REMOVAL OF PHOSPHATE (PO_4^{3-}) FROM AQUEOUS SOLUTION USING BIOCHAR DERIVED FROM PAPER SLUDGE

Hoang Le Phuong
TNU - University of Technology

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ABSTRACT

The aim of this study was to produce adsorbent from paper sludge for removal contaminants in water that has great environmental significant in utilization of waste to solve waste. Paper sludge in Hoang Van Thu paper joint stock company was collected and cleaned with tap water and distilled water. Then, it was dried and crushed to particle size of 0.25 – 0.5 mm. Finally, the paper sludge powder was carbonized at 600 ^oC for 4 hours to create the biochar (BP). Batch adsorption experiment was carried out to investigate and evaluate the effect of some factors on phosphate (PO_4^{3-}) adsorption of BP material. The results expressed that the suitable conditions for phosphate adsorption of BP occurred at solution pH of 3, initial phosphate concentration of 20 mg/L and adsorption capacity can reach 3.04 mg/g at contact time 120 minutes. The paper sludge biochar shown pretty good adsorption capacity of phosphate in aqueous solution and can be become a promising adsorbent for removal of phosphate in wastewater.

HẤP PHỤ PHOTPHAT (PO_4^{3-}) TRONG DUNG DỊCH NƯỚC SỬ DỤNG THAN SINH HỌC NGUỒN GỐC TỪ BÙN GIẤY

Hoàng Lê Phương
Trường Đại học Kỹ thuật Công nghiệp - ĐH Thái Nguyên

THÔNG TIN BÀI BÁO

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TỪ KHÓA

Hấp phụ
Hấp phụ photphat
Bùn giấy
Than sinh học
Photphat

TÓM TẮT

Mục đích của nghiên cứu là tạo ra chất hấp phụ từ bùn giấy để loại bỏ các chất ô nhiễm trong nước, điều này có ý nghĩa môi trường lớn trong việc sử dụng chất thải để xử lý chất thải. Bùn giấy thải từ công ty cổ phần giấy Hoàng Văn Thụ được thu hồi và rửa nhiều lần với nước máy và nước cất. Sau đó, bùn giấy được làm khô và nghiền đạt kích thước từ 0.25 – 0.5 mm. Bột bùn giấy thu được được các bon hoá ở 600 ^oC trong 4 giờ để tạo vật liệu than sinh học (BP). Thí nghiệm theo mẻ đã được thực hiện để đánh giá ảnh hưởng của một số yếu tố đến quá trình hấp phụ photphat (PO_4^{3-}) của vật liệu BP. Kết quả cho thấy điều kiện thích hợp cho quá trình hấp phụ photphat ở pH dung dịch bằng 3, nồng độ photphat ban đầu 20 mg/L và dung lượng hấp phụ có thể đạt 3,04 mg/g với thời gian hấp phụ 120 phút. Than sinh học chế tạo từ bùn giấy đã thể hiện khả năng hấp phụ photphat trong dung dịch nước khá tốt và có thể trở thành chất hấp phụ đầy hứa hẹn để loại bỏ photphat trong nước thải.

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Email: phuongqtn@tnut.edu.vn

1. Introduction

Phosphate (PO_4^{3-}) is the important nutrient in ecosystem. However, the excess of phosphate has caused eutrophication in freshwater ecosystem. Phosphate is released into environment mainly due to human activities such as industrial, agricultural and domestic activities [1]. The status of phosphate pollution is still increasing even though the removal of phosphate from wastewater is required before discharging it into environment.

There is variety of techniques using to remove phosphate including ion exchange, membrane separation, chemical precipitation, planted soil filter and adsorption [2], [3]. Of these techniques, adsorption is considered as one of the most effective technologies with simple operation and high efficiency [4]. Many types of adsorbents have been studied for PO_4^{3-} removal from wastewater such as hydroxides [5], fly ash [6], clay mineral [7], activated carbon [8] and biochar [9]. Recently, some types of sludges such as sewage sludge and paper sludge have been used to make biochar for adsorption of contaminants in water. Yin et al [10] used sewage sludge to create biochar for removing NH_4^+ and PO_4^{3-}. The result showed that adsorption efficiency of sewage sludge was higher than some different adsorbents. In a study reporting by Yaras and Arslanoğlu [11], paper sludge has cellulose structure with high percentage of carbon and oxygen elements. Moreover, surface morphology of paper sludge has porous structure with different sizes. Therefore, the adsorption capacity of Cu(II) ions onto biochar making from paper sludge was higher than activated carbon derived from coconut shell. Nguyen et al [12] created hydrochar from paper sludge and evaluated physical properties of this material. The results shown that the surface area, pore volume and pore size of the material were 2.2236 m^2/g, 0.0093 cm^3/g and 23.7473 nm, respectively. Although these values were less than that of magnetic modified hydrochar, it also represented that hydrochar from paper sludge has adsorption capacity for amonium in aqueous solution [12].

In Vietnam, paper sludge usually has been disposed with large amount [13]. Therefore, research on using paper sludge to product biochar for phosphate removal in water environment will have excellent environmental and economic significances. The aim of this study was to produce biochar from paper sludge and evaluate the effect of solution pH, contact time, initial phosphate concentration on phosphate adsorption of biochar.

2. Materials and methods

2.1. Preparation of biochar

The paper sludge was collected from Hoang Van Thu Joint Stock Company, Thai Nguyen province. Firstly, paper sludge was washed many times with tap water and distilled water. After cleaning with water, the paper sludger was dried at 100 ℃ for 48 h and then it was crushed to have a particle diameter from 0.25 – 0.5 mm. The obtained paper sludge powder was gradually pyrolyzed to 600 ºC in a furnace with a heating rate of 10 ºC/min for 4h. Finally, the biochar that obtained from above paper sludge powder was labeled as BP adsorbent and stored for next usages.

The pH value of the BP at the point of zero charge (pH_{PZC}) was determined using the Mular–Roberts titration technique [14].

2.2. Batch adsorption experiments

Batch model experiment was carried out to evaluate the effects of initial solution pH, contact time, adsorbent dose and initial PO_4^{3-} concentration on adsorption capacity of PO_4^{3-} on BP. The experiments were conducted in 50 mL Erlenmeyer flasks containing 25 mL of KH_2PO_4 solution. The initial solution pH was adjusted by using HCl 0.1 M and NaOH 0.1 M solution. The flasks were covered by paraffin and agitated at 120 rpm with a shaker (PH-2A, China). After the adsorption process, the mixture was filtered with filter paper that having pore size of 11 μm. The concentration of PO_4^{3-} in the solution was determined by the Vanado-molybdo phosphoric acid method with an UV–Vis spectrophotometer. All experiments were conducted in three times.

The adsorption capacity of PO_4^{3-} onto the biochar at any time t (q_t, mg/g) and equilibrium (q_e, mg/g) were calculated by the equations below:

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

$$q_t = \frac{(C_o - C_t)V}{M} \quad (2)$$

Where C_0, C_t and C_e (mg/L) are concentrations of PO_4^{3-} at beginning time, any time t, and equilibrium, respectively; V (L) is the volume of solution; M (g) is the dry weight of BP adsorbent.

3. Results and discussion

3.1. Influent of pH

The pH is one of the important factors influencing the phosphate adsorption onto BP because it affects not only the presence of phosphate hydroxyl groups but also the surface properties of the adsorbent. The effect of solution pH on phosphate adsorption capacity of BP was studied with the following conditions: BP dosage of 0.1 g/25 mL phosphate, initial phosphate concentration of 20 mg/L and contact time of 60 min at room temperature (25 ^oC). The pH of solution was changed in range from 3.0 to 10.0. The experimental results are shown in Fig. 1a. It could be observed that when initial solution pH increased from 3.0 to 10.0, the adsorption capacity and removal efficiency for phosphate of BP decreased. Namely, the phosphate adsorption capacity and removal efficiency of BP reached maximum of 2.45 mg/g and 47.3% at pH = 3.0, while these values decreased to 1.07 mg/g and 24.31% at pH = 10.0, respectively. At different pH values, the phosphate can exist in different forms. At solution pH between 2.15 and 7.2, the main phosphate species is $H_2PO_4^-$. However, when pH is between 7.2 and 12.33, HPO_4^{2-} is the main form [8]. Therefore, at high pH value, the increasing of ion OH^- concentration in the solution competed with phosphate ions for adsorption sites on BP leading to the decrease in the phosphate adsorption capability [8]. Moreover, the point of zero charge (pH_{PZC}) of BP was found to be 8.23 (Fig. 1b). This result indicated that at initial pH > 8.23, the surface of BP was negatively charged and thus caused the decrease the adsorption of anion ions at $pH > pH_{PZC}$ significantly. Generally, solution pH affects strongly adsorption capacity and surface charge of biochar. In this study, the optimal pH for adsorption of phosphate onto BP was reported at pH of 3. The similar result also was found in other studies [15].

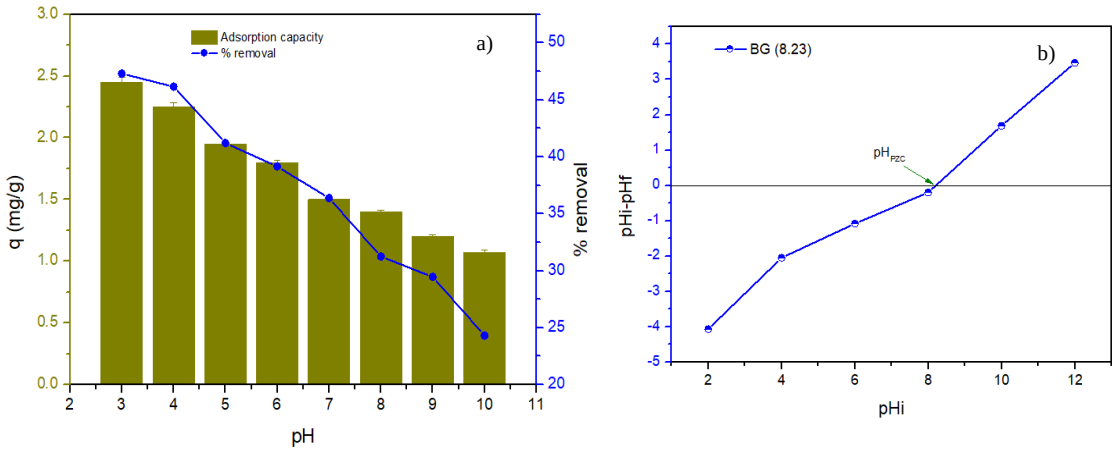

Figure 1. *(a) Effect of pH on phosphate adsorption and (b) pH_{PZC} of BP*

3.2. Effect of contact time

The affection of contact time on the PO_4^{3-} adsorption onto BP was evaluated at initial phosphate concentration of 20 mg/L, adsorbent dosage of 0.1 g/25 mL phosphate, solution pH of 3.0 and contact time from 0 to 240 min. The results are indicated in Fig. 2.

It was seen that for the first 30 min of adsorption process, adsorption capacity of phosphate onto BP increased significantly from 0.78 mg/g to 2.36 mg/g. From 60 to 120 min, the adsorption capacity increased slowly to 3.04 mg/g and become constant from 150 to 240 min. This phenomenon can be explained that at the initial stage, a large number of active sites on the surface of BP lead to adsorption capacity raised rapidly [2]. After this period of time, the number of vacant sites declined, the adsorption process slowed down and remained stable [16]. According to this result, the contact time of 120 min was considered as the best time for PO_4^{3-} adsorption onto BP and used in the subsequent experiments. This trend was similar as the result reported by other studies about adsorption of phosphate from aqueous solution [15].

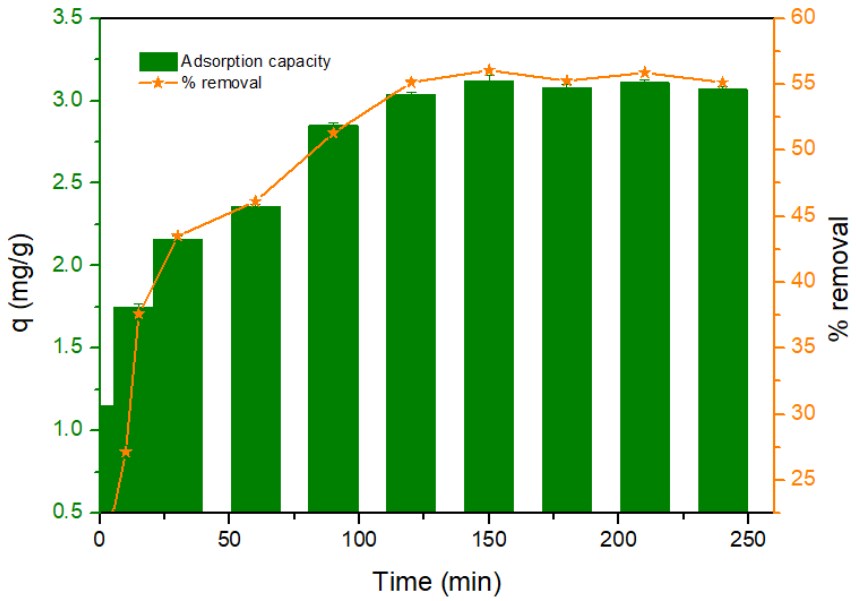

Figure 2. *Effect of contact time on phosphate adsorption by BP at initial phosphate concentration of 20 mg/L, 0.1 g BP/25 mL phosphate, initial pH of 3*

3.3. Effect of initial phosphate concentration

The experiment that studied effect of initial phosphate concentration on adsorption capacity of BP was investigated at initial phosphate concentration in range from 10 to 70 mg/L, optimum pH of 3, adsorbent dosage of 0.1 g/25 mL and contact time of 120 min. The results are showed in Fig. 3. It can be seen that adsorption capacity of phosphate onto BP increased from 0.84 to 4.27 mg/g as initial phosphate concentration increased from 5 mg/L to 50 mg/L. However, at initial phosphate concentration higher than 50 mg/L, the adsorption capacity did not increase and become stable. Besides, the removal efficiency of phosphate decreased from 61.1% to 33.6% corresponding to the increase of initial phosphate concentration from 5 to 70 mg/L. This can be explained due to the limitation of binding sites on the surface of BP. At higher initial phosphate concentration, the binding sites were occupied and saturated lead to the removal efficiency of phosphate reduced and adsorption capacity did not rise and became stability [2], [17]. The similar trends have been reported by other researchers such as research on removal of phosphate from water using activated laterite [18] or activated carbon derived from tea residue [15].

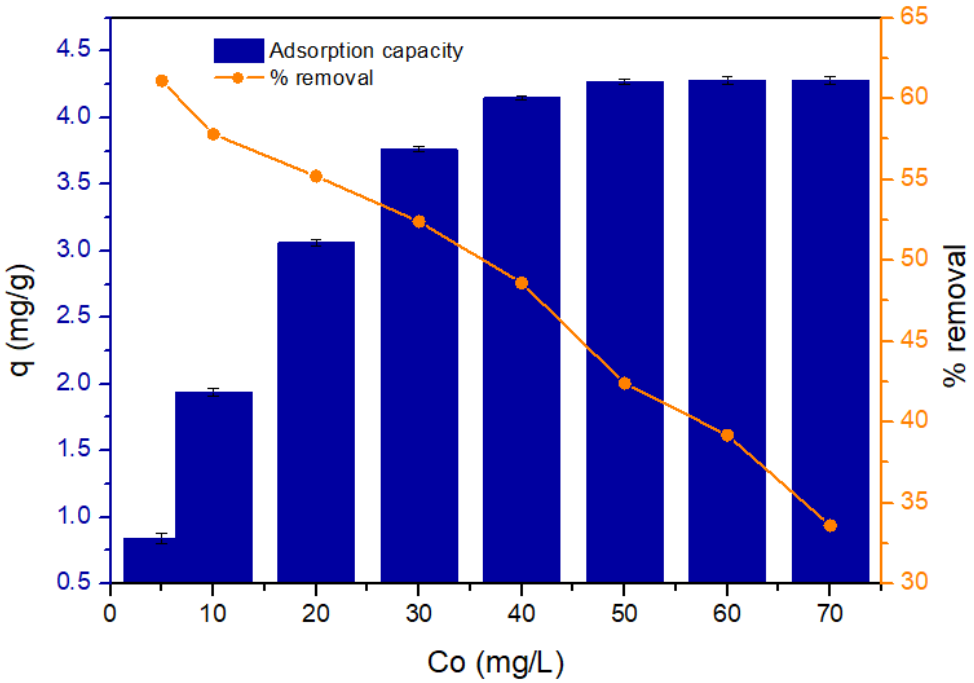

Figure 3. *Effect of initial concentration on phosphate adsorption by BP at initial phosphate concentration of 5 to 70 mg/L, contact time: 120 min, adsorbent dosage: 0.1 g BP/25 mL solution, initial pH of 3*

3.4. Effect of adsorbent dosage

Adsorbent dosage is an important factor which relates adsorbent-adsorbate equilibrium of the adsorption process [19]. In this study, the effect of BP dose on adsorption capacity of phosphate was conducted at solution pH of 3, initial phosphate concentration of 20 mg/L and contact time of 120 min. From Fig. 4, the removal efficiency of phosphate rose significantly from 38.13% to 59.7% when the BP dose increased from 50 to 200 mg/25 mL. It can be explained that with increasing adsorbent dosage, the active sites rose and lead to increase in binding sites for phosphate ions in the surface of BP [20]. However, the removal efficiency of phosphate did not increase and become stable when adsorbent dose was higher than 250 mg/L. Besides, the adsorption capacity of phosphate onto BP fell from 3.95 mg/g to 0.76 mg/g when the adsorbent dosage rose from 50 to 350 mg/25 mL. This is due to all experiments were conducted at the certain of the initial phosphate concentration and volume. Therefore, when the adsorbent dose increased, the active sites on BP surface can be saturated and caused a decrease in adsorption capacity of phosphate [21]. These results show that adsorbent dose plays an important role for adsorption process which has been reported by other researches [22], [23].

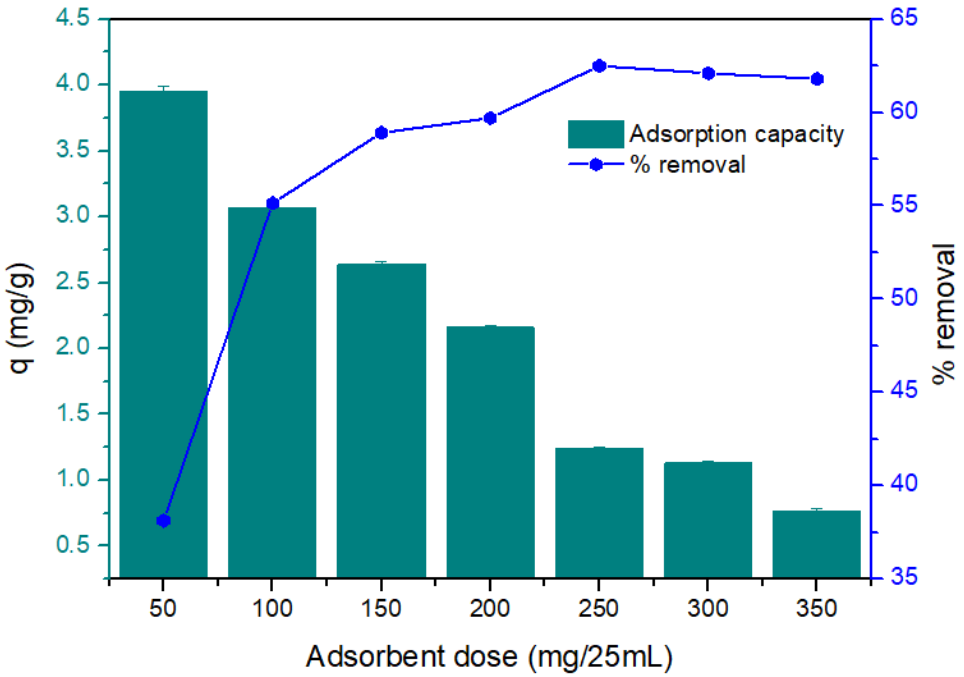

Figure 4. *Effect of BP dosage on adsorption capacity of phosphate at 20 mg/L of initial phosphate, contact time of 120 min and initial pH of 3*

4. Conclusion

The results of this study indicated that biochar from paper sludge is a promising adsorbent for removing phosphate from aqueous solution with low cost and simple producing method. In this study, the equilibrium of adsorption process was reached at 120 min, the pH of 3 was the best suitable for the adsorption. The adsorption capacity of phosphate onto BP increased when BP dosage and contact time rose. However, the adsorption efficiency was not really high. Therefore, it is necessary to modify the BP material to increase the surface functional groups and surface area. Moreover, it also needs to investigate characteristics and properties of BP as well as the kinetic and isotherm models of the phosphate adsorption onto BP to explain adsorption mechanism.

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