

## Removal of Phosphate Ions from Aqueous Solution Using Anthracite

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### Abstract

Anthracite was used as an adsorbent to remove excess phosphate from wastewater. Anthracite used in the present study is environmentally friendly and of cost effective. The adsorption study was carried out using different particle size of adsorbents, different concentration of phosphate solution ranging from 25.0 mg/L to 100.0 mg/L, different pH values ranging from 0.5 to 11.5 along with different adsorbent amount from 1.0 g to 5.0 g. Flow rate was also varied in the range of 0.6 mL/min to 1.8 mL/min. Adsorption column methods show the optimum removal of phosphate under the following conditions: initial phosphate concentration 25 mg/L, initial volume 25.0 mL, flow rate 1.0 mL/min adsorbent amount 2.0 g, particle size, < 90 $\mu$ m. This removal method may provide a solution to the removal phosphate from wastewater in Bangladesh as well as other countries of the world.

**Key words:** Phosphate, removal, anthracite, river, wastewater.

### I. Introduction

Phosphorous has been regarded as a limiting nutrient responsible for eutrophication of the water bodies, and removal of phosphate from waste effluents is thus of considerable significance before their discharge into the receiving waterways<sup>1</sup>. Phosphorous is an important element that is widely used in agriculture and industry. Low phosphorous concentration, less than 1 mg/L, can cause significant growth of algae because phosphorous is the main limiting nutrient for algal production<sup>2</sup>. Nowadays there are various techniques proposed for phosphate removal, which can be simply classified as chemical precipitation by using ferric or aluminium salts<sup>3-5</sup>, biological removal<sup>6</sup>, and adsorption<sup>7-8</sup>. Chemical precipitation and biological processes have been widely used for phosphate removal from industrial effluents<sup>9-10</sup>, however, it is still technically difficult or economically undesirable for both techniques to enhance phosphate removal as to meet increasingly stringent regulations on phosphate discharge.

In Bangladesh, the river Buriganga receives wastewater from numerous of sources along its way, which are discharged as industrial effluents, municipal sewage, household wastes and oils. The largest share of population load into this river appears to be from about 200 tannery industries in the Hazaribagh and Rayerbazar area. Studies show that up to 15,000 cubic meters of liquid wastes, 19,000 kilograms of solid waste and 17,600 kilogram of BOD load go into the Buriganga each day from these industries<sup>11</sup>.

Anthracite (Greek (anthrakites), literally "a type of coal", is a hard, compact variety of mineral coal that has a high luster. It has the highest carbon count and contains the fewest impurities of all coals, despite its lower calorific value. Anthracite is the most metamorphosed type of coal in which the carbon content is between 92% and 98%<sup>13</sup>. Moreover, it is cheaper and available compared to other adsorbents such as activated charcoal.

The aim of the present study is to explore the feasibility of using anthracite (type of coal) to remove of phosphate from water of the Buriganga River. The current technologies usually cannot achieve the goal in a cost effective manner. Adsorption seems attractive for phosphate removal due to its operation simplicity and low operation cost<sup>12</sup>. The attractive features of the adsorbent used in the present study are environment friendly and cost effective.

### II. Experimental

#### Materials and Methods

All chemicals were reagent grade from Aldrich (UK) and used without further purification. The stock solution containing 1000 mg/L of orthophosphate was prepared by dissolving KH<sub>2</sub>PO<sub>4</sub> into the de-ionized water. Anthracite (Analar, BDH) was collected from Germany. The sample was ground with grinder machine. Finally, it was characterized with standard methods<sup>14</sup>. Particle sizes of powdered anthracite were measured using different sieves. Wastewater sample was collected from the river Buriganga in a plastic bottle which were washed before collecting samples with 5% HNO<sub>3</sub>, distilled deionized water and finally with the wastewater at the sampling sites for several times. Water sample was preserved in freeze at temperature below (4-5) °C. pH of the solution was measured by using a pH meter ( TOA HN-265, Japan). Phosphate concentration in sample and synthetic solution was measured by using UV-Visible Spectrophotometer (UV-160A, Shidmadzu, Japan)<sup>14</sup>.

#### Preparation of adsorbent column and adsorption procedure

For the treatment of adsorbent (anthracite), firstly glass wool was inserted into the column which acted as a support for the adsorbent. The soaked adsorbent with water was poured into column and water was allowed to pass through the column to remove dissolved materials from the adsorbent. The adsorption experiments were carried out in columns that were equipped with a stopper for controlling the column elute flow rate (treatment rate). Adsorption parameters such as the amount of adsorbent (1-5) g, particle size (90-425)  $\mu$ m,

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treatment flow rate (0.8-1.4) mL/min, initial sample concentration (25-100) mg/L and pH was optimized. The sample solution (25mL) was passed through the adsorption column at a given flow rate. The removal treatment was performed at ambient temperature. The removal (adsorption) efficiency was calculated using the equation:

$$\text{Removal efficiency} = [(C_0 - C_e) / C_0] \times 100$$

Where,  $C_0$  = concentration of the sample solution before treatment;  $C_e$  = concentration of the sample solution after treatment

### III. Results and Discussion

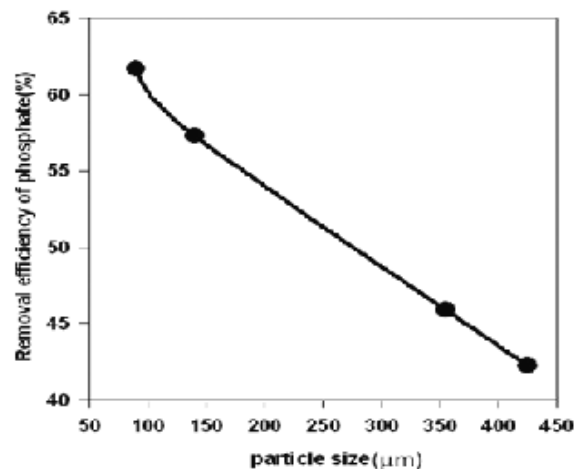
Anthracite was used without any chemical pretreatment. It was chemically stable and insoluble in water. The physicochemical characteristics of anthracite are presented in Table 1.

**Table 1. Physicochemical characteristics of Anthracite**

Property	Composition
Particle size (mm)	0.8-1.8
Ignition loss (%)	90-96
Sulphur content (%)	0.6
Ash content (%)	2-4
Moisture content (%)	1.2
Carbon content (%)	90
Chemical Resistance	Slightly soluble in acid and alkali solutions

#### Optimization of the particle size

Column adsorption experiments were carried out for the removal of phosphate from aqueous solution using four particle sizes such as <90, 90 – 140, 140 – 355 and 355 – 425 $\mu$ m.

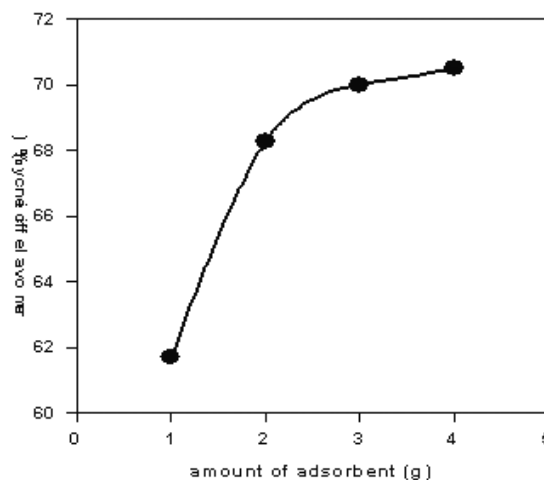


**Fig. 1.** Effect of particle size of adsorbent on the removal of phosphate by adsorption onto anthracite. Adsorbent amount: 1.0 g; conc. of phosphate solution: 50mg/L; volume of phosphate solution: 25.0 mL; flow rate: 1 mL/min.

The plot of percentage removal of phosphate against particle size is depicted in Fig. 1. It shows that removal efficiencies of adsorbents for phosphate decreases with increasing particle size. Highest removal was observed for 90  $\mu$ m adsorbents. About 61.70% phosphate was removed with particle size 90 $\mu$ m. So, the particle size 90 $\mu$ m was considered optimum. This is probably due to the fact that, with the decrease of particle size, the surface areas of the adsorbents are increased, which provide greater number of adsorption sites for phosphate to adsorb onto adsorbents.

#### Optimization of the amount of adsorbents

The effect of the amount of adsorbents on the removal of phosphate is given in Fig. 2. This shows that removal efficiency increased with increasing amount of adsorbent up to a certain value after which removal efficiencies do not change significantly with increasing adsorbent amount.

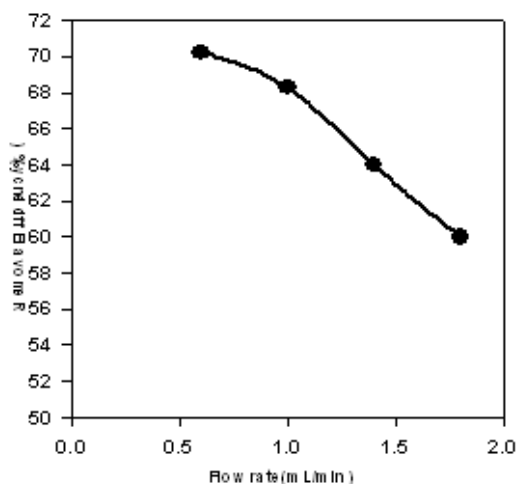


**Fig. 2.** Effect of amount of adsorbent on the removal of phosphate by adsorption. Particle size: 90  $\mu$ m; conc of phosphate solution: 50mg/L; volume of phosphate solution: 25.0mL; flow rate: 1mL/min.

The initial rapid rise in removal efficiency is due to increase in adsorption sites with increase in amount of adsorbents. With the increase in adsorbent amount, adsorption sites become abundant compared to phosphate present in the solution. It shows that removal efficiency is 61.70% when the amount is 1.0 g. For 2.0 g it is 68.26%, 3.0 g it is 70.0%, 4.0 g it is 70.50%. Moreover, higher than 2.0 g of adsorbents cover large volume of column. So, 2.0 g of anthracite is the optimized amount of adsorbent.

#### Optimization of flow rate

The influence of the treatment flow rate on the removal of phosphate is presented in Fig. 3. It shows that the removal efficiency decreases with increasing flow rate.

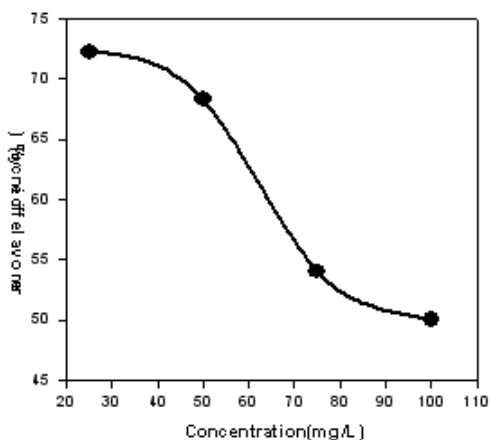


**Fig. 3.** Effect of the flow rate on the removal of phosphate by adsorption. Particle size: 90  $\mu$ m; conc. of phosphate solution: 50 mg/L; volume of phosphate solution: 25.0 mL

In general, 68.26 % of phosphate is removed at flow rate 1.0 mL/min. Higher removal efficiency is found at lower flow rate is due to the attain of longer contact time of adsorbate with adsorbents. So, 1.0 mL/min is the optimized flow rate for the removal of phosphate.

#### Optimization of initial concentration

Removal efficiency is greatly depended on the initial concentration of solution of adsorbate. Fig. 4 shows the plot of percentage removal of phosphate against initial concentration of phosphate solution.

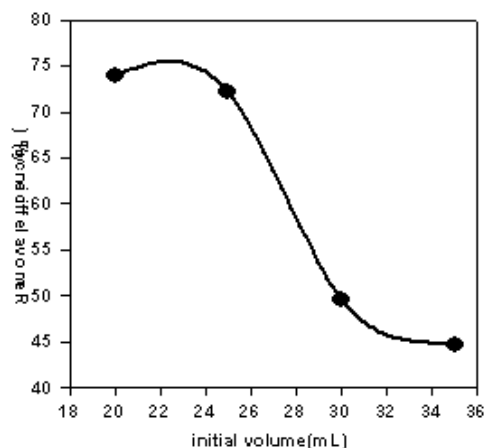


**Fig. 4.** Effect of concentration of phosphate on the removal of phosphate by adsorption; particle size: 90 $\mu$ m; volume of phosphate solution: 25mL; flow rate: 1mL/min.

It is observed that higher removal efficiency (72.20%) is achieved by using 25 mg/L of phosphate. So, 25 mg/L of phosphate solution is optimized initial concentration.

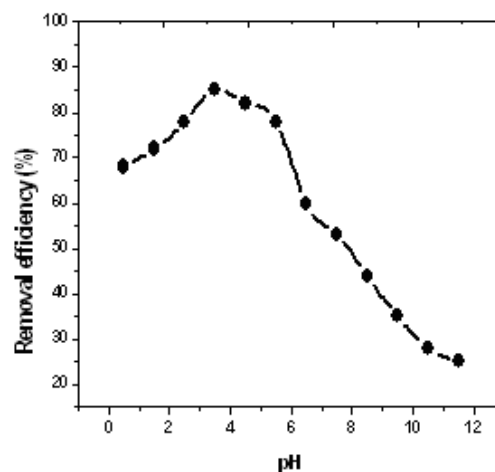
#### Optimization of initial volume

Different initial volumes with optimized concentration of 25mg/L were treated with adsorbent and the results are summarized in Fig. 5.



**Fig. 5.** Effect of initial adsorbate volume on the removal of phosphate by adsorption, initial conc. of phosphate: 25mg/L; Flow rate:1.0 mL/min; Particle size: 90 $\mu$ m

5. It shows that removal efficiency decreases with increase of initial volume. The removal efficiency is over 74.0% when the volume of phosphate solution is 20.0mL. The decrease in removal efficiency was probably due to overabundance of adsorbate in comparison with sites of adsorbents. At lower volume, all adsorbate molecules can come in contact with adsorbent sites. When initial volume increases all molecules cannot come in contact with adsorbent sites because adsorbents are not available as they are already used up. About 49.58% removal of phosphate is found for 30 mL and 44.66% for 35 mL of initial volume phosphate solution. Therefore, the volume selected for further study is 25.0 mL of phosphate solution.



**Fig. 6.** Effect of initial pH of the solution on the removal of phosphate by adsorption, particle size : <90 $\mu$ m, Volume of waste water: 25.0mL, Flow rate: 1.0mL/min.

### Optimization of pH

The effect of pH on the removal of phosphate in the presence of adsorbent is represented in Fig. 6. As the pH increases, the removal of phosphate from the solution decreases. The decreasing trend of removal of phosphate with increasing pH is dependent on surface hydrolysis reactions<sup>15</sup>. At pH 3.5 the removal efficiency is the highest. Therefore, 3.5 is the optimized pH for the removal of phosphate.

### Application of the optimized method for the removal phosphate

In order to check this optimized method a synthetic phosphate solution of 25 mg/L was passed through the column following the optimized conditions (Particle size: <90 $\mu$ m; adsorbent amount 2.0 g; flow rate 1mL/min; pH: 3.5, initial volume of sample: 25 mL etc.). The removal efficiency of this developed method is 85%.

**Table 2. Removal of phosphate with optimized method.**

Sample no.	Initial phosphate conc.(mg/L)	Final phosphate conc. (mg/L)	Removal (%)
1	0.34 $\pm$ 0.02	0.05 $\pm$ 0.02	84.84
2	0.36 $\pm$ 0.312	0.0545 $\pm$ 0.01	80.25

The optimized conditions were applied to remove phosphate from the water samples of the river Buriganga. The collected samples were passed through the column with the optimized method. The concentration of phosphate before and after passing through the column is measured. It is observed that 80-84% of the phosphate is removed from sample water. The results are presented in the Table 2.

### Probable phosphate removal mechanism

An exchange mechanism took place in the sorption of phosphate onto the adsorbent, and the sorption reaction may be written with the following probable exchange reactions. Surface hydrolysis reactions are as follows<sup>15</sup>:

(Acidic condition)



(Basic Condition)

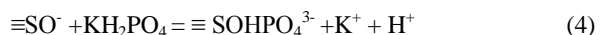


Phosphate sorption reactions:

(Acidic condition)



(Basic Condition)



Here  $\equiv\text{SOH}$  represents surface of anthracite and  $\text{KH}_2\text{PO}_4$  is used in mechanism because the removal method is optimized by using  $\text{KH}_2\text{PO}_4$ . When the pH is low the removal of  $\text{KH}_2\text{PO}_4$  is increased. Since anion adsorption is coupled with the release of  $\text{OH}^-$  ions, the adsorption is favored by the low pH value. When the pH is increased, a gradual decrease in the percentage of adsorption is observed which may be due to the competition between  $\text{OH}^-$  and phosphate ions. The observed behavior of the phosphate removal with varying pH might be attributes to various mechanisms such as electrostatic attraction/repulsion, chemical interaction and ion exchange which are responsible for adsorption on sorbent surfaces.

### IV. Conclusion

Anthracite supported column adsorption proved to be an efficient phosphate removal technique. Favorable phosphate removal by anthracite occurs at pH 3.5. Other parameters such as amount of the adsorbents, particle size, initial volume of the adsorbate, flow rate of the solution were also optimized to develop a phosphate removal method. Then the developed method was applied to the samples water of the Buriganga River showed satisfactory performance.

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