

Adsorption of phosphorus by modified clay mineral waste material relating to removal of it from aquatic system

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Abstract: This study examined the application of modified clay mineral waste material (MCMWM) for removal of phosphorus (P) from aquatic systems including surface water and wastewater related to the application of recycled solid waste materials. The effects of ionic strength and pH on P adsorption by MCMWM were investigated at pH values of 3, 5, 6, 7 and 9 with P concentrations of 10, 20, 40, 100 and 200 mg/L in solution. The P adsorption was rapidly at the early stage with 95% of P in solution being adsorbed for 10 mg/L P in solution at a high pH range within 0.5 hr. The amount of P adsorbed increased with increasing ionic strength. The amount of P adsorbed increased continuously as pH values increased from 3 to 9 for P adsorption at 10 mg/L. Other series of P concentrations in solution showed variable trends due to the rates of P adsorption being affected by pH associated with the effect of ionic strength. The maximum amounts of P adsorbed and the highest percentages of P adsorbed were obtained at pH 9 for all levels of P concentrations, and at pH 7 for the lower P concentrations in solution. Calcium (Ca) ion was found to form a bridge for P adsorption in solution as the increases in the amount of P adsorbed at high pH values was related to the performance of Ca in favoring P to be adsorbed either onto the surfaces or incorporated into the structural bonds of MCMWM. Ionic strength, pH and modification process have been found to be the important factors that influenced P adsorption in solution.

Keywords: Ionic Strength, Modified Clay Mineral Waste Material (MCMWM), pH, Phosphorus Adsorption, Recycling of Solid Waste Material

1. Introduction

Phosphorus (P) is an essential nutrient in everyday life and a key element for many physiological and biological processes [1]. Phosphorus compounds are present in surface water and domestic wastewater, originating from detergents as well as from metabolism processes, and diffuse runoff from agricultural land. It has been reported that at a concentrations higher than 0.01 mg/L P may result in eutrophication [2]. Furthermore, Ruan and Gilkes [3] had found that eutrophication occurred when P concentration in a water system is higher than 0.02 mg/L, thus set up this critical value as the criterion for the evaluation of water eutrophication in Australia. Based on the chemical bonding and formation of P in the environment, it can be divided into

iron-phosphate (Fe-P), aluminium- phosphate (Al-P), and calcium- phosphate (Ca-P), as well as those bound or adsorbed by organic matter (O-P).

The increase of P in wastewater is one of the main factors of eutrophication and level causes in Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) in rivers and lakes [4]. Many water bodies everywhere in the world are experiencing an increasing number of algal blooms due to eutrophication, which reduces the amenity value and ecological health of water bodies such as lakes, slow moving rivers and drinking water reservoirs [2]. The amount of P is now being controlled by legislation on discharge limits in many counties. With concerning the increase of P, further processing to reduce the quantity of P in wastewater is demanded [4].

The modified clay mineral waste material (MCMWM) was used for P adsorption in this study. The physical, chemical and mineralogical properties, particularly the surface and structure properties to characterize environmental significance, relating to the capacity and potential application of MCMWM in adsorption of heavy metals have been investigated [5-6]. The MCMWM contains layer silicate minerals (Fig. 1), and the mineral properties were reported elsewhere [5]. It has been reported that three types of surface structures have been found in the layer silicates [7]. For the type I structure, for example in kaoline, one basal plane consists of a hexagonal or ditrigonal arrangement of siloxane rings, i.e. all surface O-atoms are doubly coordinated to Si, which itself is in fourfold coordination with O. Type II structures are represented in the opposite basal plane composed of a slightly open hexagonal array of OH groups doubly coordinated to Al, which is itself in sixfold coordination with OH and OSi/4 groups. Finally, type III structures are represented by O(OH) groups exposed along the edges of the clay platelets, and these are singly, doubly, or triply bonded to the Al and/ or Si atoms of the octahedral and tetrahedral sheets [7].

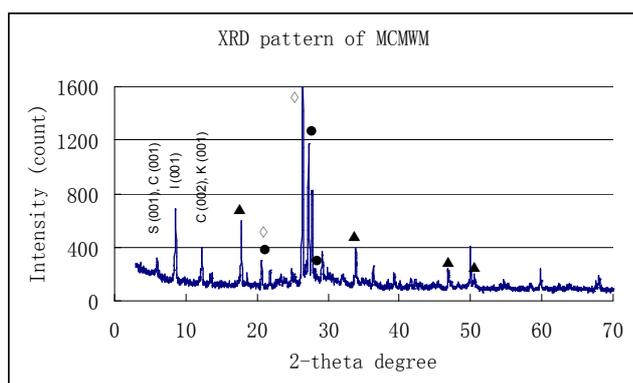


Figure 1. XRD pattern of MCMWM between 3-70° 2θ; S: smectite, C: chlorite, I: illite, K: kaolin, ▲: Ca(OH)₂, ◇: quartz, ●: feldspars

Type I surfaces tend to be very inert where there is a full balance of charge, i.e. when the lattice substitutions are absent. In cases where isomorphous substitution takes place in the tetrahedral or octahedral sheets to give rise to local deficits of positive charge, the ditrigonal hole structure is transformed into a hard Lewis base [8]. Surface charge compensation then takes place through adsorption of cations, largely in the forms of outer sphere complexes, and there is non-preferential adsorption of counter ions in the diffuse layer. The type II Surface is comparatively inert. This surface, especially when it arises from aluminum species, remains electrically neutral at the pH values which predominate in the soil. The type III surfaces, consisting of edge O(OH) group, are much different. A local deficit in the charge compensation of the O atom at the 'fractured' edges, due to the 'broken bonds', leads to a pH-dependent charge following adsorption/desorption of protons [7]. The 1:1 clay minerals which do not have isomorphous substitution in the lattice structures, are non-expanding because of hydrogen

bonding between alternating type I and II basal surfaces. Its surface properties are largely dominated by the type III groups at the edges. In contrast, the 2:1 layer clays possess only siloxane (type I) basal surfaces, and thus expose type I hexagonal arrays on both sides of the interlayer. In the absence of isomorphous substitution within the layers, such as for pyrophyllite, the layer are non-expanding since the siloxane surface reacts only weakly with water, and may be considered to be essentially hydrophobic. When isomorphous substitution takes place in the octahedral layer, for example Mg²⁺ for Al³⁺ in dioctahedral montmorillonite, the charge deficit which results in relative and uniform delocalization over the surface oxygens. Where isomorphous substitution takes place in tetrahedral sheet, such as Al³⁺ for Si⁴⁺ in illite, the charge on the three surface plane oxygen atoms coordinated to the substituent is greater than that on oxygens coordinated to silicon, and hence the charge distribution on the surface plane is less homogeneous than that for montmorillonite. Thus, the substantial differences in adsorption preferences for various ions exhibited by different clay minerals may be traced to the location and the extent of the isomorphous substitution, and to the hardness of the Lewis base sites that result [7].

Because of the dynamics, fate and transport of P in the environment attributed to its adsorption, P can play a significant role in water quality [3]. Phosphorus adsorption has been reported to be affected by a number of factors, including pH [9-11], ionic strength [12-13], type of minerals [14], organic matter content [15], and various forms of Fe and Al [15]. Among these factors the effect of pH on phosphorus sorption is probably the least understood [16-18]. While some reports have known that phosphorus sorption decreased with increase in pH in the acidic pH range [19-20], others have shown that phosphorus sorption increased with increase in pH [21-22]. There is also some evidence to show that phosphorus sorption decreased with increase in pH up to 5.0-6.0, beyond which it increased to be due largely to the difference in the exchangeable Al values of the soils [17, 23], whereas Barrow [17] cites at least six factors to be responsible. In the experiment from Eze and Loganathan [24], they found the results of quantity of the P adsorption under the different effects including ionic strength and pH.

This study dealt with the P adsorption by MCMWM at a wide range of pH values from 3 to 9, and in the various P concentrations in solution. The effects of ionic strength, pH, and modification process of MCMWM were investigated to interpret the relationships among those factors.

2. Materials and Methods

The modified clay mineral waste material (MCMWM) was supplied by a commercial company, which has been modified through physical and chemical processes in order to obtain a high porosity surface and an affinitive adsorbent. The MCMWM was finally treated by passing a sieve to obtain the powder with particle size of ≤ 0.075 mm. The

physical, chemical and mineralogical properties of MCMWM had been investigated and reported earlier [5-6].

A stock P standard solution (1000 mg/L) was firstly prepared by weighing 4.394 g of KH_2PO_4 crystals into a beaker and dissolving with little amount deionized (DI) water. The dissolved P solution was poured into a 1000 ml volumetric flask, and diluted to the mark with DI water. This P stock solution was used for making various concentrations for P adsorption.

The adsorption of P experiment was carried out following up the procedures below: (1) Various concentrations of P were firstly prepared by using the 1000 mg/L stock solution. 2, 4, 8, 20, or 40 ml of 1000 mg/L stock solution was respectively pipetted into a 100 ml of volumetric flask, and diluted to mark with DI water. The P concentrations of the series for adsorption were corresponding to 20, 40, 80, 200, 400 mg/L in solutions. (2) 0.1g (accurate to 0.0001 g) subsample of MCMWM was respectively weighed into a 50 ml tube. Then 20 ml of DI water was added to wet the solid sample, and the pH of solution was adjusted to remain at decided pH 3, 5, 6, 7, 9 by dropping either HCl or NaOH. 25 ml of various concentrations of 20, 40, 80, 200, 400 mg/L of P solution was added into each tube containing subsample, and DI water was added to mark up the mark of 50 ml. The accurate concentration of P in the solution was 10, 20, 40, 100 and 200 mg/L, respectively. The tubes were placed in a horizontal shaker to shake at a speed of 200 rpm at a temperature of 25°C for 0.5 hr. (3) The samples after shaking were filtered to obtain clear supernatants. 35 ml of clear solution was pipetted into a 50ml volumetric flask and 10 ml of Vanadate-molybdate reagent was added. After that, the solutions were diluted with DI water to the mark. After 20 mins the concentrations of P in the solutions were determined using a Vis spectrophotometer versus a blank at a wavelength of 470nm. The procedures (2) and (3) were repeated for different pH values at 3, 5, 6, 7, 9.

3. Results and Discussion

3.1. Adsorption of P Relating to P Concentration in Solution

To describe the process of P adsorption, the amount of P adsorbed per gram MCMWM was used for the evaluation of the capacity for P adsorption onto MCMWM. The amounts of P adsorbed per gram MCMWM at various pH values increased with the increase in P concentrations in solution except a couple of samples, e.g. 40 mg/L at pH 3 and 100 mg/L at pH 6 (Table 1). It is noted that when the ionic strength of P increased in solution, the reaction tend to favor P to enter the affinitive adsorption sites, thus leading the reaction towards the formation of P complex on MCMWM surfaces [25]. A basic concept of P adsorption introduced by Kuo and Lotse [26] is that, when a P ion in solution is brought in contact with the surface, and activated complex is formed. This transition site can be

identified as the configuration of the system at the maximum of the potential energy barrier [27]. The rate of reaction is the number of P ions passing over the potential energy barrier per unit time. As noticed in this experiment, the P adsorption reaction was rapid at the early stage of contact between P ions and the affinitive sites of adsorbent, e.g. the MCMWM surfaces. In particular for the P adsorption at lower concentrations, for instance, the percentage of P adsorption could reach up to 95% within half an hour when the P concentrations were between 10 and 40 mg/L. (Table 2).

Table 1. Amounts of P adsorbed per gram MCMWM at various pH values

P in solution (mg/L)	P adsorbed per gram MCMWM at various pH values (mg/g)				
	pH3	pH5	pH6	pH7	pH9
10	2.150	4.314	4.450	4.793	4.882
20	3.159	8.789	8.505	9.655	9.511
40	2.491	16.178	11.701	16.616	19.179
100	23.593	19.570	10.749	17.529	37.106
200	64.676	68.321	56.057	62.855	75.978

Table 2. Percentage of P adsorbed in solution at various pH values

P in solution (mg/L)	P adsorbed from solution at various pH values (%)				
	pH3	pH5	pH6	pH7	pH9
10	45.6	87.2	91.2	98.7	98.6
20	33.5	91.3	88.0	98.0	97.5
40	13.1	84.1	58.8	83.9	98.3
100	48.6	39.5	21.7	35.8	76.4
200	68.6	70.4	57.2	65.3	78.1

Because the P adsorption rate was high at the initial period of time of contact, followed by a decreasing trend as the adsorption was in progress [25], such decrease in the rate could be due to the reversible reaction, that is the desorption occurred along with the adsorption process. A change in the rate as the function of time determined the different adsorption performance at various levels, and this reversibility may possibly occur over a very long time [28]. An increasing P concentration in solution therefore resulted in the changes not only in abundance of P ions, as a consequence to increase the ionic strength in favoring P adsorption, but also in the increase in the amount of P desorbed from those already being adsorbed onto the surfaces of an adsorbent, at different states of equilibrium [25]. The adsorption performance of the present work did not exactly follow this pathway due to the adsorption experiments being conducted at a short period of time, which may not be in a full equilibrium state, or under a non-equilibrium condition. Ryden *et al.* [29] reported that

the amounts of inorganic P adsorbed by soil-like materials were affected by ionic strength and cation species of the matrix solution. They emphasized that particularly for non-equilibrium conditions the amounts of P adsorbed increased with increasing ionic strength. Ryden and Syers [30-31] also demonstrated that the effects of ionic strength on P adsorption was kinetic for P additions where chemisorption dominated overall adsorption but became absolute at higher P additions where a more physical, potential-determining (p.d.) adsorption mechanism accounted for an appreciable proportion of the overall amount of P adsorbed. Naidu, et al., [32] had observed that, depending on the pH, increasing ionic strength can either decrease or increase P adsorption. These phenomena had also been found in this work, indicating that the decreases in P adsorption with the increase in ionic strength were performed between 20 and 40 mg/L at pH 3 and between 40 and 100 mg/L at pH 6, while the increase in P adsorption with the increase in ionic strength was performed by all the rest concentrations (Table 1).

One of the remarkable phenomena observed in this study was that there was hysteresis or delay of P adsorption at all pH levels used, and the hysteresis appeared in 40 mg/L for pH 3 (Fig. 2a), and in 100 mg/L for pH 5, 6 and 7 (Figs. 2b, 2c and 2d), with the exception for pH 9 that exhibited almost a straight line (Fig. 2e). These phenomena were revealed by those reductions in percentage of P adsorption from the corresponding pH values and P concentrations in solution (Table 2). This finding suggested that at the early stage, P adsorption was in the non-equilibrium state. P adsorption performed in several degrees depending upon ionic strength, pH and adsorption functions including physisorption and chemisorptions that related largely to the surface and structural characteristics of an adsorbent (i.e. MCMWM) [5-6, 25, 33-35].

Another reason for hysteresis or delay of P adsorption may be the effect of pH since the hydrogen or hydroxyl in solution contributed to either favor or block P adsorption, in conjunction with the effect of P ionic strength. Furthermore, the adsorption of P onto the MCMWM could be complicated because the surfaces of MCMWM had been modified in order to create pores including nanometer-size micropores and defects within crystals for increasing the capacity of adsorption [5-6, 33, 36-37]. The effects of pH and modification process will be discussed later

The amount of P adsorbed by MCMWM varied as affected by different pH values. At the low concentration of P solution, e.g. 10 mg/L, the amounts of P adsorbed increased from 2.15 mg/g to 4.88 mg/g with the increasing values of pH from 3 to 9 (Table 1 and Fig. 3-a). However, this trend did not apply to the rest concentrations of P in solution used in this experiment. It is assumed that the effect of pH on P adsorption tended to be associated with the P concentration in solution, as this may be the combined effects from both cation and anion in solution [6, 38].

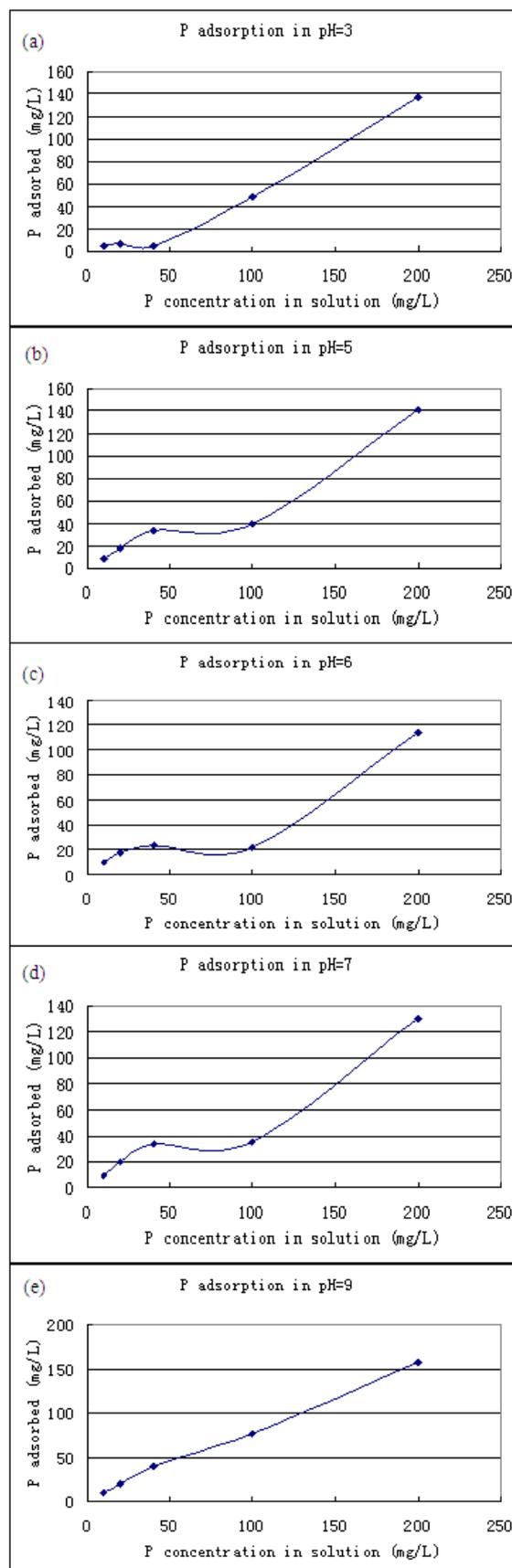


Figure 2. The amount of P adsorbed vs. P concentration in solution at (a) pH 3, (b) pH 5, (c) pH 6, (d) pH 7 and (e) pH 9.

3.2. Effect of pH on P Adsorption

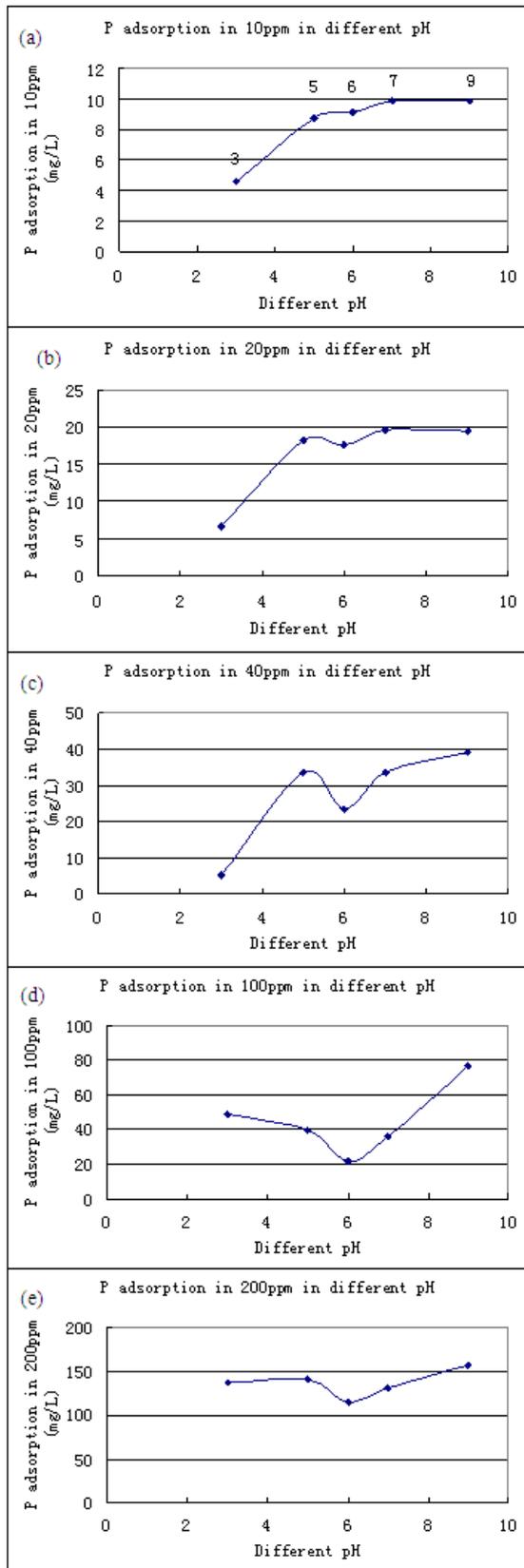


Figure 3. P adsorbed in the same concentration versus various pH values; (a) 10 mg/L, (b) 20 mg/L, (c) 40 mg/L, (d) 100 mg/L, and (e) 200 mg/L.

The lowest absorption values of P adsorption in solution were detected at pH 3, whereas the highest ones were at pH 9 (Table 1 and Fig. 3). There was a decrease in P adsorption at pH values between 5 and 6 for all levels of P concentrations in solution except for the 10 mg/L (Fig. 3a). For the 100 mg/L, the amounts of P adsorbed decreased from pH 3 to pH 6 and increased from pH 6 to pH 9, showing a “V” shape in adsorption curve (Fig. 3d).

The percentages of P adsorption in solution at various pH values are plotted in Figure 4. The lowest percentage of P adsorption was determined from the 40 mg/L sample at pH 3, 100 mg/L for all other pH values (Fig. 4). It is assumed that the percentage of P adsorption would decrease as the concentration of P in solution increased due to more P ion left in solution. The results of this study showed some variations in the percentage of P adsorption, which did not follow the hypothesis as described earlier (Table 2). This is again indicated that the percentage of P adsorption was governed by both the P concentrations and pH values, which were the combined effects of cation and anion.

The experimental data of this study showed that the P adsorption was favored under the alkaline conditions. Both the amount of P adsorbed per gram MCMWM and the percentage of P adsorbed in solution exhibited the highest average values at pH 9 (Tables 1 and 2). Since MCMWM carried both positive and negative charges in various ranges of pH values, the negative charge increased with increasing pH and the positive charge increased with decreasing pH. This co-existence of positive and negative charges is in consistency with the results reported in previous works, who proposed that positive and negative charges are spatially separated on solid particles [13, 39-40]. Barrow [41] had employed a four plane model for the adsorption of ion on a variable charged surface, explained that at high pH the surface charge is negative and that a high concentration of electrolyte causes a high number of electrolyte cations in the outer planes of adsorption, thus decreases the negative potential on the surface resulting in increased P adsorption. Bolan *et al.* [13] found that P adsorption in the soil increased between pH 3 and 4, and decreased up to pH 6 or 7 depending on the adsorbent matrixes. They also found that in some soil samples the amount of P adsorbed increased again when pH values changed from 6 to 8. The results of this study were partially consistent with their findings at the low pH range and the increasing trend of P adsorption was related to the increasing pH values under the alkaline conditions. Moreover, the maximum amount of P adsorbed by MCMWM was exhibited at pH 9 whereas that of the results of Bolan *et al.* [13] was at pH 4. Similar increases in P adsorption at high pH values have frequently been ascribed to the precipitation of calcium phosphorus because of the high levels of calcium existed [42], and as the case of the present samples containing certain amounts of Ca-minerals [5], to the formation of highly reactive polyhydroxides [43], or to the specific effect of calcium on phosphorus adsorption [44-46].

3.3. Effect of Modification Process on P Adsorption

In order to increase the adsorption capacity, the MCMWM samples had been physically and chemically modified. It was expected that modification process would increase the specific surface areas and the surface and structural defects that may play as the affinitive sites of P adsorption. The modified MCMWM material used in this study was provided by a commercial company and previously modified through physical and chemical processes. Prior to this study, the physical, chemical and mineralogical properties of the modified MCMWM materials have been investigated using BET technique for specific surface area and pore size distribution measurements, ICP-MS for heavy metal analysis, X-ray diffraction (XRD) for mineral component determination, scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX) for crystal morphology and elemental distribution, and Fourier transform infrared spectroscopy (FTIR) for mineral surface property examination [5].

After the modification processes, the particle of MCMWM became smaller with rough surfaces and structural defects. Micro-, meso-, and macro-pores, as well as voids, which contribute to the increase in specific surface area, were observed to be developed [5]. An increase in specific surface area has been reported to be related highly to the decrease in particle or crystal size [33], and the specific surface area is the most important factor in controlling the kinetic P adsorption [25]. The mineral compositions and surface/structural defects are also important factors that affect the P adsorption [25, 47-49]. Since modification processes had increased the specific surface area, structural and surface defects, and developed micropores in MCMWM. It has been reported that the most reactive sites on a surface are associated with corners, edges, and lattice disturbances [50]. Previous work has indicated that positive edge charges are probably the sites responsible for adsorption and are attributed to the exposed cation atoms (e.g. Al^{3+} and Si^{4+}) on the edge face of the crystal [51-52]. The MCMWM contains clay- and metal-minerals, and the metal oxides and clay minerals have been reported as the strong adsorbers of phosphorus ion in solution [53-57].

One of the important components in MCMWM is the Ca-contained minerals. It has been found that calcium played a significant role in influencing the chemisorptions at different pH values [24]. At the pH range of 5.0-6.0 the increase in P adsorption can be attributed to the formation of basic calcium phosphorus complex at the surface of colloid [44, 58-59] and to the formation of precipitates of these compounds in solution at pH values near neutral [60]. Calcium ion is specifically adsorbed on oxide and clay surfaces at pH values above 6.0, and it helps the adsorption of P by forming the surface complexes of basic calcium phosphorus at high concentrations of Ca^{2+} [61-62], thus Ca^{2+} fits in the cavity between two adjacent P ions and as a result

reducing the electrostatic repulsion between the negatively charged ions, allowing more P to be adsorbed [24]. The results of the present study are in agreement with what have been intensively discussed by a number of researchers.

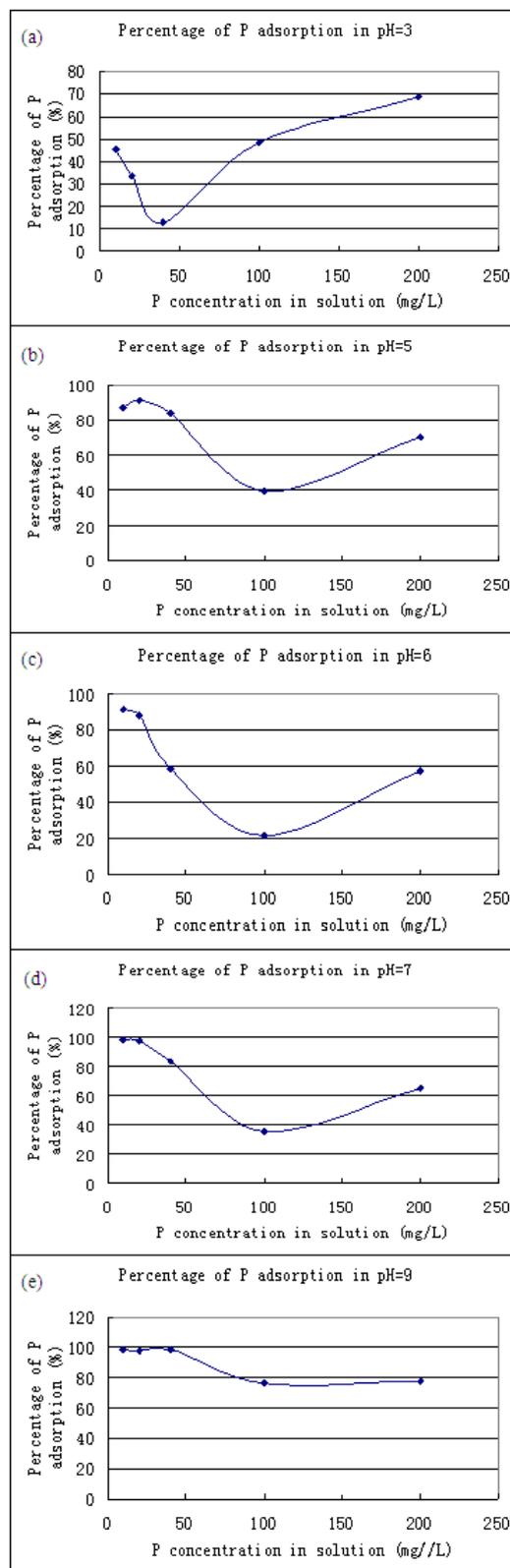


Figure 4. P adsorbed in the same concentration versus various pH values; (a) 10 mg/L, (b) 20 mg/L, (c) 40 mg/L, (d) 100 mg/L, and (e) 200 mg/L.

4. Conclusion

Phosphorus adsorption can be affected by a number of factors. The ionic strength, pH and modification process of MCMWM were studied in order to understand the relationships among these factors and their multi-effects on P adsorption by MCMWM. The findings of this research can be concluded as the following. (a) The amounts of P adsorbed increased with increasing P ionic strength. (b) When the P ionic strength increased in solution, the reaction tend to favor P to enter the affinitive adsorption sites, thus leading the reaction towards the formation of P complex on surfaces of an adsorbent. (c) P adsorption reaction was rapidly at the early stage of contact between P ions and the affinitive sites of an adsorbent, e.g. the MCMWM surfaces. (d) At the early stage, that was in the non-equilibrium state, P adsorption performed in several degrees depending upon ionic strength, pH and adsorption functions including physisorption and chemisorptions that related largely to the surface and structural characteristics of an adsorbent (i.e. MCMWM). (e) The effect of pH on P adsorption was associated with the P concentration in solution, as they are the combined effects from both cation and anion in solution. (f) P adsorption by MCMWM was favored under alkaline condition. (g) Increase in P adsorption at high pH values was due to the precipitation of calcium phosphorus because of the high levels of calcium existed to build an adsorption bridge between P ion and the surfaces of an adsorbent. (h) Modification process had increased the specific surface area, structural and surface defects, and developed internal and external pores in MCMWM, thus increased the capacity of P adsorption. The results of this work revealed the potential of its application for the removal of P in aquatic system

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