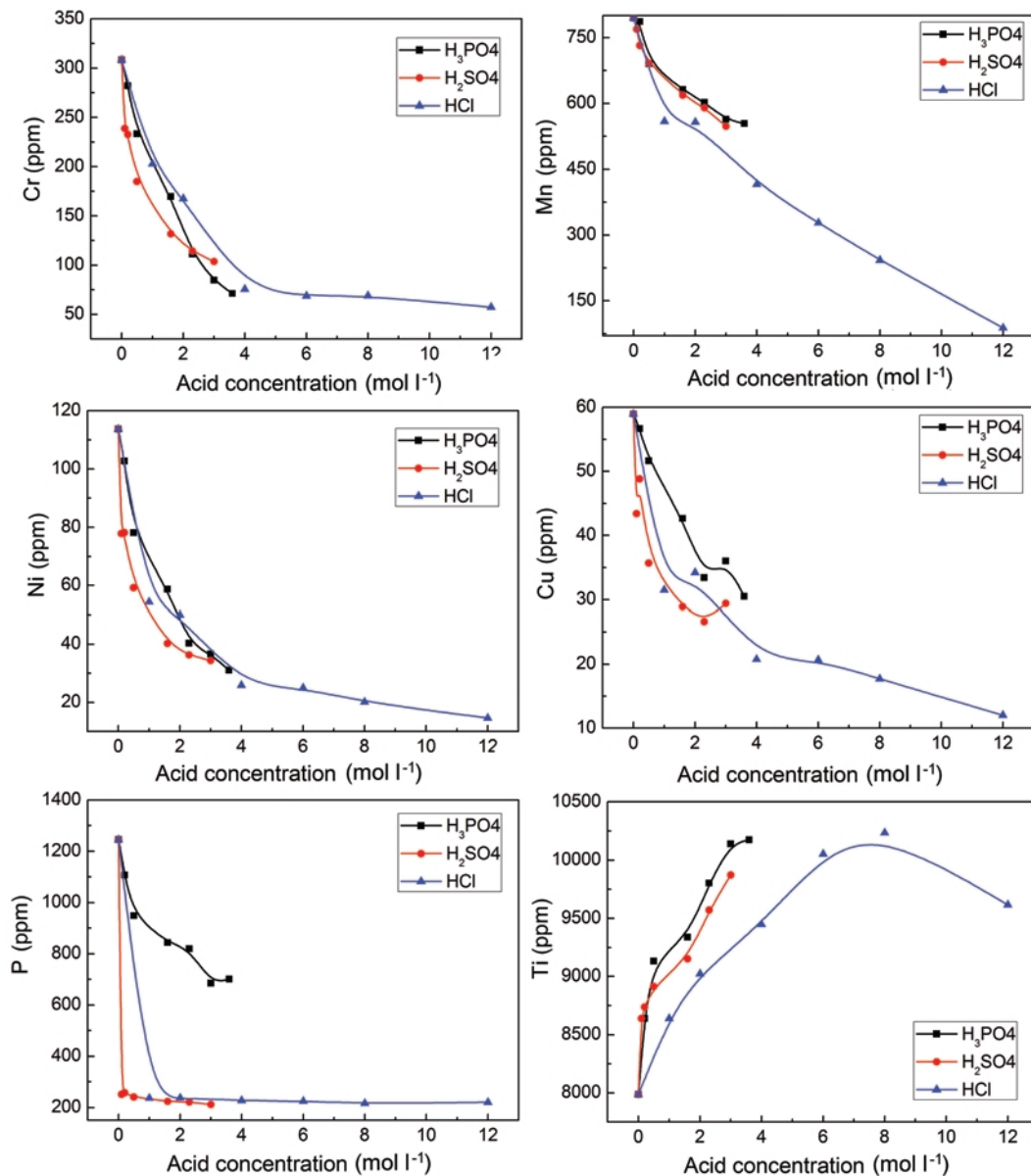

FIG. 3. Microcomponents of the natural and acid-activated palygorskite after treatment with HCl, H_2SO_4 and H_3PO_4 of various concentrations.

may also be responsible for the existence of these microcomponents. Acid activation could cause an evident dissolution of most of these microcomponents except for Ti (Fig. 3). The contents of these microcomponents decrease with increasing acid concentration in common with the main components. The effect of acid type seems to be complicated by the dissolution of these microcomponents. For example, the content of Mn decreased more noticeably with increasing HCl concentration than was the case with H_2SO_4 and H_3PO_4. The effect of acid activation on the dissolution of Cu is in the order $H_2SO_4 >$ HCl $> H_3PO_4$, whereas HCl and H_3PO_4 have similar effects on the dissolution of Ni. The P content in palygorskite after treatment with H_3PO_4 is evidently greater than those treated with HCl and H_2SO_4, which may be attributed to the adsorption of a small fraction of the anions in H_3PO_4 solution onto palygorskite. A weak acid attack by HCl and H_2SO_4 is sufficient to decrease the P content in palygorskite to 200 ppm, and further increasing their concentration has no influence on its content. The Ti content in palygorskite is very high and increases with increasing acid concentration, differing from other microcomponents. This is attributed to the fact that Ti (like Si) is stable to acid attack, and its relative content obtained from the XRF results increases with the gradual dissolution of other components of palygorskite with increasing acid concentration. The presence of Ti in the palygorskite samples may be attributed to its presence as insoluble minerals, probably rutile or ilmenite.

It can be concluded from Figs 2 and 3 that acid activation has a significant influence on the chemical composition of palygorskite. The contents of most palygorskite components decrease with increasing acid concentration except for Si and Ti. H_2SO_4 and H_3PO_4 show greater acid-activation activity and the effect on the dissolution of components of palygorskite is greater than HCl. However, the effect of acid type seems to be complicated by the dissolution of the microcomponents.

Effect of acid activation on adsorption-desorption isotherms

As reported previously, acid activation decomposes impurities (carbonate and cement) in palygorskite, disaggregates the crystals, changes the composition, generates more active OH^- groups on the surface and increases the surface area as well as the number of adsorption sites by disaggregation of palygorskite particles (Myriam *et al.*, 1998). The effects of acid activation on surface area and pore structure were further investigated in detail, since acid concentration and acid type have different influences on the chemical composition of palygorskite as shown in Figs 2 and 3.

Figure 4 shows the N adsorption-desorption isotherms of natural and acid-activated palygorskite after treatment with HCl, H_2SO_4 and H_3PO_4 of various concentrations. As can be seen, the isotherms of natural and acid-activated palygorskite are similar and belong to typical type II in the IUPAC classification. The amount of N adsorbed increases gradually with increasing relative pressure when $P/P_0 < 0.45$, in which the adsorption and desorption lines completely coincide with each other, indicating a monolayer adsorption (Yan & Zhang, 1979). This phenomenon also means that the adsorption of N occurs mainly in the micropores and forms a N monolayer on the wall. The amount of N adsorbed increases rapidly and small hysteresis loops are observed when $P/P_0 > 0.45$, indicating the existence of many meso- and macropores in all the palygorskite samples.

An evident increase in the amount of adsorbed N is observed after palygorskite is treated with HCl of various concentrations throughout the range of relative pressures investigated. For example, the amount of adsorbed nitrogen is 29 cm^3 g^{-1} for natural palygorskite at $P/P_0 = 0.10$, whereas it is 63, 70, 73, 74, 73 and 74 cm^3 g^{-1} after treatment with 1, 2, 4, 6, 8 and 12 mol l^{-1} HCl aqueous solution, respectively. Approximately another 40 cm^3 g^{-1} of N could be adsorbed by the HCl solution (concentration <2 mol l^{-1}) activated palygorskite. These data indicate that HCl solution of small concentration (such as 2 mol l^{-1} HCl solution) is sufficient to increase the number of micropores of palygorskite and a further increase of acid concentration has little influence on the amount of adsorbed N when $P/P_0 < 0.10$. It can also be seen from the upper graph in Fig. 4 that the amount of adsorbed N is 211 cm^3 g^{-1} for natural palygorskite at $P/P_0 = 0.99$; meanwhile, it is 280, 311, 390, 412, 396 and 397 cm^3 g^{-1} after treatment with 1, 2, 4, 6, 8 and 12 mol l^{-1} HCl aqueous solution, respectively. In contrast to the small influence of acid concentration on the amount of adsorbed N when $P/P_0 < 0.10$, the amount of adsorbed N at $P/P_0 = 0.99$ increases rapidly with
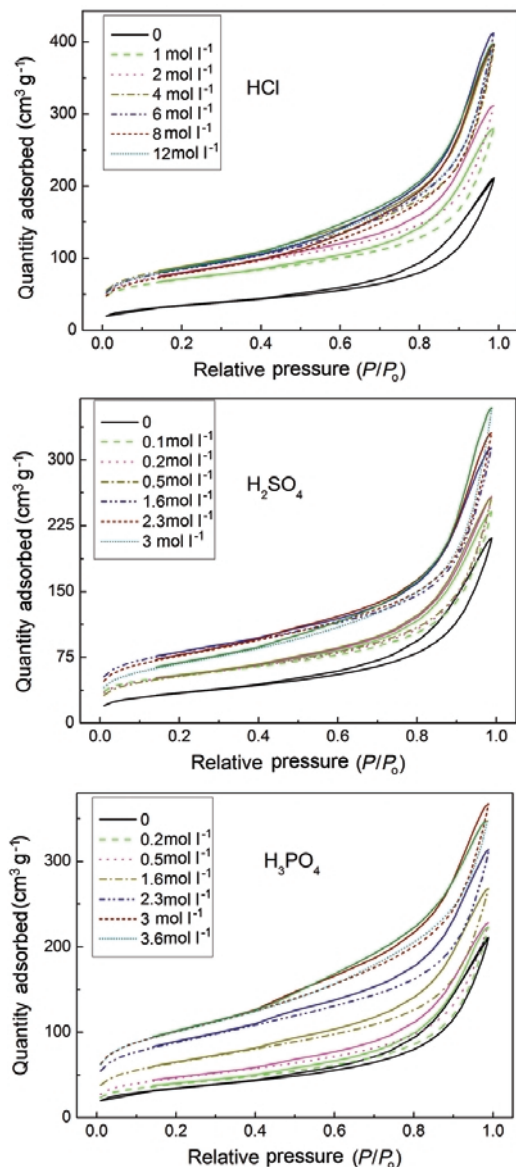
FIG. 4. Nitrogen adsorption-desorption isotherms of natural and acid-activated palygorskite after treatment with HCl, H$_2$SO$_4$ and H$_3$PO$_4$ of various concentrations.

increasing acid concentration. Approximately another 201 cm^3 g^{-1} of N could be adsorbed by palygorskite activated with 12 mol l^{-1} HCl. Only about 45 cm^3 g^{-1} of the 200 cm^3 g^{-1} of absorbed N is attributed to the newly generated micropores of palygorskite as shown above, which indicates that

acid activation by HCl not only increases the number of micropores, but also generates a larger proportion of meso- and macropores.

From the central graph in Fig. 4, it can be seen that acid activation by H$_2$SO$_4$ also enhances the amount of adsorbed N. However, the variation with acid concentration is different from that seen with HCl activation. The increase of H$_2$SO$_4$ concentration from 0.1 to 0.5 mol l^{-1} has no obvious influence on the amount of adsorbed N when P/P_0 = 0.10. The amount of adsorbed N at P/P_0 = 0.10 increases sharply from 46 to 72 cm^3 g^{-1} when the H$_2$SO$_4$ concentration increases from 0.5 to 1.6 mol l^{-1}, and then decreases to 67 and 58 cm^3 g^{-1} on further increasing the H$_2$SO$_4$ concentration to 2.3 and 3 mol l^{-1}, respectively. This decreasing tendency on increasing H$_2$SO$_4$ concentration may be attributed to the fact that SO$_4^{2-}$ of higher concentration restricts the attack of H$^+$ on palygorskite. This phenomenon remains to be further investigated. It can also be seen from this graph that H$_2$SO$_4$ solution of normal concentration (1.6 mol l^{-1}) aids the generation of micropores, whereas higher concentrations promote an increase in the number of meso- and macropores (the amount of adsorbed N increases from 211 to 359 cm^3 g^{-1}). In addition, the amount of N adsorbed by H$_2$SO$_4$-activated palygorskite is always smaller than that treated with HCl throughout the range of relative pressures investigated, which indicates that HCl is a more efficient activator than H$_2$SO$_4$.

In contrast to the abrupt increase in the amount of adsorbed N with increasing HCl concentration and the decrease in the amount of adsorbed nitrogen with further increasing H$_2$SO$_4$ concentration, the amount of adsorbed N increases gradually from 29 to 88 cm^3 g^{-1} with increasing H$_3$PO$_4$ concentration from 0 to 3.6 mol l^{-1} at P/P_0 = 0.10 as shown in the third graph of Fig. 4. The amount of adsorbed N at P/P_0 = 0.99 also increases gradually to 367 cm^3/ g with the H$_3$PO$_4$ concentration increasing to 3 mol l^{-1}, and then decreases to 347 cm^3 g^{-1} following a further increase to 3.6 mol l^{-1}. This may be attributed to the same cause as the H$_2$SO$_4$ activation, as interpreted above.

It can be concluded from Fig. 4 and Table 1 that 3 mol l^{-1} H$_3$PO$_4$ is a more efficient activator in increasing the number of micropores of palygorskite, whereas 12 mol l^{-1} HCl is more appropriate for use in enhancing the number of meso- and macropores.

Junping Zhang et al.

TABLE 1. The additional amount of nitrogen adsorbed (cm^3 g^{-1}) by acid activated palygorskite (best samples) at $P/P_0 = 0.10$ and $P/P_0 = 0.99$ compared with natural palygorskite.

P/P_0	12 mol l^{-1} HCl	3 mol l^{-1} H_2SO_4	3 mol l^{-1} H_3PO_4
0.10	45	29	59
0.99	201	148	156
~0.10−0.99[a]	156	119	97

[a] The amount of adsorbed nitrogen at $P/P_0 = 0.99$ subtracted from that adsorbed at $P/P_0 = 0.10$.

Effect of acid activation on pore-size distribution

The pore-size distribution of natural and acid-activated palygorskite samples are shown in Fig. 5. As can be seen, there are two peaks, one at ~4 nm attributed to the mesopores between layers of palygorskite and one at 20 nm attributed to the non-structural pores between microparticles of palygorskite. The first small and narrow peak corresponds to the inner surface area, whereas the second large and broad peak corresponds to the outer surface area of palygorskite (Dai & Liu, 2005; Chen, 2003). This indicates that a large proportion of the pore volume and surface area are attributed to non-structural pores among microparticles of
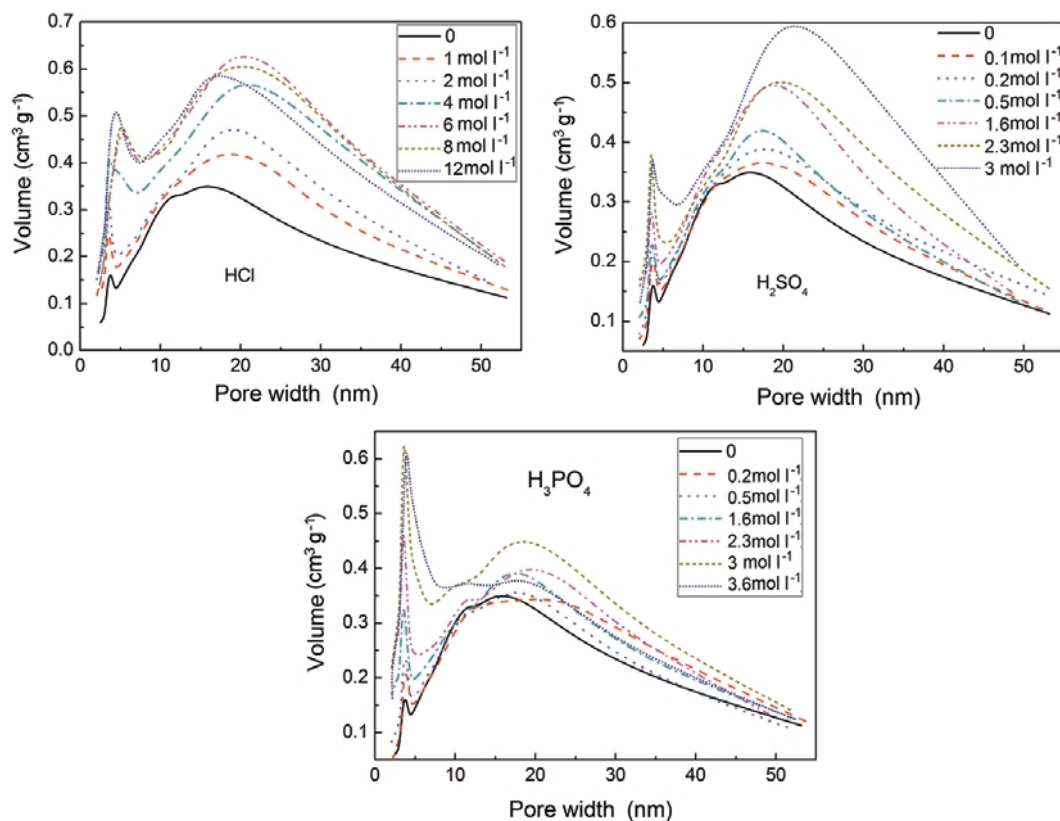

FIG. 5. Pore-size distribution of natural and acid-activated palygorskite with HCl, H_2SO_4 and H_3PO_4 of various concentrations.

palygorskite. The pore volume of palygorskite increases with increasing acid concentration. An increase of intensity of these two peaks was observed with increasing acid concentration whichever acid was used. For palygorskite samples treated with HCl, both peaks increase with increasing HCl concentration, whereas H_2SO_4 activation has a greater effect on the second peak and H_3PO_4 activation has a greater effect on the first peak. These results are in accord with the variation of N adsorption-desorption isotherms of natural and acid-activated palygorskite with HCl, H_2SO_4 and H_3PO_4 of various concentrations as shown in Fig. 4.

It can also be seen from Fig. 5 that the pore size of the second peak increases with increasing acid concentration except for the palygorskite sample treated with 12 mol l^{-1} HCl. Acid activation may eliminate impurities between the microparticles of palygorskite, and then increase the pore size

between the microparticles. An increase in pore size of the first peak is also observed with increasing acid concentration for the samples treated with HCl, but not for those treated with H_2SO_4 and H_3PO_4.

Effect of acid activation on surface area

Surface area is one of the most important physicochemical properties of palygorskite, especially when it is used as an adsorbent to remove heavy-metal ions and dyes. Chen *et al.* (2007) found that the specific surface area of acid-activated palygorskite has great influence on Cu(II) adsorption. The effects of acid concentration and acid type on the surface area of palygorskite are shown in Figs 6 and 7. S_{BET} and S_{micro} of natural palygorskite are 123 and 12.7 m^2 g^{-1}, respectively, as shown in Table 2. S_{BET} was greatly enhanced after acid activation as can be seen from Fig. 6, increasing to 249 m^2 g^{-1} after activation with 1 mol l^{-1} HCl, and then increasing gradually to 305 m^2 g^{-1} with increasing HCl concentration to 4 mol l^{-1}. Further increasing HCl concentration to 12 mol l^{-1} has no obvious influence on the S_{BET} of palygorskite. An increase was also observed after treatment with dilute H_2SO_4 (0.1 mol l^{-1}). S_{BET} of palygorskite increases gradually to 284 m^2 g^{-1} with increasing H_2SO_4 concentration to 3 mol l^{-1}. No abrupt increase was observed and it increases almost linearly to 358 m^2 g^{-1} with increasing H_3PO_4 concentration to 3 mol l^{-1}. S_{micro} of palygorskite increases sharply from 12.7 m^2 g^{-1} to 83 and
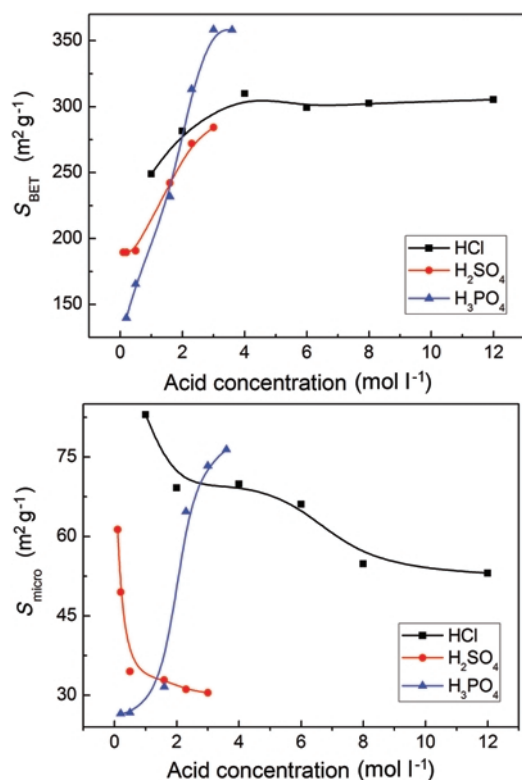

FIG. 6. Variation of S_{BET} and S_{micro} of acid-activated palygorskite with HCl, H_2SO_4 and H_3PO_4 of various concentrations.
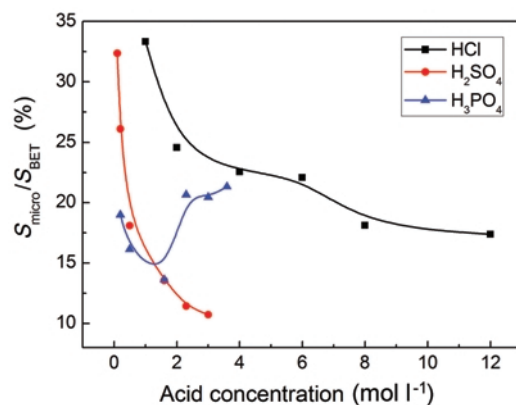

FIG. 7. Variation of S_{micro}/S_{BET} of acid-activated palygorskite with HCl, H_2SO_4 and H_3PO_4 of various concentrations.

TABLE 2. Surface area and pore volume of natural palygorskite.

Sample	S_{BET} (m^2 g^{-1})	S_{micro} (m^2 g^{-1})	S_{micro}/S_{BET} (%)	V_{total} (cm^3 g^{-1})	V_{micro} (cm^3 g^{-1})	V$_{micro}$/V$_{total}$ (%)
Natural palygorskite	123	12.7	10.3	0.283	0.005	1.77

61 m^2 g^{-1} after activation by 1 mol l^{-1} HCl and 0.1 mol l^{-1} H$_2$SO$_4$, respectively, and then decreases to 53 and 30 m^2 g^{-1} with further concentration increase to 12 and 3 mol l^{-1}, respectively. S_{micro} of palygorskite increases gradually when the H$_3$PO$_4$ concentration is <1.6 mol l^{-1}, and then increases rapidly with further increases of concentration. The micropores of palygorskite are passivated by the silica generated by the acid treatment, which avoids later attack of acid and is responsible for the decreased S_{micro} following increasing HCl and H$_2$SO$_4$ concentration (Mendioroz *et al.*, 1987). The differences between S_{BET} and S_{micro} after treatment with H$_3$PO$_4$ compared with those of HCl and H$_2$SO$_4$ may be interpreted as follows. HCl and H$_2$SO$_4$ are strong acids, whereas H$_3$PO$_4$ is only a weak acid. The H$^+$ concentration of H$_3$PO$_4$ solution is obviously lower than those of HCl and H$_2$SO$_4$ at the same concentration. H$_3$PO$_4$ should always have the lowest acid activation effect on palygorskite if the effects of anions are ignored. However, S_{BET} and S_{micro} of palygorskite activated by H$_3$PO$_4$ of a greater concentration are abnormally larger than those of HCl and H$_2$SO$_4$. Thus, anions of H$_3$PO$_4$ solution certainly play an important role in the acid-activation process. H$_3$PO$_4$ aqueous solution is mainly composed of H$_3$PO$_4$ and H$_2$PO$_4^-$ with a small fraction of HPO$_4^{2-}$ and PO$_4^{3-}$. H$_2$PO$_4^-$ may be the key factor for the abnormal phenomenon after treatment with H$_3$PO$_4$. A small fraction of H$_2$PO$_4^-$ may be closely adsorbed onto palygorskite, which may be responsible for the greater P content of palygorskite after treatment with H$_3$PO$_4$, as shown in Fig. 3. The adsorbed H$_2$PO$_4^-$ may cause disaggregation of the crystals of palygorskite owing to electrostatic repulsion, similar to hexametaphosphate (Andreola *et al.*, 2006). S_{micro}/S_{BET} decreases with increasing concentration of HCl and H$_2$SO$_4$ (Fig. 7), implying that it is the main influence of acid activation on the outer surface area of palygorskite. S_{micro}/S_{BET} initially decreases with increasing H$_3$PO$_4$ concentration to 1.6 mol l^{-1}, and then increases with

further increasing concentration, indicating the greater influence of H$_3$PO$_4$ activation on the inner surface area.

Effect of acid activation on pore volume

The effects of acid activation on V_{total} and V_{micro} of palygorskite were also investigated and are shown in Figs 8 and 9. As can be seen from Table 2, V_{total} and V_{micro} of natural palygorskite are 0.283 and 0.005 cm^3 g^{-1}, respectively. V_{micro} of natural palygorskite used in this study is very small.

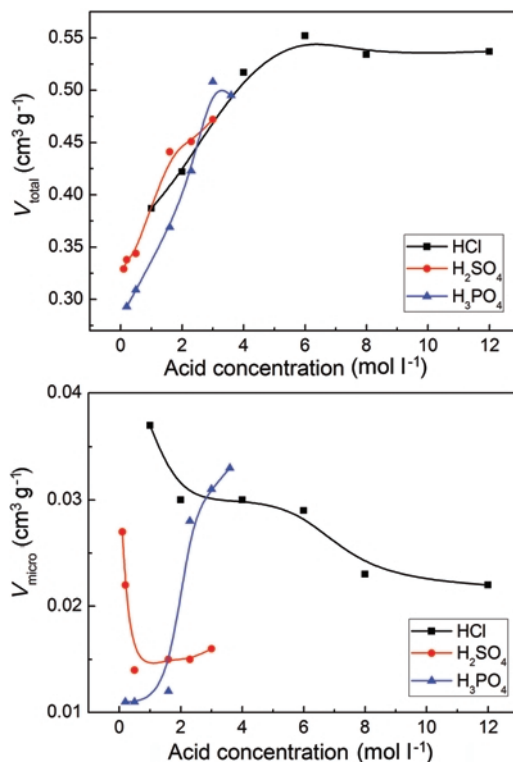FIG. 8. Variation of V_{total} and V_{micro} of acid-activated palygorskite with HCl, H$_2$SO$_4$ and H$_3$PO$_4$ of various concentrations.
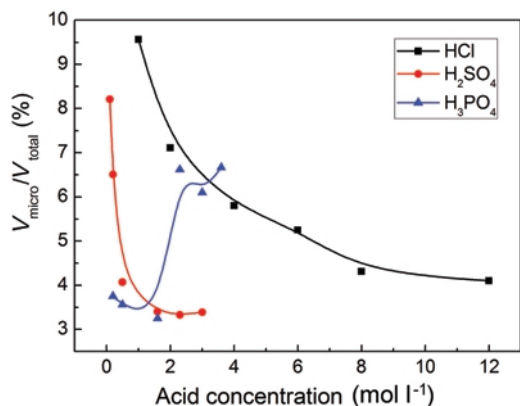
FIG. 9. Variation of V_{micro}/V_{total} of acid-activated palygorskite with HCl, H_2SO_4 and H_3PO_4 of various concentrations.

V_{total} increases with increasing acid concentration and is in the order HCl > H_2SO_4 > H_3PO_4 when their concentration is <2.3 mol l^{-1}. Further increase of the HCl concentration has no obvious influence on V_{total} and the order of V_{total} is HCl > H_3PO_4 > H_2SO_4. These results indicate that acid activation has changed the pore structure of palygorskite and HCl is the most efficient activator for increasing the pore volume compared with H_2SO_4 and H_3PO_4. The variation tendencies of V_{micro} and V_{micro}/V_{total} with acid concentration are similar to those of S_{micro} and S_{micro}/S_{BET}, as shown in Fig. 9.

CONCLUSIONS

Palygorskite from Xuyi (Jiangsu, P.R. China) was activated by HCl, H_2SO_4 and H_3PO_4 of various concentrations. XRF and BET techniques were used to study the effects of acid concentration and acid type on its chemical composition and pore structure. Most components (Al, Fe, Mg, K, Ca, Cu, Mn, Cr, etc.) of palygorskite were eroded and dissolved into aqueous solution in acidic media except for Si and Ti. A greater acid concentration aids dissolution. Acid concentration and acid type have a great influence on the surface area and pore volume. HCl is the most efficient at increasing the number of meso- and macropores of palygorskite, and then enhancing the external surface area and mesopore volume. However, H_3PO_4 is more appropriate for increasing the number of micropores, and then improving the microporous surface and micropore volume. The influence of acid concentration and

acid type on chemical composition and pore structure of palygorskite revealed in this study helps to understand its role in many practical applications.

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