

Study on Adsorption and Recovery of Phosphate in Aqueous Solution by MgO Loaded Activated Carbon

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Abstract

The eutrophication of water bodies has become a serious global pollution problem. How to deal with eutrophication of water bodies scientifically and effectively is now an important issue in the environmental field. Various methods have advantages and disadvantages, and the adsorption method has the performance of convenient operation and simple application conditions. Compared with other methods, it has the advantages of higher selectivity and recyclability. Among them, magnesium oxide-loaded activated carbon has a strong ability to remove phosphate. This subject studied the effects of initial solution pH, phosphate concentration, reaction time, dosage, and coexisting ions on the removal of phosphate by magnesium oxide loaded activated carbon. The results show that the magnesium oxide loaded activated carbon has a high removal efficiency for phosphate, and it is affected by the initial solution pH, dosage and some coexisting ions.

Keywords: Activated carbon; Magnesium oxide; Phosphorus; Adsorption.

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I. INTRODUCTION

Phosphate is a nutrient for the growth of animals and plants. In nature, the main forms of phosphorus are phosphate and various organic phosphorus compounds. With the development of mining, chemical manufacturing, machinery and electronics industries. Excessive phosphate released into water will lead to water eutrophication in oceans, rivers and lakes. Water eutrophication will cause different damage depending on the environment. For example, water eutrophication will provide rich nutrition for algae. The excessive reproduction of algae occupies the living space of other organisms, the self purification ability of water body is weakened, the water quality is gradually deteriorated, and even seriously destroys the original ecological balance and species diversity of aquatic organisms, threatening the growth and health of aquatic organisms and human beings. In recent years, water eutrophication has become a serious global pollution problem. In 2007, the outbreak of cyanobacteria in Taihu Lake has warned people of the severity of water eutrophication [1]. Therefore, the treatment of phosphorus containing wastewater is becoming more and more urgent. How to scientifically and effectively treat water eutrophication is an important topic in the field of environment.

At present, the main phosphorus removal methods include: chemical precipitation method, membrane separation method, biological method, adsorption method, etc. [2] In recent years, the commonly used adsorbents are activated carbon, zeolite, slag, fly ash and activated alumina. This is mainly due to the large specific surface area, strong adsorption capacity, convenient manufacture and low cost of these materials. Compared with other phosphorus removal methods, the advantage of this adsorption method is that it has no secondary pollution, especially the physical adsorbent, which can be recycled after dephosphorization. [3] However, the phosphorus removal effect of adsorption method also has some limiting factors: adsorbent and wastewater quality. This is the key reason that limits the wide application of adsorption phosphorus removal. If the important technical problems of improving the adsorption efficiency and regeneration efficiency of adsorbents with different water quality can be solved, the space for adsorption and phosphorus removal will be larger. [4] Various methods have advantages and disadvantages, and adsorption method has the properties of convenient operation and simple application conditions. Compared with other methods, it has the advantages of high selectivity and recyclability. Soybean residue is an industrial waste with high protein content and high nitrogen content [5,6,7]. Therefore, soybean residue is used as raw material for manufacturing activated carbon in this work.

II. MATERIALS AND METHODS

2.1. Preparation of bean dregs derived activated carbon

Dissolve 10 g MgCl₂ reagent in water and stir 10 g soybean residue at room temperature (25 °C), put the colloid obtained after stirring into the mold, and put the mold into the tubular furnace. Under the protection of N₂, heat it to 800 °C at the rate of 5 °C / min and calcine it for 1 h, and finally obtain magnesium oxide loaded activated carbon. Add 20 g of soybean residue into the colloid and put it into the mold, and put the mold into the tubular furnace. In the tubular furnace, it is heated to 800 °C at the rate of 5 °C / min under the protection of N₂ and calcined for 1 h, and finally the solid product activated carbon is obtained. They are named BDC-MgO and BDC according to their components.

2.2. Batch adsorption test

Add 100 ml of K₂HPO₄ solution with concentration of 2 mol / l into 6 beakers respectively, adjust the pH to 1, 2, 4, 7, 10 and 12 respectively with 0.1 mol / L and 1 mol / L HCl solution and 0.1 mol / L NaOH solution measured by pH meter, and add 0.02 g of dried BDC-MgO into a group of triangular conical flasks (the group without BDC-MgO is used as the control group), Then use a pipette to transfer 20ml of K₂HPO₄ solution with adjusted pH value to the corresponding two groups of triangular conical flasks, put all the two groups of triangular conical flasks into the shaking table, adjust the temperature to 25 °C and take them out after shaking at a constant speed for 192 h, and then draw the calibration curve and determine the sample.

For the determination of phosphate concentration in solution, molybdenum antimony anti spectrophotometry is used in this experiment [8,9]. According to the chemical characteristics of phosphate, molybdate solution and ascorbic acid solution are used to make color developing agent to form blue complex, which is usually called phosphorus molybdenum blue. The main steps are:

(1) drawing of calibration curve: take 7 50 ml volumetric flasks, add 0, 0.5, 1, 3, 5, 10 and 15 ml of phosphate standard solution respectively, and add deionized water to 50 ml respectively.

① Color development: add 1 ML10% ascorbic acid to each colorimetric tube and mix well. After 30 s, add 2 ml molybdate solution to each tube, fully mix and place for 15 min.

② Measurement: measure the absorbance with a 10 mm or 30 mm cuvette and an ultraviolet spectrophotometer at the wavelength of 700 nm with a zero concentration solution as the reference.

(2) sample determination: take 50 supernatants of the samples filtered by the filter membrane μ L add it into a 25 ml colorimetric tube, dilute it to the mark with deionized water, add 0.5 ML10% ascorbic acid to the test tube respectively, and mix well. After 30 s, add 1 ml molybdate solution, fully mix and place for 15 min. Follow the steps of drawing a calibration curve for color development and measurement. Subtract the absorbance of the blank experiment and find out the phosphate concentration contained in the correction curve.

The formula for calculating phosphate adsorption value is as follows:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where Q_e (mmol/g) is the equilibrium adsorption capacity for Phosphate of activated carbon, m (g) is the mass of the activated carbon, V (L) is the volume of the Phosphate solution, C₀ (mmol/L) represents the initial concentration of Phosphate, C_e (mmol/L) is the adsorption equilibrium concentration of Phosphate.

III. RESULTS AND DISCUSSION

3.1. Effect of solution pH

pH is an important factor affecting the adsorption capacity of adsorbent. [10] The pH in the solution can not only affect the ionization morphology of phosphate, but also affect the adsorption performance of adsorbent through the distribution characteristics of surface charge of adsorbent [8]. The experiment was carried out at pH 1-12. The results showed that the adsorption process of phosphate depended on the pH in the reaction system. When the pH in the reaction system is 1.0 and 2.0, the phosphorus adsorption capacity of BDC-MgO is very small. It can be seen from Fig. 1 that the Q_E value in this pH range is zero. This is because the phosphate form is mainly H₃PO₄, which is not easy to be adsorbed by BDC-MgO. When the pH increases to 2.0-10.0, the adsorption value of BDC-MgO for phosphate shows an upward trend. At this time, the main form of phosphate is H₂PO₄⁻, which is easy to be adsorbed by metal oxides because of its low adsorption free energy. [11] At the same time, the active component (MgO) of BDC-MgO is easy to be lost in strong acid environment. Increasing pH value can stabilize MgO and reduce its loss. Therefore, in this pH range, if you want to improve the adsorption efficiency of phosphate, you can increase the pH value. When the pH is in the range of 10.0-12.0, the adsorption capacity of BDC-MgO for phosphate gradually decreases with the increase of pH value, because the pH value in this range is greater than the zero charge of BDC-MgO. Because the surface of BDC-MgO has been deprotonated and negatively charged, the electrostatic repulsion force between BDC-MgO and phosphate will

be generated. In addition, the effective adsorption sites for phosphate are affected by the increase of hydroxyl ions in the solution, which further limits the adsorption efficiency of BDC-MgO. Another reason for the gradual reduction of phosphorus adsorption efficiency [12,13] is that under strong alkaline conditions, more adsorption sites (S2-HPO₄, S3-PO₄) are required due to the existing form of phosphate. Similar conclusions have also been verified by Shi Chuan [14,15] and others.

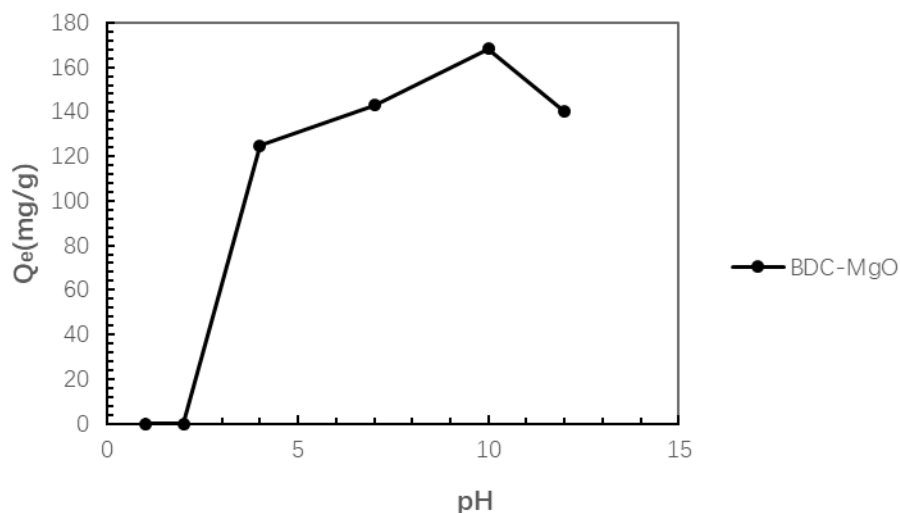


Fig. 1: The effect of different pH on the adsorption of phosphorus by BDC-MgO

3.2 Effect of dosage

It can be concluded from Fig. 2 that the adsorption value of BDC-MgO for phosphate mainly decreases with the increase of BDC-MgO dosage. [16,17] The main reason is that when the phosphorus concentration in the water is constant, increasing the dose of BDC-MgO means the increase of the total specific surface area and adsorption sites of BDC-MgO. When the dosage of BDC-MgO is sufficient, the surface of BDC-MgO provides sufficient adsorption sites to completely adsorb the phosphorus in the solution, but it continues to increase on the basis of sufficient dosage of BDC-MgO, There will be many spare adsorption sites on its surface, so the adsorption rate of BDC-MgO will be reduced. [18]

It can be seen that when the dosage of BDC-MgO is 20 mg, the adsorption value of BDC-MgO for phosphate in water is 139 mg/g, and when the dosage of BDC-MgO is 30 mg, the adsorption value of BDC-MgO for phosphate in water is 143 mg/g. it can be seen that when the dosage of BDC-MgO is increased from 20 mg to 30 mg, the removal effect of BDC-MgO on phosphate is slightly improved, [19] It indicates that the adsorption point is close to sufficient at this time; However, when the dosage exceeds 30 mg, the adsorption effect of BDC-MgO on phosphate gradually decreases, [20] indicating that there are spare adsorption sites on the surface of BDC-MgO, so the adsorption rate of BDC-MgO will decrease.

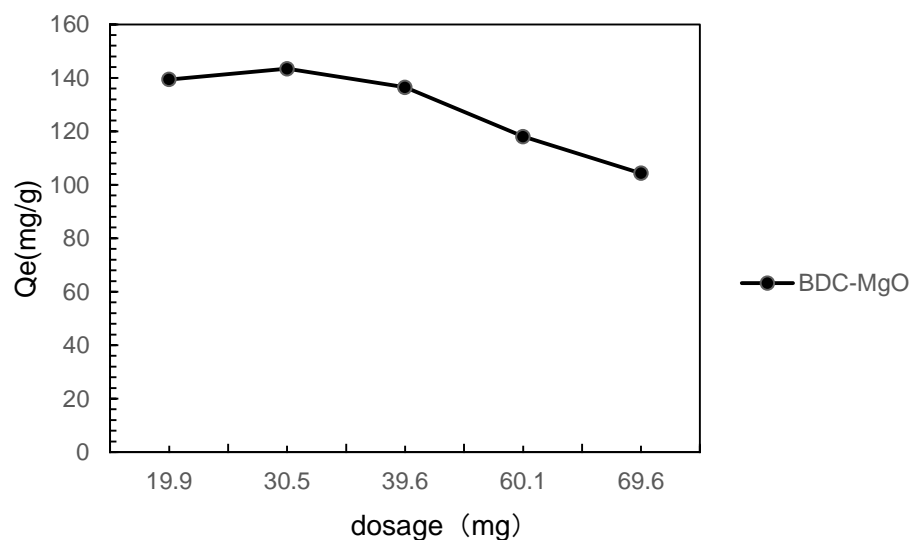


Fig. 2 The effect of BDC-MgO on phosphorus adsorption under different dosages

3.3 Influence of coexisting ions

Since the actual water to be treated usually contains anions such as NO_3^- , Cl^- , SO_4^{2-} and HCO_3^- , [21] this topic will explore the adsorption state of BDC-MgO on phosphate in the presence of coexisting anions through controlled experiments.

As shown in Fig.3, SO_4^{2-} has little effect on phosphate in adsorbed water [22]; NO_3^- and Cl^- can promote the adsorption of phosphate in water by activated carbon; HCO_3^- inhibits the adsorption of phosphate in water by activated carbon. At this time, the reason for the limited adsorption performance of BDC-MgO for phosphate: CO_3^{2-} produced by HCO_3^- ionization may compete with phosphate for the effective active site in BDC-MgO.

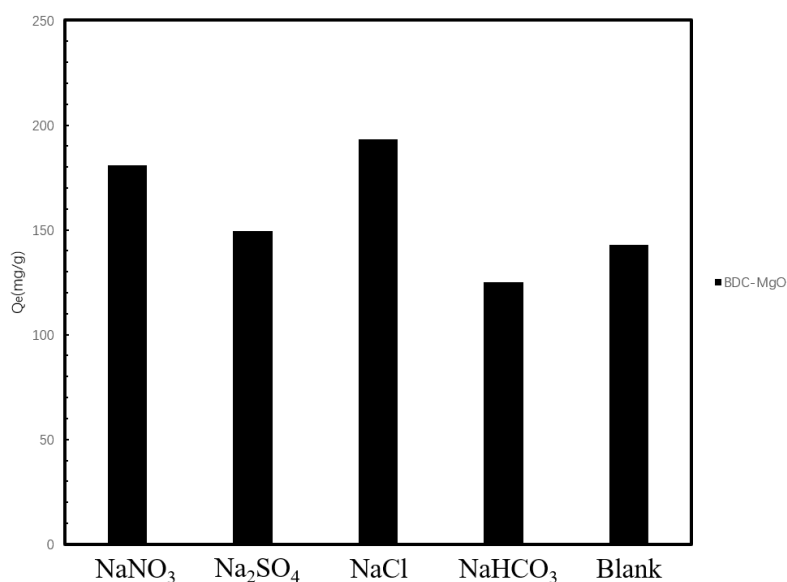


Fig. 3 The effect of different coexisting anions on the adsorption of phosphorus by BDC-MgO

IV. CONCLUSION

In this study, batch laboratory tests have proved that MgO supported activated carbon has good phosphate adsorption properties. However, there are still some problems in relevant experiments, and further experimental research is needed to be improved:

(1) In the experiment of this subject, the effects of initial solution pH, initial phosphate concentration, reaction time, dosage and coexisting ions on the removal of phosphate by MgO loaded activated carbon were studied. Other factors also affected the adsorption of MgO loaded activated carbon, such as temperature in adsorption state. The particle size of adsorbent is used to determine the optimal conditions for magnesium oxide supported activated carbon to adsorb phosphate.

(2) In the adsorption experiment, only the adsorption characteristics of MgO supported activated carbon were studied, and the desorption characteristics also need to be further studied.

(3) In the experiment of this study, because the test results have certain limitations during the limited experimental period, further testing is necessary to optimize the long-term results.

(4) The research of this subject is limited to the laboratory, and the follow-up research should expand the test scale to verify the phosphate adsorption effect of MgO loaded activated carbon in practical application. At the same time, this study focuses on the physical and chemical properties of BDC-MgO and its phosphoric acid adsorption performance and mechanism, while ignoring the economic benefits of relevant material types. Subsequent research can further supplement relevant research contents and provide sufficient theoretical basis for practical application in this field.

REFERENCES

- [1] Aamir, M., Tolouei-Rad, M., Giasin, K., Nosrati, A., 2019. Recent advances in drilling of carbon fiber-reinforced polymers for aerospace applications: a review. *Int. J. Adv. Manuf. Technol.* 105, 2289–2308.
- [2] Xie F, Wu F, Liu G, Mu Y, Feng C, Wang H, et al. 2014. Removal of Phosphate from Eutrophic Lakes through Adsorption by in Situ Formation of Magnesium Hydroxide from Diatomite. *Environmental Science & Technology*;48:582-590.
- [3] Ji X, Lee K T, Holden R, Zhang L, et al. 2010. Nanocrystalline intermetallics on mesoporous carbon for direct formic acid fuel cell anodes. *Nature Chemistry*, 2(4),286-293.
- [4] Goergen, C., Baz, S., Mitschang, P., Gesser, G., 2017. Highly drapable organic sheets made of recycled carbon staple fiber yarns, 21st International Conference on Composite Materials, Xi'an, China. p. 2017.
- [5] Karuppappan Gopalraj, S., K'arki, T., 2020. A review on the recycling of waste carbon fibre/glass fibre-reinforced composites: fibre recovery, properties and life-cycle analysis. *SN. Appl. Sci.* 2 (3), 433.
- [6] Heidarian, P., Kouzani, A.Z., Kaynak, A., Paulino, M., Nasri-Nasrabadi, B., 2019. Dynamic hydrogels and polymers as inks for three-dimensional printing. *ACS. Biomater. Sci. Eng.* 5 (6), 2688–2707.
- [7] Si, H., Zhou, L., Wu, Y., Song, L., Kang, M., Zhao, X., Chen, M., 2020. Rapidly reprocessable, degradable epoxy vitrimer and recyclable carbon fiber reinforced thermoset composites relied on high contents of exchangeable aromatic disulfide crosslinks. *Composites Part B* 199, 108278.
- [8] Ma, H, Li, J.B., Liu, W.W., Miao, M., Cheng, B.J., Zhu, S.W., 2015. Novel synthesis of a versatile magnetic adsorbent derived from corncob for dye removal. *Bioresour. Technol.*190,13–20.
- [9] M.M. Mian, G.J. Liu, B. Yousaf, B. Fu, R. Ahmed, Q. Abbas, M.A.M. Munir, R.J. Liu, One-step synthesis of N-doped metal/biochar composite using NH₃-ambiance pyrolysis for efficient degradation and mineralization of Methylene Blue, *J. Environ. Sci.* 78 (2019) 29–41.
- [10] X.Y. Xu, Y.L. Zheng, B. Gao, X.D. Cao, N-doped biochar synthesized by a facile ball-milling method for enhanced sorption of CO₂ and reactive red, *Chem. Eng. J.*368(2019)564–572.
- [11] W.C. Yu, F. Lian, G.N. Cui, Z.Q. Liu, N-doping effectively enhances the adsorption capacity of biochar for heavy metal ions from aqueous solution, *Chemosphere* 193(2018)8–16.
- [12] M.M. Mian, G.J. Liu, B. Yousaf, B. Fu, H. Ullah, M.U. Ali, Q. Abbas, M.A.M. Munir, L. Ruijia, Simultaneous functionalization and magnetization of biochar via NH₃ ambiance pyrolysis for efficient removal of Cr (VI), *Chemosphere* 208 (2018)712–721.
- [13] P. Yoo, Y. Amano, M. Machida, Adsorption of nitrate onto nitrogen-doped activated carbon fibers prepared by chemical vapor deposition, *Korean J. Chem. Eng.* 35(2018) 2468–2473.
- [14] Y. Teng, E.H. Liu, R. Ding, K. Liu, R.H. Liu, L. Wang, Z. Yang, H.X. Jiang, Bean dregs-based activated carbon/copper ion supercapacitors, *Electrochim. Acta* 194(2016) 394–404.
- [15] Y. Teng, K. Liu, R.H. Liu, Z. Yang, L. Wang, H.X. Jiang, R. Ding, E.H. Liu, A novel copper nanoparticles/bean dregs-based activated carbon composite as pseudocapacitors, *Mater. Res. Bull.* 89 (2017) 33–41.
- [16] Li, R., Wang, J.J., Gaston, L.A., Zhou, B., Li, M., Ran, X., Quan, W., Zhang, Z., Hui, H., Wen, L., 2018b. An overview of carbothermal synthesis of metal-biochar composites for the removal of oxyanion contaminants from aqueous solution. *Carbon* 129,674–687.
- [17] Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Chen, M., 2016. Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. *Bioresour. Technol.* 214, 836–851.
- [18] Jia, W., Wu, L., Li, J., Tang, D., Zhang, G., 2018. Simultaneous and efficient removal of fluoride and phosphate by Fe-La composite: adsorption kinetics and mechanism. *J. Alloy. Comp.* 753, 422–432.
- [19] Wang, S., Gao, B., Zimmerman, A.R., Li, Y., Ma, L., Harris, W.G., Migliaccio, K.W., 2015a. Removal of arsenic by magnetic biochar prepared from pinewood and natural he-matite. *Bioresour. Technol.* 175, 391–395.
- [20] Taifan, W.E., Bučko, T., Baltrusaitis, J., 2017. Catalytic conversion of ethanol to 1,3-butadiene on Mg O: a comprehensive mechanism elucidation using DFT calculations. *J. Catal.* 346, 78–91.
- [21] Khurshid, M., Abdkader, A., Cherif, C., 2019. Process development for uni directional tape structure based on recycled carbon fiber and thermoplastic fibers for fiber reinforced plastics, 19th World textile conference on textiles at the crossroads. pp. 1–6.
- [22] Wong, K.H., Turner, T.A., Pickering, S.J., 2014. Challenges in developing nylon composites commingled with discontinuous recycled carbon fibre, 16th European conference on composite materials.