Synthesis of Mg-Decorated Carbon Nanocomposites from MesoCarbon MicroBeads (MCMB) Graphite: Application for Wastewater Treatment

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ABSTRACT: The potential application of a carbon nanocomposite from battery anode materials modified with magnesium (Mg) was explored to remove phosphate from aqueous solutions. Thermogravimetric analysis (TGA) shows that the Mg content of the prepared Mg/C composite is around 23.5%. Laboratory batch adsorption kinetics and equilibrium isotherm experiments demonstrate that the composite has an extremely high phosphate adsorption capacity of 406.3 mg PO₄/g, which is among the highest phosphate removal abilities reported so far. Results from XRD, SEM-EDX, and XPS analyses of the postsorption Mg/C composite indicate that phosphate adsorption is mainly controlled by the precipitation of P to form Mg₃(PO₄)₂·8H₂O and MgHPO₄·1.2H₂O nanocrystals on the surface of the adsorbent. The approach of synthesizing Mg-enriched carbon-based adsorbent described in this work provides new opportunities for disposing spent batteries and developing a low-cost and high-efficiency adsorbent to mitigate eutrophication.

1. INTRODUCTION

Phosphorus, as a limiting nutrient and an essential element for the growth of organisms and plants, is an indicator of surface water quality. However, excessive point and/or nonpoint discharges of phosphate into water bodies such as lakes, rivers, and seas lead to the eutrophication of freshwater and deteriorate aquatic ecosystems subsequently, which has been occurring throughout the world.1,2 To address the eutrophication issue, it is necessary to remove phosphate from aqueous solutions before their discharge into surface runoff and natural water bodies.3,4 However, phosphate removal has long been facing technical difficulties in wastewater treatment systems because of the lack of efficient and convenient approaches.

Current phosphate removal technologies for municipal sewage and industrial effluents mainly include biological, chemical, and physical treatment methods.5,6 Recently, simple physical adsorption has attracted considerable attention because it is comparatively more efficient and cost-effective.5,7 However, the most common adsorbents such as activated carbon, fly ash, slay, and oxide tailings exhibit relatively low phosphate adsorption capacity, which is lower than 20.0 mg/g.8−11 Pioneering work by Yao et al. on engineered carbon decorated with MgO nanoparticles demonstrated significantly improved phosphate removal capacity. These engineered carbon materials were obtained through the pyrolysis of anaerobically digested sugar beet tailings or Mg-enriched tomato leaves. The superior phosphate sorption ability is attributed to the presence of the nanosized MgO particles on the biochar surfaces, which can facilitate the precipitation of phosphate on carbon surfaces.12,13 In other words, the concentration of Mg in the engineered biochar controls its phosphate removal ability. However, the inherent nature of low Mg contents (<1%) in regular feedstock for carbon production, such as agricultural residues, seriously affects the phosphate
removal capability of magnesium and thus limits its practical application. Therefore, it is very important to develop new approaches for the fabrication of Mg-enriched engineered carbon to improve the rate of phosphate removal.

From the environmental perspective, producing nanosized magnesium (Mg) compounds on the surface of carbon recovered from waste materials is considered as a more eco-friendly approach with additional benefits to the economy. In our previous study, we preliminarily investigated the phosphate removal capacity of Mg-enriched engineered carbons (MesoCarbon MicroBeads, MCMB) from the anode materials of lithium-ion batteries (LIBs), which demonstrated that the Mg modification dramatically promotes the phosphate removal ability of MCMB and that the phosphate removal rate reaches as high as 95%. In this study, we conduct a series of experiments to determine phosphate sorption kinetics, mechanisms, and characteristics of Mg-enriched engineered carbons (MCMB) from LIBs. The specific objective of this study is to investigate the physicochemical properties of the original and post sorption Mg/C nanocomposites and the mechanisms governing the adsorption of phosphate onto the Mg/C nanocomposite in detail. This study provides clear evidence that building nanosized magnesium (Mg) compounds on the surface of carbon materials from the anode materials of LIBs has great potential to effectively remove phosphate from wastewater.

2. EXPERIMENTAL SECTION

2.1. Preparation of Mg/C Nanocomposites. MCMB graphite powder (Kejing Company, China) was used to synthesize nanostructured Mg/C composites in this study. MCMB was immersed in concentrated nitric acid and stirred at room temperature overnight. After being washed with deionized (DI) water and dried in an oven at 80 °C, 5 g of oxidized MCMB was added to 30 mL of 2.07 mol/L magnesium nitrate (Mg(NO3)2•6H2O, Beijing Chemical Works) solution. The mixture was stirred and then oven-dried to remove water and was heated at 10 °C/min up to 600 °C for 1 h under a N2 flow. The Mg/C composite produced from pyrolysis was washed several times with DI water and then oven-dried at 80 °C followed by grinding it into fine powder for the subsequent experiments.

2.2. Phosphate Adsorption. Phosphate solutions were prepared by dissolving potassium phosphate dibasic anhydrous (K2HPO4, Beijing Chemical Works) in DI water. The adsorption kinetics experiment was carried out by mixing 0.05 g of the Mg/C composite to 25 mL of phosphate solutions with an initial phosphate concentration of 153.2 mg/L (50 mg P/L) in 50 mL plastic centrifuge tubes. The tubes were then shaken at 200 rpm in a mechanical shaker at room temperature (22 ± 0.5 °C). At appropriate time intervals, the tubes were withdrawn and the mixtures were immediately filtered through mixed cellulose ester (MCE) membrane filters of pore size 0.22 μm.

The adsorption isotherm experiment was carried out similarly by mixing 0.1 g of Mg/C to 50 mL of phosphate solutions of different concentrations ranging from 30.6 to 1532.3 mg/L (10–500 mg P/L) in centrifuge tubes. The tubes were then shaken in a mechanical shaker for 24 h at room temperature (which is sufficient to reach adsorption equilibrium). The supernatant solution was separated from the adsorbent to determine the adsorbed phosphate concentrations. The phosphate concentrations in the liquid-phase samples were determined using the ascorbic acid method (ESS Method 310.11) and a spectrophotometer (UB 2800, Hitachi, Japan). It should be noted that the concentration of Mg(OH)2/MgO in the solution is negligible (∼100 ppm). The phosphate concentrations in the solid phase were calculated based on the initial and final aqueous concentrations. All experimental treatments were performed in duplicate, and the average values are reported. The post adsorption Mg/C samples were collected, rinsed with deionized water, and dried at 80 °C for further characterizations.

The effects of pH on phosphate adsorption by Mg/C were investigated by mixing 0.05 g of Mg/C to 25 mL of 153.2 mg/L phosphate solutions, with an initial solution pH ranging from 1 to 11 (i.e., 1.6, 3.1, 4.1, 5.4, 7.3, 8.6, and 10.4). The mixtures were shaken for 24 h and filtered to analyze aqueous and adsorbed phosphate concentrations using the same procedure. It should be pointed out that the final pH after adsorption is around 10 for all samples.

2.3. Characterizations. Thermogravimetric analysis (TGA) of carbon before and after Mg modification was carried out under a stream of air at a heating rate of 10 °C/min using a thermogravimetric analyzer (TG/DTA 6200 LAB SYS). The X-ray diffraction (XRD) analysis was carried out using a computer-controlled X-ray diffractometer (Rigaku Ultima IV, Rigaku, Japan), and data were collected in the 2θ range of 10°–90° at a scan rate of 8° per minute to investigate the crystallographic structures and the crystallite size on the post sorption Mg/C composite. A scanning electron microscope coupled with energy-dispersive X-ray spectroscopy (SEM-EDX, Quanta FEG 250, FEI, USA) was used to analyze the surface morphology of the post sorption Mg/C composite and to determine their surface elemental composition at the same spot that was used for SEM. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PHI Quantera-II spectrometer (Ulvac-PHI, INC, Japan) to further analyze the elemental composition on the post sorption Mg/C sample.

3. RESULTS AND DISCUSSION

The thermal stability of the Mg/C composite prepared is estimated using thermogravimetric analysis in a temperature range of 40–850 °C in an air atmosphere, with a heating rate of 10 °C/min. The TGA results show that the Mg/C composites have similar and comparable thermal stability to the unmodified samples, indicating that the thermal stability of the carbon sample was not affected by the Mg-modification process (Figure 1). The negligible weight loss from room temperature to about 200 °C is likely due to the dehydration of the samples. A marked weight loss of about 6.5% is observed for the Mg/C composite in the temperature range of 332–380 °C. According to the previous studies, Mg usually exists as Mg(OH)2 and MgO on the surface of the carbon matrix in the Mg/C composite. Such weight loss could be attributed to the decomposition and transformation of Mg(OH)2 to MgO. Decomposition of the main carbon chain starts at about 690 °C and continues up to 850 °C with the evolution of carbon dioxide. Almost all of the weight was removed as gaseous products for the unmodified C sample, whereas the residue of Mg/C composite is approximately 38.9% corresponding to the MgO content. The Mg concentration of the Mg/C composite is calculated to be 23.5% by weight ratio (38.9% × M(Mg)/M(MgO) = 38.9% × 24.3/40.3) based on the MgO content in the sample.
Adsorption kinetics is one of the most pivotal factors in predicting the rate of adsorption reactions and provides valuable information to understand the mechanism of the sorption. The phosphate adsorption capacity on the Mg/C sorbent as a function of contact time is provided in Figure 2A. The results suggest that the adsorption process is clearly time-dependent. As the reaction time increases, the amount of phosphate adsorbed increases until reaching its equilibrium. Specifically, the adsorption rate was quite high during the first hour, followed by a much slower sorption in the next few hours, and eventually reached its equilibrium at about 4 h (Figure 2A). This type of adsorption process is due to the significant differences in the phosphate concentration (i.e., concentration gradient). The concentration differences between the solution and the sorbent were gradually removed, and the active sites on the sorbent were used up during the first 4 h (Figure 2A). This type of adsorption process is due to the significant differences in the phosphate concentration (i.e., concentration gradient).

To further clarify the characteristics of the phosphate adsorption process onto Mg/C, mathematical models were applied to simulate the data of sorption kinetics, including the pseudo-first-order, pseudo-second-order, Ritchie Nth-order, and Elovich models, as shown below:

First order: \[
\frac{dq}{dt} = k_1(q_e - q_t)
\]  

Second order: \[
\frac{dq}{dt} = k_2(q_e - q_t)^2
\]  

Ritchie Nth-order: \[
\frac{dq}{dt} = k_n(q_e - q_t)^n
\]  

Elovich: \[
\frac{dq}{dt} = \alpha \exp(-\beta q_t)
\]

where \(q_t\) (mg/g) and \(q_e\) (mg/g) represent the amount of phosphate adsorbed at time \(t\) and at equilibrium, respectively; \(k_1\) with unit h\(^{-1}\), \(k_2\) with unit g/(mg h), and \(k_n\) with unit g\(^n\)/ (mg\(^n\) h) are adsorption rate constants for the four kinetic models, respectively. In the Elovich model, \(\alpha\) (mg/(g h)) represents the initial adsorption rate and \(\beta\) (g/mg) is the desorption constant. The first-, second-, and the Nth-order models describe the kinetics of the solid–solution system based on mononuclear, binuclear, and N-nuclear adsorption, respectively, in terms of the sorbent capacity. The pseudo-second-order kinetics model is based on the assumption that the rate-limiting step is determined by the chemical sorption, or chemisorption, process involving valence forces through sharing or exchanging of electrons between the adsorbent and the adsorbate, whereas the Elovich model is an empirical equation considering the contribution of desorption. Except for the Elovich model, all of the other three tested models fit the kinetics data quite well, with \(R^2\) exceeding 0.95 (Figure 2A). Both the kinetics parameters and the correlation coefficients from the four adsorption models are listed in Table 1. The correlation coefficients \(R^2\) vary in the order of Nth order > first order > second order > Elovich. The result reveals that the Nth-order model is the most suitable one to describe the adsorption kinetics of phosphate on Mg/C, that is, the phosphate sorption on the Mg/C composite is likely controlled by multiple mechanisms. Additionally, it indicates that the chemical bonding between adsorbent active sites and phosphate might dominate the adsorption process.

Adsorption equilibrium isotherm is the key for describing how adsorbates interact with adsorbents and providing information on the capacity of adsorbents removing pollutants under certain conditions. Five well-known models were employed to analyze the experimental data and describe the
Table 1. Best-Fit Kinetics and Isotherms Model Parameters for Phosphate Adsorption to Mg/C

| model                  | parameter 1 | parameter 2 | parameter 3 | $R^2$ |
|------------------------|-------------|-------------|-------------|-------|
| Adsorption Kinetics    |             |             |             |       |
| first-order            | $k_1 = 1.935$ (h$^{-1}$) |             |             |       |
| second-order           | $k_2 = 0.03473$ (g/mg·h) |             |             |       |
| Nth-order              |             |             |             |       |
| Elovich                | $\beta = 11.06$ (g/mg) |             |             |       |
| Adsorption Isotherms   |             |             |             |       |
| Langmuir               | $K = 0.07305$ (L/mg) | $q_e = 73.25$ (mg/g) |             | 0.9634 |
| Freundlich             | $K_f = 74.39$ (mg$^{1/n}$ L$^n$/g) | $q_e = 73.59$ (mg/g) | $n = 1.155$ | 0.9639 |
| Langmuir–Freundlich    | $K_f = 0.1106$ (L/mg$^n$) | $q_e = 74.39$ (mg/g) |             | 0.9762 |
| Redlich–Peterson       | $K_f = 0.5418$ (L/g) | $a = 77.36$ (L$^n$/mg$^n$) | $n = 0.7999$ | 0.9954 |
| Temkin                 | $b = 40.46$ (J/g/mg) | $A = 2.602$ (L/mg) |             | 0.9708 |

where $C_e$ (mg/L) represents the sorbate concentration at equilibrium and $Q$ (mg/g) is the maximum capacity for different models; $K$ (L/mg), $K_f$ (mg$^{1/n}$ L$^n$/g), $K_d$ (L$^n$/mg$^n$), and $K_f$ (L/g) are the coefficients for the first four models, respectively; $n$ (dimensionless), $a$ (L$^n$/mg$^n$), and $b$ (J/g/mg) and $A$ (L/mg) are constants for the Freundlich, Redlich–Peterson, and Temkin isotherm models, respectively. The Langmuir isotherm is applicable for the monolayer adsorption of an adsorbate on a homogeneous surface of the adsorbent, which provides information on uptake capabilities and also reflects the usual equilibrium process behavior. Freundlich isotherm reveals information regarding the heterogeneous adsorption and is not restricted to the formation of a monolayer. The Langmuir–Freundlich isotherm model is a combination of Langmuir and Freundlich models derived for predicting the heterogeneous adsorption systems, whereas other models are empirical equations, which are often used to describe chemisorptions onto the surface of a heterogeneous site.

All these models exhibit results that agree well with the experimental data (Figure 2B), and all coefficients of determination ($R^2$) exceed 0.97. On the basis of the values of $Q$ calculated using the Langmuir equation, the maximum phosphate adsorption capacity of Mg/C reaches up to 406.3 mg/g, which is much higher than those of all other carbon-based adsorbents for phosphate removal from aqueous solutions reported previously. This dramatically improved performance is probably due to the pure and uniform carbon (graphite) structure of Mg/C composite compared with that of conventional amorphous biochar, which serves as an effective matrix for precipitating phosphate from aqueous solutions by providing more active sites. In addition, the Langmuir–Freundlich model with an $R^2$ value of 0.991 and the Redlich–Peterson model with an $R^2$ value of 0.995 fit the data slightly better than the other three models. Therefore, the adsorption of phosphate onto Mg/C could be controlled by multiple processes onto the heterogeneous surface and governed by multiple mechanisms, which is consistent with the findings from previous kinetics studies.

The pH value of the solution generally plays an important role in the physicochemical reaction at the water–solid interface. To investigate the effect of pH on the phosphate removal, the Mg/C sample is examined by changing the initial pH of the solutions from 1.6 to 10.4. In general, pH does not show much impact on phosphate removal ability of Mg/C nanocomposite, indicating that this carbon material have strong affiliation to phosphate in aqueous solutions in almost the entire pH range. The phosphate adsorption was the highest when the pH is 5.4, suggesting the existence of an optimum pH for the maximum phosphate adsorption, and it is in the typical pH range of municipal and living effluents. Increasing the pH to 10.4 or decreasing it to 1.6 slightly decreases the adsorption of phosphate (Figure 3). This result is consistent with that of the previous studies: the optimum pH (although it is not significant in this study) for phosphate removal by the carbon nanocomposite surface should be around 5.2 theoretically, at which pH almost all phosphate exists in the form of H$_2$PO$_4^-$ (i.e., mononuclear adsorption). If the pH is higher or lower than the optimum value (i.e., 5.2), polynuclear interactions may be triggered to consume more adsorption sites and thus decrease
phosphate adsorption. Hence, the strong affiliation to phosphate and the broad pH suitability and flexibility of Mg/C make it well suited for the practical application in the wastewater treatment systems when compared with the traditional chemical and biological technologies, most of which are very sensitive to the operation conditions (mainly pH) and whose phosphate removal efficiency may be much lower.\textsuperscript{31}

During the phosphate adsorption process, Mg–P crystals gradually formed on the surface of adsorbent matrix. The XRD spectrum of the postsorption Mg/C sample shows strong signals of new Mg–P crystals in the form mainly of \( \text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \) and a little of \( \text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O} \) as well as of the preexisting Mg oxyhydroxides because Mg usually exists as Mg(OH)\(_2\)/MgO nanoparticles on the Mg/C surface during sintering (Figure 4).\textsuperscript{20} The particle sizes estimated using the Scherrer formula\textsuperscript{32,33} are calculated to be 29.5 ± 5.0 and 39.0 ± 7.6 nm for \( \text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \) and \( \text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O} \), respectively. The XRD results suggest that the precipitation of phosphate by Mg released from the nanocomposite could play an important role in the phosphate removal from aqueous solutions. P anions play an important role in facilitating the dissolution of Mg(OH)\(_2\) and MgO in the solution. Given the lower surface energy, the P salts formed, \( \text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \) and \( \text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O} \), prefer to nucleate and further grow on the carbon surface.\textsuperscript{19} In addition, after adsorption, the final pH of the solutions increased to around 10.9 from 5.2 and the phosphate could only exist as \( \text{PO}_4^{3-} \) and \( \text{HPO}_4^{2-} \), which further explains the formation of \( \text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \) and \( \text{MgHPO}_4 \cdot 1.2\text{H}_2\text{O} \).

The morphology of the nanoscale Mg–P crystals formed was further examined using scanning electron microscopy (SEM), and the composition was determined using energy-dispersive X-ray spectroscopy (the SEM–EDX analysis) (Figure 5A–C). As shown in the SEM image, the postsorption Mg/C shows a large amount of Mg–P nanorods covering the entire carbon surface with an average thickness of 54.6 nm (Figure 5B) compared with that before the adsorption process showing a large amount of nanoplates.\textsuperscript{17} These nanocrystals were probably converted from the nanoplatelet particles (i.e., Mg(OH)\(_2\) and MgO) on the surface of the original Mg/C composite. The significant alteration in the morphology of nanoparticles before and after P sorption suggests that the precipitation could significantly impact the P removal by the Mg/C nanocomposite. The EDX spectrum at the same spot as that of SEM images further identifies these nanorods as Mg–P particles because of the presence of high peaks of phosphorus, magnesium, and oxygen besides carbon and these four elements are well-distributed (Figures 5C and 6). EDX also indicates that the molar ratio between P and Mg is 0.86. This number is between the P and Mg molar ratio in \( \text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \) (0.67) and that in

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**Figure 4.** XRD spectrum of the postsorption Mg/C sample.

**Figure 5.** SEM images (A,B) and corresponding EDX spectra (C) of the postsorption Mg/C.

**Figure 6.** EDX mapping elements of carbon, oxygen, magnesium, and phosphorus of the postsorption Mg/C nanocomposite.
MgHPO₄·1.2H₂O (1.00), which further demonstrates that the newly formed precipitation on Mg/C is mainly composed of both Mg₅(PO₄)₃·8H₂O and MgHPO₄·1.2H₂O. In addition, EDX results also give the molar ratio of P/O as 0.10, which is smaller than that in Mg₅(PO₄)₃·8H₂O (0.13) and in MgHPO₄·1.2H₂O (0.19). The extra oxygen content from the above calculation may be attributed to the functional groups on the carbon surface, which further suggests that the functional groups on the Mg/C composite did not interact with phosphate, and therefore they do not contribute to the phosphate removal from aqueous solutions.

To further investigate the precipitation process, XPS was performed to analyze the P on the Mg/C composite. Figure 7 shows the XPS spectra of Mg 2p and P 2p regions, which demonstrate the presence of two Mg–P compounds on the postadsorption carbon surface, that is, Mg₅(PO₄)₃ and MgHPO₄ (Figure 7B,C). The spectrum of P 2p shows that the molar percentage of Mg₅(PO₄)₃ and MgHPO₄ on the composite surface is around 27.8% and 72.2%, respectively (Figure 7C). On the basis of these results, the molar ratio calculated between P and Mg is 0.82, which is very close to that of the EDX analysis (0.86). The Mg 2p spectrum shows a large quantity of Mg(OH)₂ (65.3%) besides Mg–P compound (34.7%) on the postadsorption carbon surface, which reveals that the adsorbents are capable of adsorbing more P anions from the aqueous solution until the depletion of Mg(OH)₂. XRD, SEM, EDX, and XPS analyses of the postadsorption Mg/C composite collectively indicate that the precipitation of Mg–P nanocrystals plays an important role in P removal from aqueous solutions using the Mg/C composite prepared.

4. CONCLUSIONS

As an example of preparing adsorbents for the wastewater treatment from battery anode materials, the Mg-decorated graphite nanocomposite shows an extremely high phosphate adsorption capacity of 406.3 mg/g, which is among the highest phosphate removal abilities reported so far. The sorption experiments and postadsorption characterizations indicate that phosphate adsorption is mainly controlled by the precipitation of P to form Mg₅(PO₄)₃·8H₂O and MgHPO₄·1.2H₂O nanocrystals on the surface of the adsorbent. The approach of synthesizing Mg-enriched carbon-based adsorbent in this study provides new opportunities in developing a low-cost and high-efficiency adsorbent to mitigate eutrophication and introduces a novel direction for recycling spent batteries.

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Notes

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