



Removal of Orthophosphate by Adsorption onto Activated Magnesium Oxide in Aqueous Solution†

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In this study, the adsorption properties of an activated magnesium oxide powders *via* precipitation method for orthophosphate was examined. The effect of different parameters such as pH, contact time, adsorbate concentration and temperature was investigated. The adsorption kinetics data were best described by the pseudo-second-order rate equation and equilibrium was achieved after 40 min. The adsorption isotherm of the activated MgO was approximated by a Langmuir type and the maximum adsorption capacity was 95.24 mg/g. The thermodynamic parameters like ΔG , ΔH and ΔS for the adsorption of phosphate ions have been evaluated and it has been found that the reaction was spontaneous and endothermic in nature.

Key Words: Orthophosphate, Activated magnesium oxide, Adsorption.

INTRODUCTION

Phosphorus is one of the primary nutrients that cause eutrophication in aquatic environments¹. An elevated level of phosphate in a water system stimulates the growth of photosynthetic algae and toxic cyanobacteria^{2,3}. Removal of phosphate from wastewater by chemical treatment⁴⁻⁷ and biological treatment⁸⁻¹⁰ has been widely investigated. Among numbers of removing techniques, adsorption is known more useful and economical¹¹⁻¹⁴. Magnesium oxide is an important inorganic material that had been widely utilized in catalysis, additives in refractory, painting and superconductor products¹⁵⁻¹⁷. Furthermore, it had been utilized as a sorbent in water treatment to remove toxic ions and organic pollutants, such as Cr, F, B, As and orange G¹⁸⁻²¹. However, no report had been made on the removal of phosphorus by MgO from aqueous environment and systematic study on the performance as well as mechanism of phosphorus removal by MgO is still missing. In this study, active MgO powder was synthesized by a precipitation process followed with a calcination process to convert the dense Mg(OH)₂ obtained into active MgO. Their phosphorus removal performance was investigated with lab-prepared water samples. With further development, this technology may offer a simple single-step treatment option to treat water with high or low concentration phosphorus contaminant.

EXPERIMENTAL

Preparation and characterization of activated MgO: All chemicals are analytical-grade reagents and were used without further purification. MgCl₂·6H₂O and NH₃·H₂O (Kermel Chemical Reagent Co. Ltd., Tianjin, China) were used as the magnesium source and the precipitation agent, respectively. In a typical synthesis, 3 mmol of MgCl₂·6H₂O was first dissolved in distilled water to form a solution at the amount of 40 mL and 40 mL of 0.15 mol/L ammonia solution was added dropwise into the above solution under continuous magnetic stirring. The resulting precipitate was centrifuged, washed with distilled water several times and dried at 70 °C to form Mg(OH)₂ powder. To obtain activated MgO, these as-prepared Mg(OH)₂ powder were then calcinated in a muffle furnace at 450 °C for 3 h with the temperature increase rate of 10 °C/min and furnace cooling. Commercial MgO powders (light, 98.5 %, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used to compare with activated MgO on the phosphorus removal performance. X-ray diffraction (XRD) analysis was carried out on Phillips X'Pert diffractometer with CuK_α radiation. Specific surface areas of Mg(OH)₂ powder and activated MgO were conducted by methylene blue method⁸.

Batch experiments: For phosphorus sorption, a series of stock phosphorus solutions with high concentrations (ranging

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from 30 to 400 mg/L) were prepared. Phosphorus solutions with lower concentrations were prepared by diluting the 100 mg/L stock P solution. All the P sorption experiments were conducted with 250 mL P solutions under magnetic stirring to disperse sorbent to ensure its good contact with P solutions. In the kinetic study of P sorption on activated MgO, different activated MgO dosages were used to examine the sorbent loading effect on the removal of P. In the sorption equilibrium experiments, P solutions with different initial concentrations at different temperatures (288, 298, 308 and 408 K) were used while the activated MgO dosage was fixed at 1 g/L and the contact time was set at 2 h. Three different initial P concentrations of 1, 50 and 200 mg/L were chosen in the comparison study of the P sorption performance between activated MgO, Mg(OH)₂ and commercially available MgO. In this study, the sorbent loadings were fixed at 1 g/L for activated MgO, commercial MgO and 1.445 g/L for Mg(OH)₂, respectively. Thus, the Mg:P molar ratios for them in water samples were the same. After recovering the sorbent by centrifugation, the supernatants were analyzed by molybdenum blue method to determine the remaining concentrations of P in the water samples.

RESULTS AND DISCUSSION

Characterization of Mg(OH)₂ and activated MgO: Fig. 1 shows the XRD patterns of as-prepared Mg(OH)₂ and the activated MgO obtained by the calcination of Mg(OH)₂ at 450 °C. For Mg(OH)₂, all the diffraction peaks belong to Mg(OH)₂ (JCPDS No. 07-0239) and no impurity peaks could be observed. The diffraction peaks are very sharp, which indicates that the Mg(OH)₂ obtained is well-crystallized. For activated MgO, all the diffraction peaks belong to MgO (JCPDS No. 65-0476) and no remaining Mg(OH)₂ peaks could be observed. This observation suggests that Mg(OH)₂ was converted to MgO completely after the calcination at 450 °C for 3 h. The specific surface area of activated MgO was determined to be 59.5 m²/g, which is more than six times as that of Mg(OH)₂ (9.8m²/g). Thus, these activated MgO created by the precipitation process and subsequent calcination have a relatively large surface area, which are beneficial for its sorption capability.

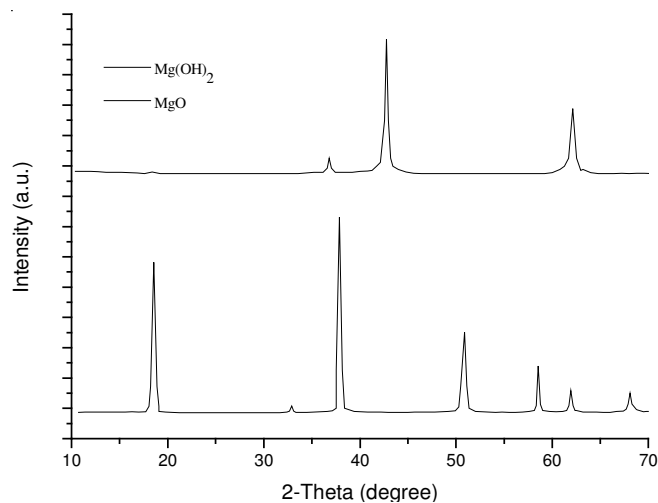


Fig. 1. X-ray diffraction patterns of Mg(OH)₂ and activated MgO

Effect of pH on phosphorus sorption: Experiments were performed at different pH. The removal increased from 22.24 mg/g to 88.35 mg/g with an increase of pH from 5 to 7 and, thereafter removal decreased from 88.35 mg/g to 58.76 mg/g with an increase of pH from 7 to 11 at 25 °C and concentration of 200 mg/L. The optimum pH for the removal of phosphorus in activated MgO was 6-7. The adsorption was most favoured in neutral solution. At the range of pH 5-6, the adsorption occurs through electrostatic attraction and ion exchange mechanism of phosphate hydrolysis products (H₂PO₄⁻, HPO₄²⁻). Also, high pH decreases the binding capacity of phosphorus on the adsorbent surface because of their competition with OH⁻ ions.

Sorption kinetics: Water samples with two initial P concentrations were used in the batch experiments. The low P concentration used was 1 mg/L and the high P concentration used was 50 mg/L. With the increase of contact time, the remaining P concentration in the water samples decreased rapidly. For example, when the loading concentration of activated MgO was 1g/L, approximately two thirds of P was removed from water in just 15 min. With the increase of the loading concentration of activated MgO, the sorption rate increased and the equilibrium time shortened. With the loading concentration increased from 0.2 to 1.0 g/L, the equilibrium P concentration in water dropped from 0.28 to 0.06mg/L. The P sorption kinetic data could be best fitted into a pseudo-second-order rate model (Fig. 2).

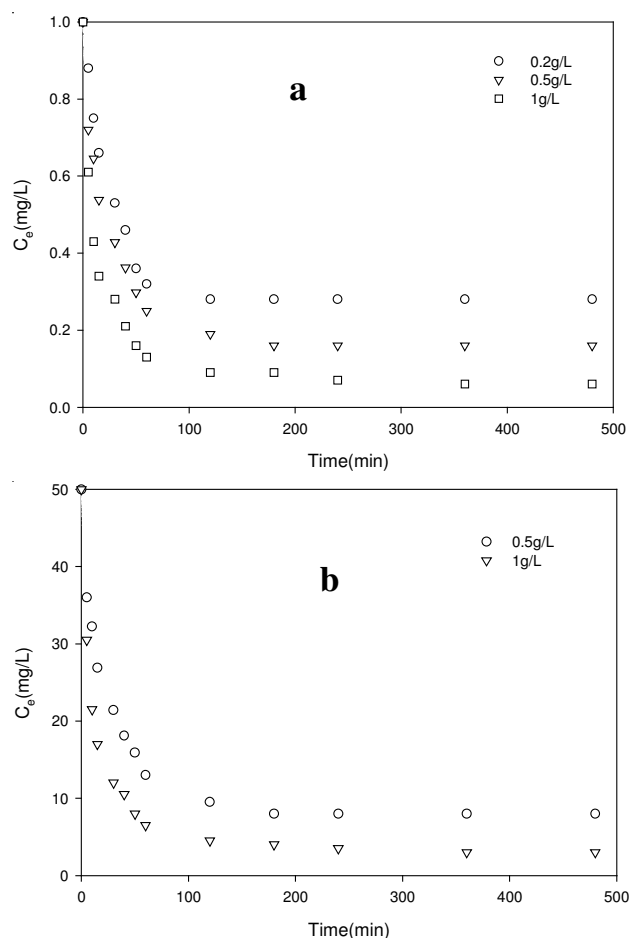


Fig. 2. Sorption kinetics of P on activated MgO at different dosages (0.2 g/L, 0.5 g/L and 1 g/L) (a) initial P concentration is 1 mg/L and (b) initial P concentration is 50 mg/L

Sorption isotherm: The sorption capacity of activated MgO on P was investigated by the equilibrium sorption isotherm study. The amount of P sorbed increased rapidly with the increase of the equilibrium P concentration in the relatively low equilibrium P concentration range and gradually reached a plateau when the equilibrium P concentration was over 40 mg/L. The equilibrium sorption data could be best fitted with the Langmuir isotherm and the maximum adsorption capacity was 95.24 mg/g (Fig. 3).

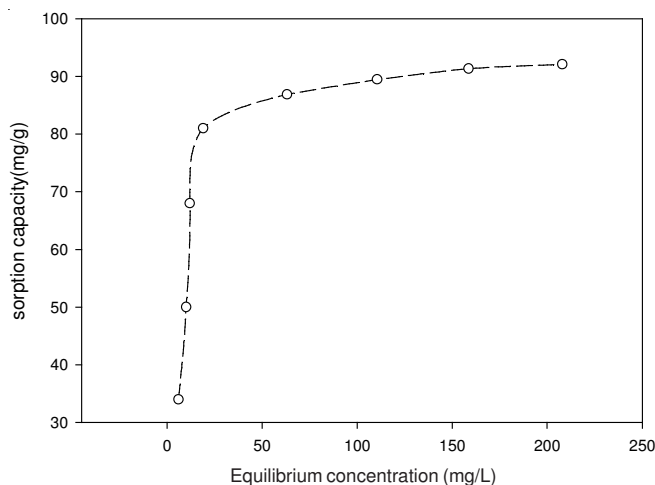


Fig. 3. Equilibrium sorption isotherm of P on activated MgO (T: 298 K; V: 250 mL; activated MgO dosages: 1 g/L)

Sorption thermodynamics: The thermodynamic equilibrium constants (K_d) of the adsorption process were computed by plotting $\ln(Q_e/C_e)$ versus Q_e . ΔG was then calculated with $\Delta G = -RT \ln K_d$. ΔH and ΔS were calculated from the slope and intercept of the plot of $\ln K_d$ vs. $1/T$ using Van't Hoff equation. The negative values of ΔG and positive values of ΔH indicate that the adsorption of phosphate onto activated MgO is spontaneous and endothermic. The values of ΔG decreased from -5.78 to -6.75 KJ/mol in the temperature range of 288-318 K. The endothermic adsorption of phosphate onto the activated MgO was enhanced by an increase in temperature. The values of ΔH are high enough to ensure strong interaction between the phosphate and the adsorbents. The positive values of ΔS state clearly that the randomness increased at the solid-solution interface during the phosphate adsorption onto the activated MgO and show that some structural exchange may occur among the active sites of the sorbent and the ions. The increase in adsorption capacity of activated MgO at higher temperatures may be caused by the activation of the adsorbent surface.

Comparison of phosphorus sorption performance between activated MgO and Mg(OH)₂ powder: Activated MgO have a much better performance to remove P from water than Mg(OH)₂ with the same Mg:P molar ratio, especially when the initial P concentration is high. The reaction between MgO and water gradually produces Mg(OH)₂ during the sorption process and the surface area of the sorbent will change gradually during the reaction. Thus, these *in situ*-formed Mg(OH)₂ should preserved most of the large surface area of activated MgO. Owing to the difficulty to determine the special surface area of the *in situ*-formed Mg(OH)₂ during its reaction with P, we measured the special surface area of *in situ* formed Mg(OH)₂

after being stirred for 24 h in water. It is determined at 23.6 m²/g, which is still much higher than that of the as-prepared Mg(OH)₂ (9.8 m²/g). The newly formed surface should also have higher activity. Thus, activated MgO have much better sorption performance than the as prepared Mg(OH)₂.

Comparison of phosphorus sorption performance between activated MgO and commercial MgO: To demonstrate the superior P removal effect of our activated MgO, we compared it with commercial MgO powders. The results demonstrate the decrease of P concentration in water samples with the increase of the treatment time by these two sorbents. With the same sorbent loading of 1 g/L, activated MgO showed a much faster P removal rate than that of commercial MgO powders. Over 92 % P in the water sample was removed by activated MgO in 1 h, while only about one third of P was removed by commercial MgO powders for the same treatment time. For the commercial MgO powders, the sorption equilibrium could not be reached even after 12 h treatment.

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