



FEASIBILITY STUDY OF RICE BASED BIOCHARS FOR THE REMOVAL OF PHOSPHATE FROM FERTILIZER INDUSTRY WASTE WATER

Sneha Suresh¹, Bindu G.²

^{1,2}Department of Civil Engineering, Government Engineering College Trichur (India)

ABSTRACT

Phosphate released from fertilizer industries effluent imposes serious environmental risk due to its toxic and non biodegradable nature. Conventional methods for the removal of these nutrients from aqueous solutions are ineffective and expensive. Biochar is a novel and feasible green environmental sorbent. The use of biochar as a low-cost sorbent to remove phosphate from aqueous solutions is an emerging and promising wastewater treatment technology. Present study focuses on the application of rice based biochars for the removal of phosphate from waste water. Batch experiments were conducted to evaluate the various parameters such as the nature of biochar, pH, dosage of adsorbent and reaction time which influences the adsorption efficiency. A removal efficiency of 89.2% is obtained for rice husk biochar produced at 600°C.

Keywords – Activated carbon, Adsorption, Biochar, Fertilizer industry wastewater, Phosphate

I. INTRODUCTION

Fertiliser industry is a prime contributor of phosphate to aqueous systems. As phosphate is a limiting nutrient of eutrophication, its removal during the treatment process from any source of wastewater prior to disposal into the environment is an important issue. The high concentration of phosphate in fertilizer industry wastewater effluents results in the increase of nutrients levels in water. This will stimulate extensive phytoplankton growth and causes algal blooms, which then disrupts the normal aquatic ecosystem functioning. The recycle and reuse of these nutrients could possibly control these major environmental threats. This work focuses on the application of biochar to capture phosphate from fertilizer industry waste water.

Adsorption onto activated carbon is a very traditional way to treat wastewaters. However, large-scale application of this technology is often limited by high capital and regeneration costs of the commercially available activated carbon. Extensive research concerning the identification of suitable and relatively cheap materials for the production of low-cost adsorbents; capable of removing significant quantities of contaminants from aqueous waste is carried out. Utilization of biochar as activated carbon precursor is getting increased attention as it is renewable, widely available, cheap, and environmental friendly.

Biochar is a novel and feasible green environmental sorbent. Biochar is a porous carbonaceous solid produced by thermochemical conversion of organic matter in an oxygen depleted atmosphere. Biochar is a carbon produced during the pyrolysis of biomass under oxygen-limited conditions and at relatively low temperatures (<700°C) [1]. Biochar is defined more descriptively as the porous carbonaceous solid produced by the thermochemical conversion of organic materials in an oxygen depleted atmosphere that has physicochemical

properties suitable for safe and long-term storage of carbon in the environment. The sorption capacity of biochar depends highly on parameters such as pyrolysis conditions, including residence time, feedstock types, temperature, and heat transfer rate. Similarly, the physicochemical properties such as surface area, surface charge, and chemical functionality are influential factors controlling the sorption of inorganic and organic contaminants. Being a renewable resource and due to its economic and environmental benefits, biochar is a promising resource for environmental technology used for water contaminants treatment.

This work studies the adsorption ability of biochars produced from rice straw and rice husk for the removal of phosphate from fertilizer industry wastewater. Optimisation of the removal efficiency of phosphate was done by conducting batch experiments by varying the dosage of biochar, pH of wastewater and reaction time for the adsorption of phosphate from the effluent.

II. MATERIALS AND METHODOLOGY

2.1 Sampling of waste water

Fertilizer industry effluent was collected from fertilizer industry, Kochi, India in the months of December and January. Grab sampling technique was used for sampling. The sample was transferred into clean plastic sample bottles which were immediately transported to the laboratory and stored at 40°C. Experiments were carried out after the samples reached ambient temperature.

2.2 Characteristics of fertilizer waste water

Table 1 Characteristics of fertilizer waste water

Parameter	Concentration
pH	8.87
Conductivity(mS/cm)	2.46
TDS(mg/L)	1480
COD(mg/L)	248
Nitrate(mg/L)	232.57
Phosphate(mg/L)	112.5

2.3 Biochar production

Two types of chars were used in the experiment. The rice husk and straw was locally collected for preparing biochar and was ground into powder (<0.2 mm) sieved and dried at 105 °C for 1.0 h prior to pyrolysis. Rice husk and Rice straw biochars were prepared by low-temperature pyrolysis at approximately 300°C and 600°C. The samples were screened, and biochars that were less than 0.1 mm in size were selected for use.

2.4 Nitrate and phosphate adsorption

To test the phosphate adsorption capacities Rice husk and Rice straw biochars were placed in beakers containing 50 ml of waste water at its initial pH 8.89. In order to determine the effect of adsorbent dosage, reaction time and wastewater pH trial runs were conducted by arbitrarily selecting three ranges of each parameter.



Table 2 Trial Experimental Runs

Parameters	Values		
pH	3	6	9
Dosage(g)	0.25	0.5	1
Reaction Time(min)	30	60	180

The flasks were shaken with a shaker at 100 rpm at room temperature. After adsorption, the concentration of phosphate was determined via ascorbic acid colorimetry at wavelengths of 880 nm. Afterwards, the collected samples were filtered for further determining the residual concentrations of these ions. The removal percentage phosphate from aqueous solutions was calculated. From the trial experimental runs the suitable range for pH, dosage and time was obtained. Further the experiments were conducted in a closer interval obtained from trial run results.

2.5 Effect of adsorbent dosage and contact time

The effect of adsorbent dosage and contact time on phosphate adsorption was studied by adjusting the solution at optimum pH of 3 and by varying adsorbent dosage ranging from 0.1 to 0.3 g L⁻¹. The mixtures were shaken with a speed of 100 rpm using a shaking assembly. The reaction time was varied from 30 to 120 minute. Residual concentration in the filtered solution was determined by spectrophotometer.

2.6 Effect of solution pH

For determination of the pH effect on the phosphate adsorption by biochar, initial pH of phosphate solutions were adjusted at different pH values (2–4) by using 0.1 M HCl and 0.1 M NaOH. Optimum biochar dosage was added to 50 ml solution and the mixture was shaken at 100 rpm for optimum reaction time. The phosphate concentration in the filtered solution was analyzed immediately by UV spectrophotometer.

III. RESULTS AND DISCUSSIONS

3.1 Optimization of Process Parameters

Identifying the influencing factors and optimizing the phosphate removal efficiency is of primary importance in this study. Identification of significant variables is done using One factor at a time method [2]. The most widely used screening and optimization strategy is the Design of Experiment (DOE) method, by which certain factors are selected and deliberately varied in a controlled manner, in order to study their effects, facilitate process comprehension and even to improve the performance.

Experiments were initiated for screening the significant factors. Batch studies were conducted with working volume of 50 mL synthetic wastewater, with Rice husk and Rice straw biochars. The variables chosen for the present study were adsorbent dosage, reaction time and pH. Initial trials were conducted to study the effect of process parameters on the process.

3.1.1 Effect of Adsorbent Dosage and Contact Time

The removal of phosphate was studied using synthetic wastewater containing initial phosphate concentration. Adsorption of phosphate using rice husk biochars was investigated varying contact time (30 min to 120 min) and adsorbent dose (0.1 to 0.3g) at 100 rpm of agitating speed .It was observed that the removal efficiency increases with increasing the contact time. Maximum phosphate 89.2% removal was observed using 0.2 g/L dose in 60 min for ricehusk biochar produced at 600°C and 82.6% for ricestraw biochar produced at 600°C.

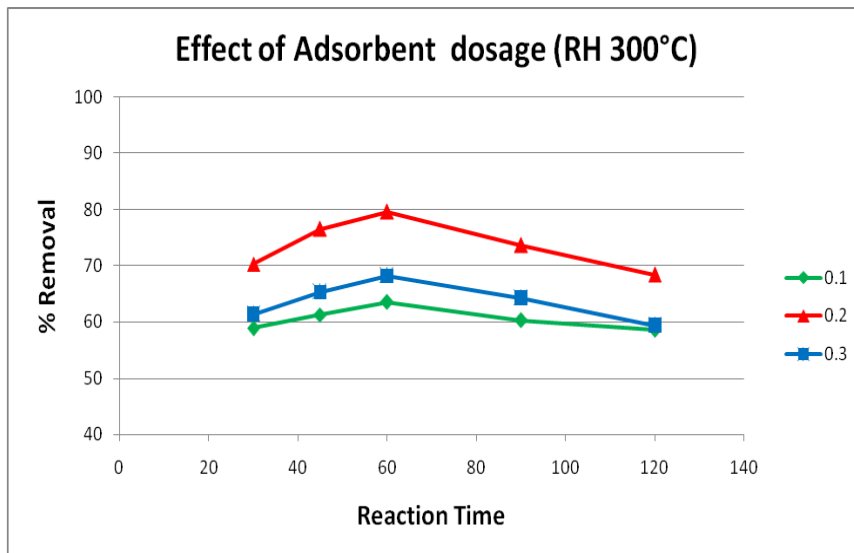


Fig. 1 Effect of Rice husk 300 °C biochar dosage in the removal of phosphate

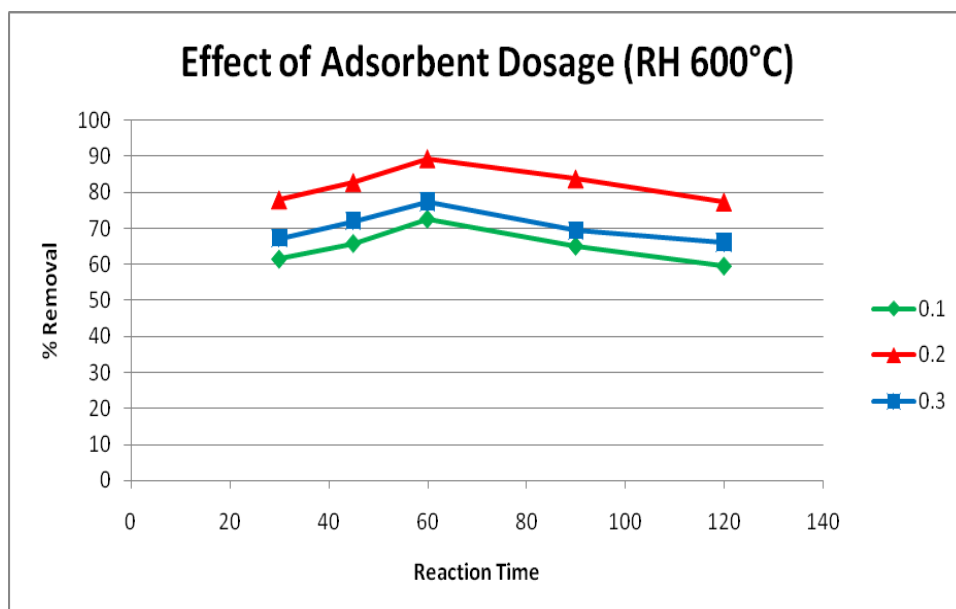


Fig. 2 Effect of Rice husk 600 °C biochar dosage in the removal of phosphate

Increase in adsorbent dose increases the percentage removal of phosphate as it provides more free sites leading to increase in net surface area of adsorbent [3]. However, further increase in the adsorbent dose may cause aggregation of adsorbent resulting in decrease in available adsorption sites. Maximum removal efficiency was at 0.2g dosage for rice husk while for rice straw it was at 0.6g

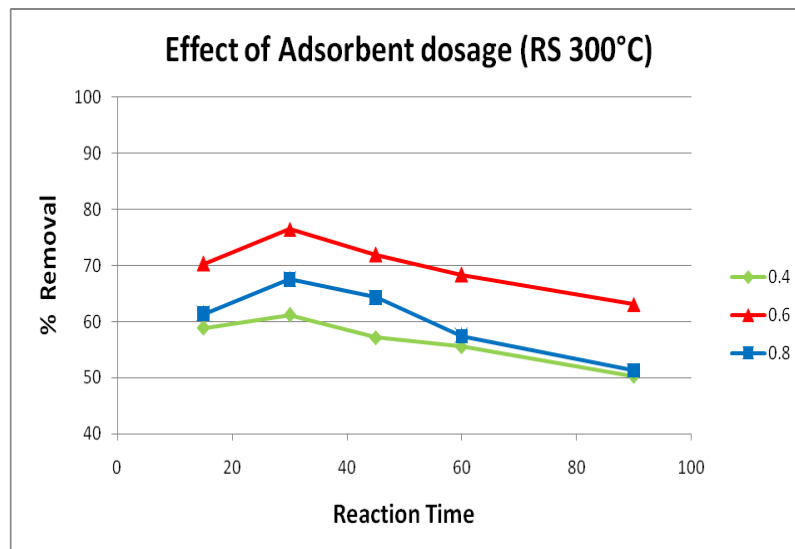


Fig. 3 Effect of Rice straw 300 °C biochar dosage in the removal of phosphate

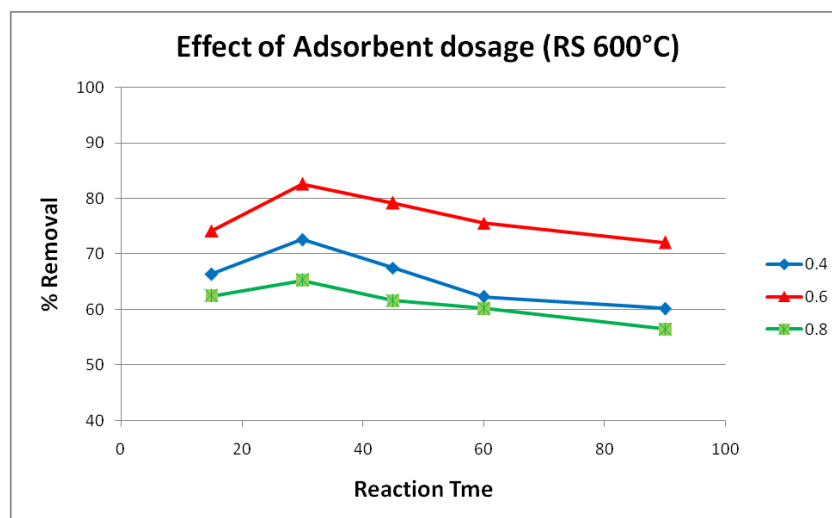


Fig.4 Effect of Rice straw 600 °C biochar dosage in the removal of phosphate

The adsorption capability of biochar was also significantly influenced by the natural compositions of feedstock. Given the same pyrolysis condition, the adsorption capacity of biochars for contaminants varied with the types of raw biomass. The removal ability varies with different biochar feedstock sources as the mineral components originated from the feedstocks play an important role in the adsorption properties of biochar [4]. The lower adsorption at 300°C carbonization temperature can be attributed to the inadequacy of heat energy generated at low carbonization temperature for any substantial evolution of volatile matters essential for pore development. At 600°C, more volatile matters were released progressively during carbonization, thereby resulting in the development of some new pores and hence the adsorption of nitrates increased progressively.

In nature, rice husk is tough, insoluble in water, woody characterized by its abrasive inherent resistance behaviour and silica-cellulose structural arrangement. Its major constituents comprising of cellulose, hemicellulose, lignin, hydrated silica and ash content. The presence of polar groups on the surface increases the

ion exchange capacity of the adsorbents [5].Rice husk biochar also showed the presence of silica content which has a high adsorptive capacity.Better removal efficiency was obtained for Rice straw produced at 600 °C.

Adsorption rate initially increased and the maximum removal efficiency was reached at 60 minutes contact time after which the removal reduced for ricehusk biochar whereas for rice straw the maximum removal was found to be at 30minutes . It is clear that the sorption rate was rapid at the initial stage and gradually slowed down afterwards. The slower sorption was likely due to the decrease in sorption sites on the surface of the biochars.

3.1.2. Effect of pH

The degree of ionization and speciation of adsorbate is mainly affected by pH of solution. Hence the removal of phosphate was studied using synthetic wastewater containing initial concentration of phosphate and nitrate and ranging pH from 2 to 4.

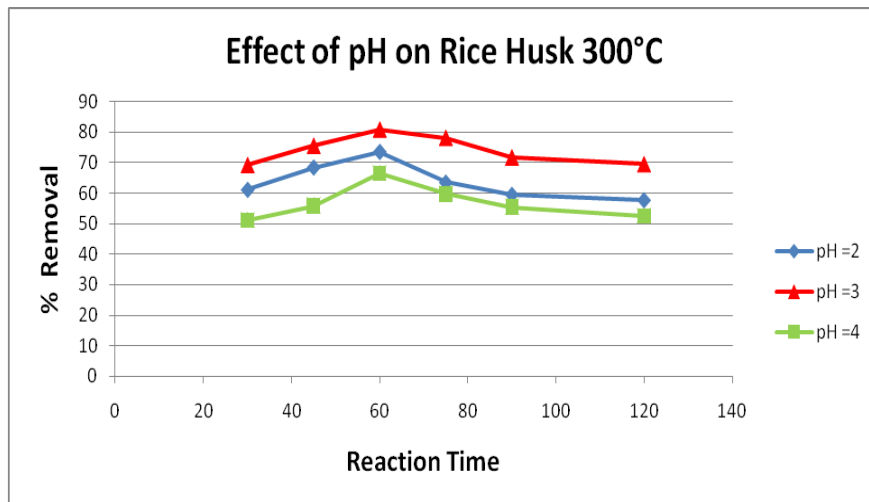


Fig. 5 Effect of pH on the removal of phosphate using rice husk 300 °C biochar

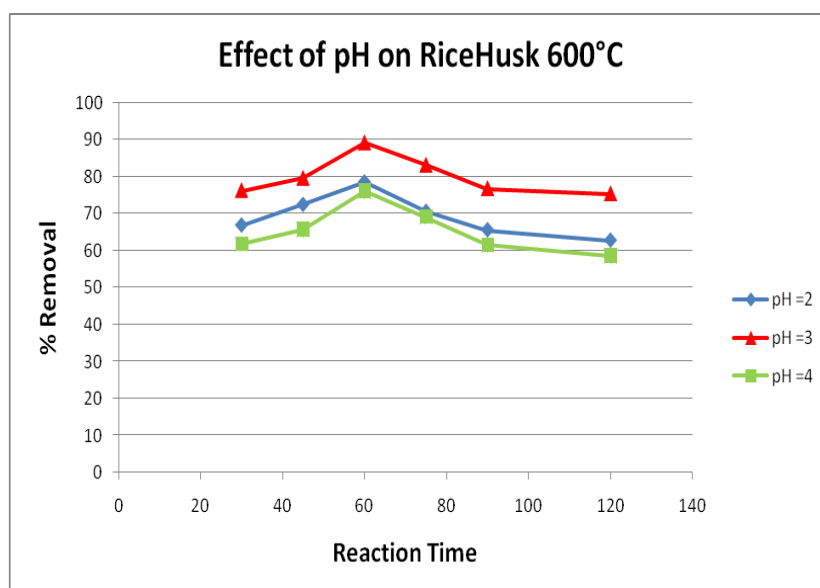


Fig. 6 Effect of pH on the removal of phosphate using rice husk 600 °C biochar

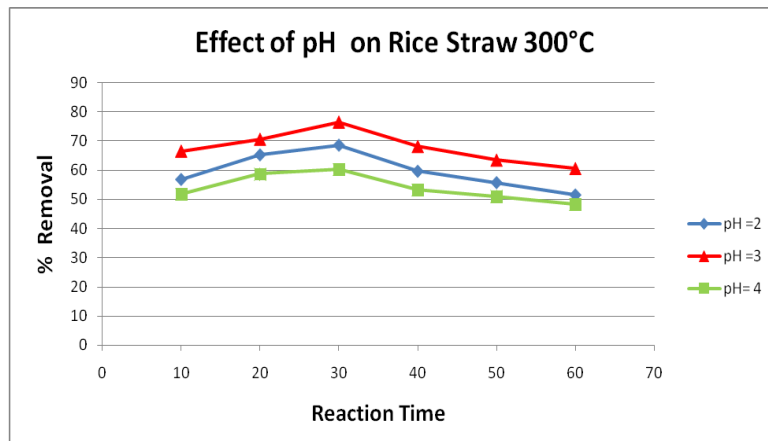


Fig.7 Effect of pH on the removal of phosphate using rice straw 300 °C biochar

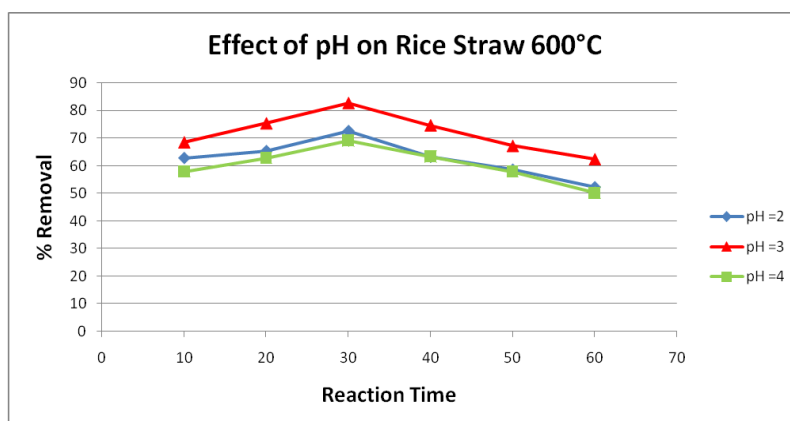


Fig. 8 Effect of pH on the removal of phosphate using rice straw 600 °C biochar

The results show that the percentage removal decreases with increases in pH of the solution and that the phosphate removal is more efficient under acidic condition. Maximum removal efficiency was obtained at a pH of 3 for both rice husk and rice straw biochar. Biochars produced at 600°C is found to be more effective than that produced at 300°C. The maximum removal efficiency was found to be 89.2% for rice husk biochar whereas for rice straw biochar it was 82.6%. This difference in the removal efficiency can be attributed to the difference in the feedstock composition.

High pH leads to dissociation of functional groups thereby carries more negative ions which resist phosphate ions interacting with the surfaces, thus decreasing phosphate adsorption. Adsorption is also affected by the type and ionic state of the functional group present in the adsorbent and the chemistry of the adsorbate solution[6]. At lower pH the attraction of positive ions towards the PO_3^{-4} ions to form the stable ion is more hence pH of solution also affects the removal percentage of phosphate. Decrease in removal of phosphate ions at higher pH is probably due to the higher concentration of hydroxyl ions, present in the reaction mixture which competes with the PO_3^{-4} ions for the sorption sites[7]. The lower adsorption of phosphate at higher pH may be due to the increased repulsion between the more negatively charged PO_3^{-4} species and negatively charged surface sites.

IV. CONCLUSION

The use of biochar as a low-cost sorbent to remove phosphate from aqueous solutions is an emerging and promising wastewater treatment technology. Biochars produced at 600°C is found to be more effective than that produced at 300°C, which is consistent with their specific surfaces. Maximum removal efficiency was at 0.2g dosage for rice husk while for rice straw it was at 0.6g. Adsorption rate initially increased and the maximum removal efficiency was reached at 60 minutes contact time after which the removal reduced for rice husk biochar whereas for rice straw the maximum removal was found to be at 30minutes. Similar to Rice husk biochar, Rice straw biochar also showed better removal efficiencies at a lower pH .Maximum removal efficiency was obtained at a pH of 3 for both rice husk and rice straw biochar .The maximum removal efficiency was found to be 89.2% for rice husk biochar whereas for rice straw biochar it was 82.6%. This difference in the removal efficiency can be attributed to the difference in the feedstock composition. Rice husk biochar also showed the presence of silica content which has a high adsorptive capacity.

V. ACKNOWLEDGEMENTS

Authors are thankful to the Authorities of Government engineering college Trichur and FACT, Kochi for granting permission for collecting effluent samples for this work.

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