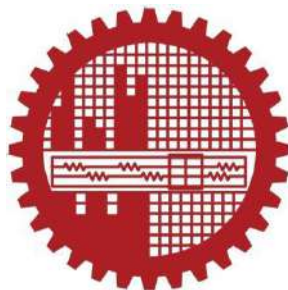# REMOVAL OF PHOSPHATES FROM EUTROPHIC WATER BY UTILIZING SYLHET SAND AND RICE HULL ASH AS LOW-COST ADSORBENT

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Certification of Thesis

REMOVAL OF PHOSPHATES FROM EUTROPHIC WATER BY UTILIZING SYLHET SAND AND RICE HULL ASH AS LOW-COST ADSORBENT

BY

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Roll No. 0417032704, Session: April 2017, has been accepted as satisfactory in partial fulfillment of the requirement for the degree of Master of Science (M.Sc.) in Chemistry & certify that the student has demonstrated satisfactory knowledge of the field covered by this thesis in an oral examination held on February 08, 2023.

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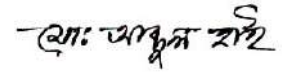
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It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

Md. Abdul Hai

I dedicate this thesis to....

My Beloved Mother

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Scheme

List of Abbreviations of Technical Symbols and Terms

1. Phosphorous (P)

2. Rice hull ash (RHA)

3. Sylhet sand (SS)

4. Parts per million (ppm)

5. Stannous Chloride Method (SCM)

6. P adsorbed rice hull ash (PARHA)

7. P adsorbed Sylhet sand (PASS)

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<div align="right">Md. Abdul Hai</div>

Abstract

Phosphorous is an important nutrient moreover discharge of phosphate into aquatic environment by various human activities causes the deterioration of water quality and causes as threat to the environment by facilitated algal bloom. Hence, the effective removal of phosphate from wastewater is essentially required. Various methods or techniques have been applied for the removal of phosphate from wastewater. Among the various techniques applied, adsorption has been found to be most attractive phosphate removal method, due to its high efficiency, simplicity and economic validity. In this study, we exploited the strong selective interaction of phosphate with Fe containing Rice hull ash (RHA) and Sylhet sand. Sylhet sand didn't need any modification & used directly for the adsorption process. On the contrary, RHA was modified by $FeCl_3$ for this study for adsorbing phosphates. The efficiency of locally available RHA and Sylhet sand examined in batch and column mode for the removal of phosphate using synthetic wastewater. Characterization of adsorbents was done by using Fourier transform infrared (FTIR), X-ray diffraction spectrophotometric analysis (XRD). Adsorption studies shows the optimal conditions for phosphate removal were pH 5 and a 3-hour contact time. Fe-treated rice hull ash removed 78.5% of the phosphate from a 5-ppm test solution. The Sylhet sand achieved a 49.6% reduction. When an actual sample of runoff from the Tangua hoar was subjected to the sorbents, the rice hull ash removed 83.8% and the Sylhet sand removed 83% for same test solution. Both materials were found to be re-usable for several cycles of phosphate removal. Phosphate removal study shows that, 42.9% & 71.6% recovery of adsorbed phosphorous from Rice hull ash and Sylhet Sand respectively. Among the desorbed phosphorous 74% could be recovered by precipitating as $FePO_4$. The overall removal capacities of the two sorbent materials were 2.37 µg/g rice hull ash (RHA) and 0.475 µg/g Sylhet sand. This ratio of about 5 to 1 is reflected in the quantities of sorbents that were used in this series of experiments. This data shows that Sylhet Sand is an effective adsorbent to remove excess phosphate from waste water.

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CHAPTER 1

Introduction

1.1 General Remarks

Phosphorus is mainly used in agriculture sector as fertilizer and in households as detergent, resulting in release of phosphate into the water body [1,2]. The other major source of phosphate includes weathering of rocks as well as industrial activities [3]. Phosphate is essential for the growth of aquatic life and plants, however high concentration of phosphate in water leads to the algal bloom and toxic condition [4]. Eutrophication mainly occurs when the phosphorous concentration is higher than the 0.02 mg/L in water bodies [5] and several studies reports that even the groundwater quality in the region is collapsed [6]. Leaching of phosphorous into the ground water through the subsoil also affect the drinking water quality leading to potential risk to human health and animals [7]. Kidney damage and osteoporosis have been reported due to the expenditure of high concentration of phosphate [8]. The continuous discharge of phosphorous level in water system animates the growth of toxins in the water bodies [9]. Hence, there is a need to develop a process for both removal and recovery of phosphorous from domestic and industrial wastewater. A number of studies have been reported using physical, chemical and biological processes for the removal of phosphate from wastewater [10]. Although, advance techniques such as electro dialysis, reverse osmosis, membrane process, flocculation are considered successful [11], but they require high capital investment and operation cost. Therefore, most of the researcher's looks for locally available adsorbent as they offer are efficient, viable and cost-effective solutions. Various studies have shown the application of different waste materials such as red mud [12], fly ash [13], coal fly ash [14], waste scallop shell [15], wheat residue [16], lanthanum doped carbon, calcine egg, nanocomposite, Fe-Al-Mn, modified carbon residue, red seaweed, fruit juice residue, aerobic digestion for the removal of phosphate from the wastewater.

Agro residue rice husk is the outer covering of paddy and accounts for 20–25% of its weight. It accounts for about one fifth of the gross rice production of 545 million metric ton of the worldwide [17]. The annual generation of rice husk in Bangladesh is in the range of 7-8 million tons [18]. RHA is an agricultural waste obtained from the rice mill. Rice hull removal during rice refining, creates disposal problem due to its low commercial value. Also, the handling and transportation of RHA is erratic due to its low density. Much of the rice produced from the processing of rice is either burnt or dumped as waste. Burning of rice hull in open fields cause environmental and health problems in the surrounding areas especially in developing countries. Therefore, it is very important to fully utilize the RHA.

In recent years, attention has been focused on the utilization of unmodified and modified rice hull, as adsorbent for the removal of various contaminants [19]. The present study deals with the utilization of agro-waste RHA & Sylhet sand for the removal and recovery of phosphate from wastewater.

1.2 Environmental impacts of phosphate

Phosphate is an inorganic compound which is considered is an agricultural fertilizer. Phosphate is an essential element for life of organism; it is one of the most important elements of DNA [20]. Certain amount of phosphate is essential but excess amount of phosphate can cause algal bloom and also toxic cyanobacterial bloom. Which consume the dissolved oxygens caused eutrophication [21].

1.2.1 Environmental Pollutants

Pollution is one of the most serious problems facing humanity and other life forms on our earth today. Environmental pollution is defined as "the contamination of the physical and biological components of the earth/atmosphere system to such an extent that normal environmental processes are adversely affected." Pollutants can be naturally occurring substances or energies, but they are considered contaminants when in excess of natural levels [22]. Any use of natural resources at a rate higher than nature's capacity to restore itself can result in pollution of air, water, and land. Pollution is a significant problem facing the environment. As the world's population Environmental continues to grow, so does the amount of potentially toxic substances that are released into the ecosystem. Environmental pollutants can be derived from a number of sources.

Phosphorous can be found in the environment most commonly as phosphates (PO_4^{3-}). Phosphates are important elements in the human body, because they are a part of DNA materials and they take part in energy distribution. Phosphate can also be found commonly in plants [23]. Recommended intake is 800 mg/day a normal diet provides between 1000 and 2000 mg/day, depending on the extent to which phosphate rich foods and consumed [24].

1.2.2 Health hazard of excess phosphorous

Too much phosphate can cause health problems, such as kidney damage and osteoporosis, shown below in figure 1.1 [25]. Phosphate shortage can also occur. These are caused by extensive use of medicine. Too little phosphate can cause health problem. Recent studies have demonstrated that phosphate also seems to damage blood vessels and induce aging processes [26]. It also appears that excessive phosphate consumption is associated with increased prevalence of cardiovascular diseases in the general population. Too much phosphate in the blood is known as hyperphosphatemia [27].
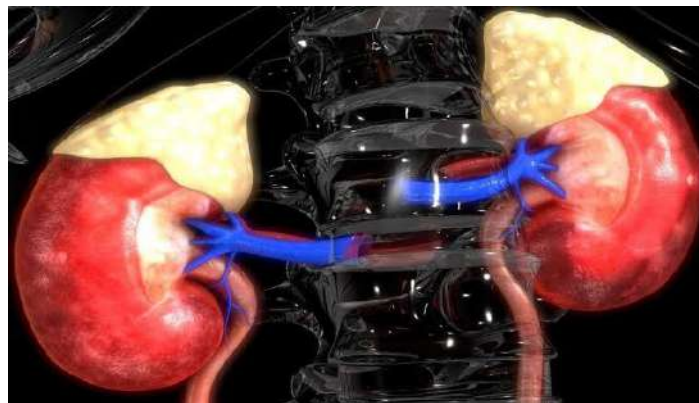
Figure 1.1 Hyperphosphatemia due to excess phosphate

Phosphorous in its pure form has a white colure. White colored phosphorous is the most dangerous form of phosphorous that is known to us When white P is occurs in nature this can be a serious danger to our health, white p is extremely poisonous and in many cases exposure to it will be fetal [28]. In most cases people that died of white p exposure had been accidentally swallowing rat poison. Before people die from white p exposure, they often experience nausea, stomach cramps and drowsiness. White p can cause skin burns. While burning, white p may cause damage to the liver, the heart or the kidneys [29].

1.2.3 Eutrophication

The process by which a lake, pond, or stream becomes eutrophic, typically as a result of mineral and organic runoff from the surrounding land. The increase growth of plants and algae that accompanies eutrophication depletes the dissolved oxygen content of the water and often cause a die-off of the other organisms is shown below in figure 1.2 [30].

Figure 1.2 Image of a eutrophic lake

1.2.4 Eutrophication process

Eutrophication can be a natural process that occurs over due to natural runoff of soil nutrients and decay of organic matter. Eutrophication is typically the result of human activities that contribute excess amounts of nitrogen and phosphate into water [31]. Agricultural fertilizers are one of the main human causes of eutrophication. Leaching from the excessive use of fertilizers causes a nutrient build up in neighboring rivers or lakes. As a result of the increased nutrients plants within the lake or river grow rapidly, including algae on the surface of the water. Figure 1.3 shows bellow the eutrophication process in environment [32]. The growth of algae is called an algal bloom, when this occurs it prevents sunlight from getting through the surface and down to the plant life on the riverbed, as a result they die [33]. The death of this plant life results in reduced oxygen in the water, and the plant matter is broken down by decomposer bacteria which use up any remaining oxygen within the water. As a result of the lack of oxygen in the water any animal life - fish and other organisms - die.
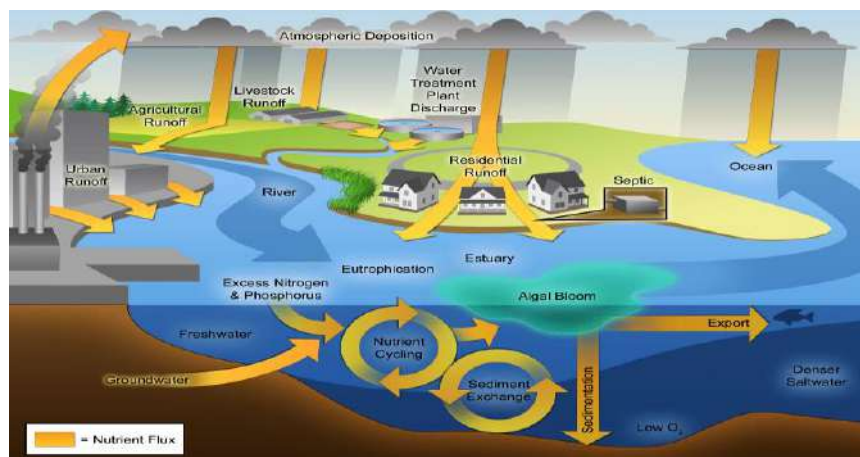
Figure 1.3 Eutrophication process in environment

1.3 Algal bloom caused by excess nutrient in north east area of Bangladesh

Swamp area in the northeast region of Bangladesh has occupied by extensive seasonal flood in April 2017. The toxic agent released by cyanobacteria killed about 1200 tons of fish and thousands of ducks reported in the local newspaper is shown in figure 1.4 [34]. Evidence from a primary investigation it has known that Cyanobacteria blooms were caused by the release of phosphate fertilizers from croplands.

Figure 1.4 Fish & duck death due to excess phosphate at Hakaluki haor

1.3.1 Livestock death at haor

Recent fish and bird deaths from flash flooding in northeast Bangladesh are probably due to blue-green algae that flourished in the water. Much fertilization with urea and phosphates had been done on rice paddies prior to the floods. These are rich sources of available nitrogen and phosphorus nutrients that the blue-green algae (also called cyanobacteria) love [35]. Once the floodwaters mobilized the fertilizer, the cyanobacteria were in ideal conditions to multiply. Their rapid growth leads to conditions that can easily cause massive die-offs of animals such as have been widely reported elsewhere in the world. Figure 1.5 collected from daily newspaper shows livestock died at Sunamgonj Haor.

Cyanobacteria have been implicated for deaths in fish, bird, livestock and even human populations [36]. Events in which algae reproduce dramatically are call "blooms". Water samples from Dakher haor and Khercher haor showed phosphorus levels that were two to three times higher than normal, 0.07 and 0.09 mg/L respectively as opposed to less than 0.03 normally. At Tanguar Haor, where few wildlife deaths were found, the phosphorus level was lower at 0.05 mg/L.

Figure 1.5 Livestock died at Sunamgonj haor

1.3.2 The main reason behind the disaster

Cyanobacteria release poisons known as cyan toxins. Some of these are among the most powerful toxic substances known. Cyanobacteria can produce neurotoxins (affecting the nervous system), hepatoxins (damaging the liver), cytotoxins (affecting cell metabolism) and endotoxins (triggering allergic immune responses) [36, 37, 38]. The specific toxins depend on which particular species of cyanobacteria are present [39]. To completely understand these animal deaths, it will be necessary to determine which blue-green algae contributed to these blooms. Preliminary examination of water samples from the area had visible suspensions of blue-green algae.

Fish living in the algal blooms had a double dose of trouble. Not only were they possibly subject to cyanotoxins, they were also in waters that were depleted in dissolved oxygen for them to breath [40]. The algal blooms create much organic material that must be decomposed, both metabolic wastes and dead cells. As they decompose, they consume the dissolved oxygen that the fish need. Water samples from Dakar haor and Khacher haor showed biochemical oxygen demands (BOD, a measure of how much organic material could be decomposed) that were five to six times higher than normal, 12.77 and 13.56 mg/L versus a normal 2.5 mg/L. These same two locations had dissolved oxygen levels that were less than a quarter of normal values, 1.5 and 1.2 mg/L versus a normal 5 mg/L. At Tanguar Haor, where fewer wildlife deaths were reported, the BOD level was slightly elevated at 3.12 mg/L and the dissolved oxygen content was a normal 5.4 mg/L.

Table1.1 Physico-chemical parameter of Tanguar Haor, Dhaker haor, Khercher haor are given below in a table.

Parameter	Tanguarhaur	Dhakerhaur	Khercherhaur	Normal range
CO_2	0.2 mg/L	0.2 mg/L	0.2 mg/L	0.759-0.663 mg/L
O_2	5.4 mg/L	1.5 mg/L	1.2 mg/L	5 mg/L
Alkalinity	1 mg/L	1 mg/L	1 mg/L	20-200 mg/L
Hardness	5 ppm	15 ppm	5 ppm	0-530 ppm
Ammonia-nitrogen	0.21 mg/L	0.06 mg/L	0.31 mg/L	Toxic level 0.53-22.8 mg/L
PH	7.2	6.7	6.8	3<PH<11
Salinity	33.1ppm	54.4 ppm	47.8 ppm	Less than 1000 ppm
Conductivity	54.4 µs/cm	96.3 µs/cm	82.9 µs/cm	150-500 µs/cm
Total dissolved solid	38.2 ppm	68.5 ppm	58.6 ppm	500 ppm

Fish die when there is no oxygen in the water.

	normal	1/4 normal	1/4 normal	normal
Parameter	Tanguarhaur	Dhakerhaur	Khercherhaur	Normal range
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Conductivity	54.4	96.3	82.9	150-500 µs/cm
Total dissolved solid	38.2 ppm	68.5 ppm	58.6 ppm	500 ppm

Algal blooms create huge number of cells. As these die off, they decompose and use up oxygen that the fish need to breathe.

Table1.2 BOD & P parameter of Tanguar Haor, Daker haor, Khercher haor are given below in a table.

Parameters	Tanguar Haor	Daker haor	Khercher haor	Normal range
Phosphorous	0.05 mg/L	0.07 mg/L	0.09 mg/L	<0.03 mg/L in fresh water
BOD	3.12 mg/L	12.77 mg/L	13.56 mg/L	2.5 mg/L

Physico-chemical parameter show that, acid mine drainage however the extremely low DO level suggests possibility of algal bloom.

1.4 Removal of phosphate

There are many acceptable methods for treatment of removal phosphate such as ion exchange, [43,44] chemical precipitation [45], Filtration, coagulation, reduction, and adsorption [46]. Adsorption have been widely applied in this field. Among those common methods, the adsorption method is considered as the most facile, and cost-effective [47].

1.4.1 Adsorption

Sorption is an effective, reliable, and environmentally friendly treatment process for the removal of phosphates [49]. At this study we use domestic adsorbent RHA and Sylhet sand which very available in our country and cost effective. On the other hand, RHA contain huge amount of silica as a result sorption capability of RHA is so high [50]. Sylhet sand also contain huge amount of silica. In this experiment we treated RHA by 0.1M $FeCl_3$ as a result RHA contain Fe which can easily bind with phosphate [51,52]. Brown colored Sylhet sand also contain Fe so both of the sorbent has high capability of removal phosphate is shown in figure 1.6 [53]. As binding affinity are less between sorbent and sorbet than other removal process of phosphate, so recovery of phosphate is also easy from these adsorbents [53,55].
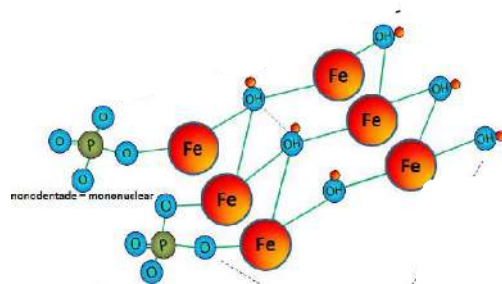
Figure 1.6 Phosphate bonding with Fe and Fe binding with silica

1.5 Importance of recovering Phosphate

Phosphorous recovery from adsorbent can be a source of raw material for the phosphate industry, especially the production of phosphate fertilizers for agriculture [56]. If successful method is developed for effective and economical recovery of P, the current thinking that P is a contaminant will change to one that deems it is resource [57]. This view has increased in recent years because some have argued that P is a limited and non-renewable resource and the reserves of high-grade phosphate rock that are used to make p fertilizers will be largely exhausted before the end of this century, unless another source of high-grade p is identified [58,59]. However, others reported that assuming current rates of production, phosphate rock concentrate will be available for the next 300-400 years [60].

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CHAPTER 2

Experimental

2.1 Materials and instruments

2.1.1 Chemicals and reagents

The chemicals and reagents used in this research were analytical grade and used without further purification. Deionized water and double distil water was used as solvent to prepare most of the solutions of this work. The chemicals and reagents which were used in this research are given below:

i. Sulfuric acid (98%) (Merck, Germany)

ii. Sodium hydroxide (NaOH) (Merck, Germany)

iii. Glycerol (99.0%) (Merck, Germany)

iv. Nitric acid (68.0%) (Merck, Germany)

v. Potassium phosphate monobasic (99.0%) (Merck, India)

vi. Hydrochloric acid (37%) (Merck, Germany)

vii. Ammonium metavanadate (98.0%) (Merck, India)

viii. Ammonium heptamolybdate (99.98%) (Merck, India)

ix. Stannous chloride (98.0%) (Merck, India)

x. Sodium metasilicate (98.0%) (Sigma-Aldrich)

xi. Brilliant green (90.0%) (Sigma-Aldrich)

xii. Calcium chloride (97.0%) (Merck, India)

2.1.2 Instruments

Analysis of the samples was performed using the following instruments:

i. Fourier Transform Infrared Spectrophotometer (SHIMADZU FTIR-8400)

ii. Scanning Electron Microscopy (JSM-7600F, Tokyo, Japan)

iii. Energy-dispersive X-ray spectroscopy (EDS) (Philips, Expert Pro, Holland)

iv. X-ray diffraction spectroscopy (XRD) (Philips, Expert pro, Holland)

v. Centrifuge machine (Hettich, Universal 16A)

vi. pH meter (Hanna, HI 8424, Romania)

vii. Digital Balance (AB 265/S/SACT METTLER, Toleto, Switzerland)

viii. Oven (Lab Tech, LDO-030E)

ix. Hach spectrophotometer (USA DR6000)

x. UV- visible Spectrophotometer (Shimadzu, AA-7000, Japan)

xi. Rotary shaker (BST/RS-425, India)

2.2 Study area

The sample was collected from different place of Sunamgonj swamp (haor) area is Shown in figure 2.1. Sample was collected from Tanguar Haor, Dakher haor, Hakaluki haor and khercher haor. The sample used in this study was collected from in 1-liter different polyethylene containers and stored with preservatives prior to its use in the experiments. Sample also collected from Gazipur lake near by paddy plant field is shown in figure 2.2.

Figure 2.1 Sunamgonj haor region

Figure 2.2 Tanguar Haor & Gazipur paddy field region

General Scheme:1

General Scheme

Sample / stock solution — Determine concentration → • UV

Sand — Characterization → • FTIR • SEM-EDX • XRD

RHA — Characterization → • FTIR • SEM-EDX • XRD

Sand → Batch study → Sand+ Effluent

RHA → column study → RHA + Effluent

Sand+ Effluent → Sand, effluent

Characterization → • FTIR • SEM-EDX • XRD

effluent → Determine concentration by → • UV

RHA + Effluent → effluent, RHA

effluent → • UV

RHA — Characterization → • FTIR • EDX • XRD

2.3 Collection of adsorbents

The adsorbent was collected from different place of Bangladesh. The Sylhet sand were collected from Sylhet district. The RHA was collected from Dinajpur Rice mill is shown below in figure 2.3. Adsorbent was preserved in safely at dry place.

Figure 2.3 Sylhet sand & Rice hull

2.3.1 Collection & preparation of adsorbent (Sylhet sand)

The sorbent materials were obtained locally in Bangladesh. The sand was collected from the Sylhet district. The sorbents were preserved in a dry condition until prepared for sorption studies. Before using, the Sylhet sand was washed 3 to 4 times in distilled water and 0.10 M HCl. The washed sand was then dried in a 60°C oven for 24 h [1].

2.3.2 Collection & preparation of adsorbent (RHA)

The rice hulls were also washed 3 to 4 times in distilled water then washed with 0.10 M H_2SO_4. It was oven-dried for 24 h at 60°C. After drying, the rice hulls were burned in ambient air [2,3]. Finally, the rice hulls were transferred to a different crucible and calcined at 600°C in a muffle furnace for 6 h to remove volatiles in the sample (Fig. 2.4).

Figure 2.4 Burned Rice hull & RHA

2.4.1 Phosphate adsorption experiments by column

Columns for flow experiments were conducted by placing 2.0 g of RHA as an adsorbent in a 10-mL syringe (Figure 2.5). The 5-ppm phosphorous test solution was run continuously through the column, about 50 mL of solution at pH 5. The effluent was collected in a beaker and passed through a 0.45-μm pore-sized syringe filter [4,5]. The concentration was determined with a UV-Vis spectrophotometer at 690 nm after developing its color with the stannous chloride reagents [6]. Additional 50-mL aliquots of 5 ppm test solution were passed through the column until a breakthrough event was detected. All experimental trials were replicated 5 times. Different concentrations of phosphorous test solutions were tried to assess column performance under other conditions. Finally, phosphorous was determined in actual samples from the Tanguar Haor.


Figure 2.5 Column experiment by RHA

2.4.2 Adsorption in batch mood:

Batch adsorption Experiments

Batch sorption experiments were conducted on synthetic waste waters by mixing 10 g Sylhet sand with 25 mL of different concentrated synthetic wastewater in 100- mL conical flasks. The flasks were installed on a rotary shaker set to 150 rpm at 25^0C [7]. Sorption studies were performed with pH ranging from 4.0 – 10.0, and contact times ranging from 60 to 240 min. After adsorption, the solution was filtered through a 0.45-µm syringe filter. Subsequent tests were conducted on Sylhet sand to generate adsorption isotherm data. A range of pH was used in order to evaluate its effect.

General Scheme: 2
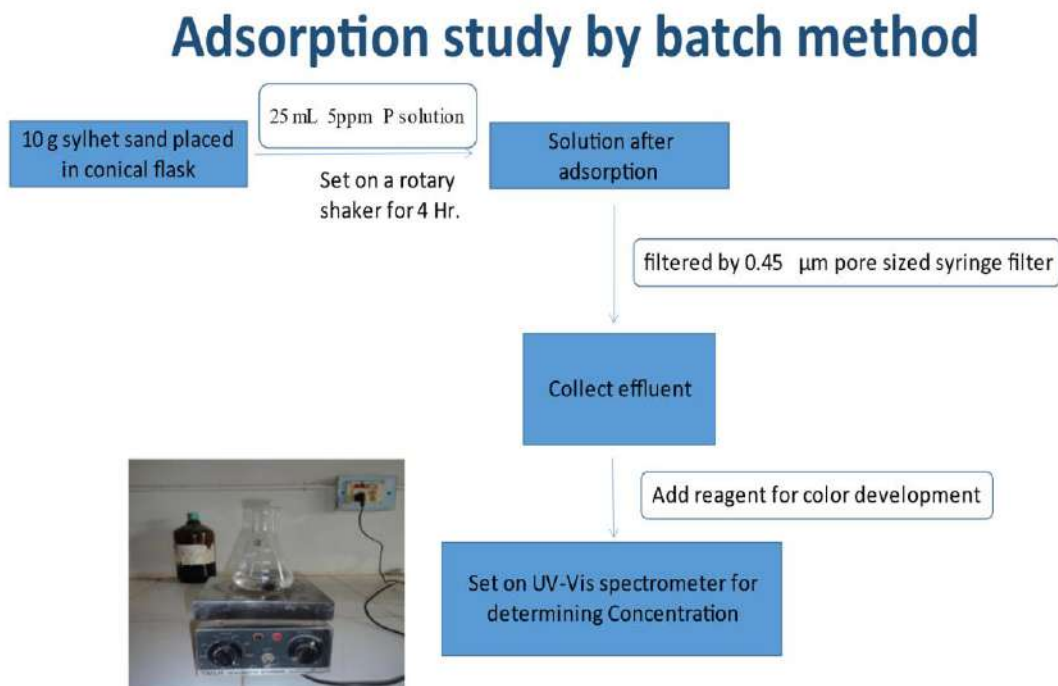
2.4.3 Removal Efficiency (%)

The removal percentage (%) for either batch or column modes was computed using a standard formula

$$\text{Removal percentage} = \frac{W_i - w_f}{W_i} \times 100\% \qquad (1)$$

Where W_i is the amount of phosphorous in mg before adsorption and w_f is amount of phosphorous in mg from eluent (the solution we get after adsorption).

2.5 Stock solution preparation:

By Dissolving 2.195 g anhydrous potassium mono basic phosphate (KH_2PO_4) in 100mL distilled water makes 5000ppm 100 ml stock solution. By diluting about100 times makes 50 ppm and after diluting 10 times makes 5 ppm stock phosphorous solution.

By using $S_1V_1 = S_2V_2$ equation, different test solution was prepared from stock solution.

It's very important to make sure about the clearance that, every test solution was diluted to 0.4 ppm to fit our calibration curve for stannous chloride method.

For 5 ppm test solution, 2 mL phosphorous solution was added with 25 mL solution to convert 0.4 ppm. For 1 ppm test solution, 10mL phosphorous solution was added with 25 mL solution to convert 0.4 ppm test sample.

2.6 Vanadomolybdophosphoric Acid Colorimetric Method

2.6.1 Vanadate-molybdate reagent:

Solution A: 2.5 g ammonium molybdate, $(NH4)_6Mo_7O_{24}.4H_2O$ was dissolved in 30 mL distilled water.

Solution B: 0.125 g ammonium metavanadate (NH_4VO_3) was dissolved in 30 mL distilled water and heated to boiling point. It was Cooled and then added 33 mL of conc HCl. After Cooling Solution B to room temperature, Solution A was poured into Solution B, mixed, and diluted to 100 mL [8].

2.6. 2 Color development in sample by Vanadate-molybdate reagent:

35 mL of sample was placed containing several different concentrations, in a 50-mL reagent bottle. Then added 10 mL vanadate-molybdate reagent and diluted with distilled water. A blank was prepared in which 35 mL distilled water was substituted for the sample. After 10 min, absorbance was measured of sample versus a blank at a wavelength of 400 to 490 nm, depending on sensitivity desired [9]. The color was stable for days and its intensity is unaffected by variation in room temperature.

Figure 2.6 Phosphate with vanadate-molybdate reagent

2.7. Stannous Chloride Method

2.7.1 Principle*:*

Molybdophosphoric acid was formed and reduced by stannous chloride to intensely colored molybdenum blue. This method was more sensitive than Vanadomolybdophosphoric Acid Colorimetric Method and makes feasible measurements down to 0.01 mg/L by using of increased light path length.
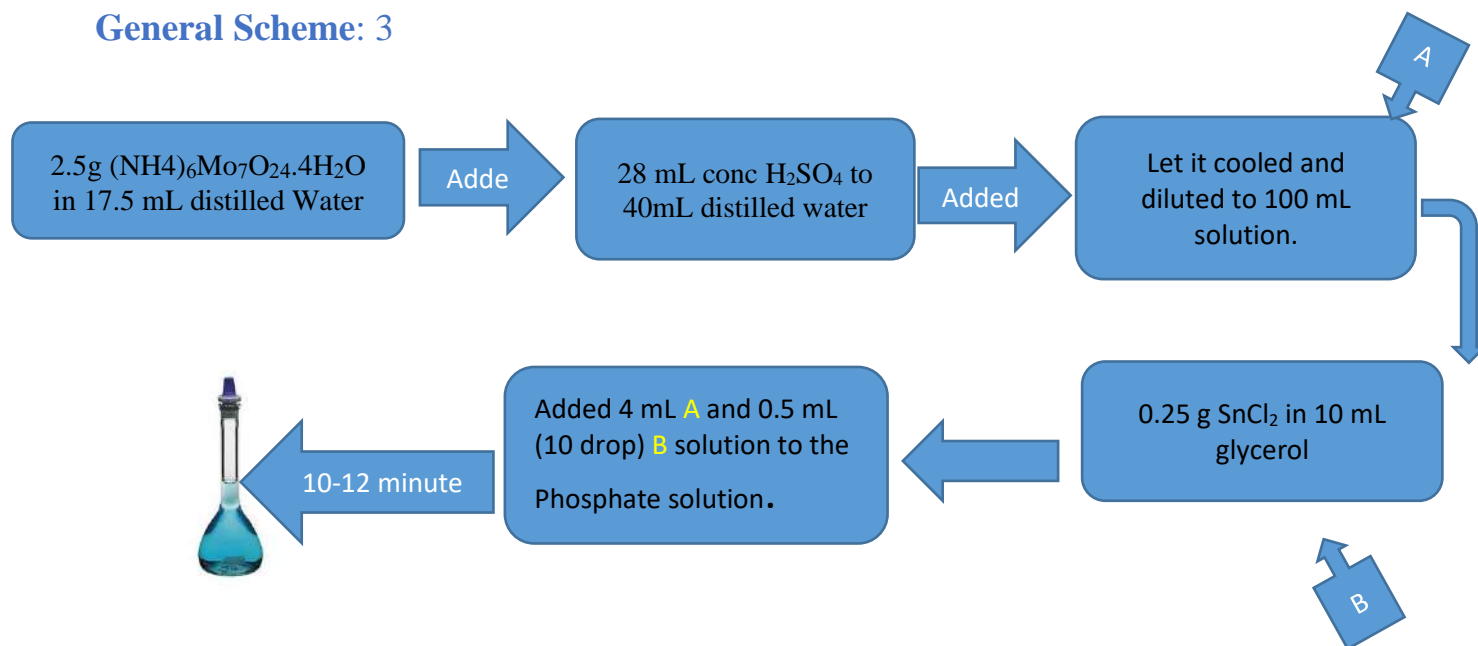
2.7.2 Ammonium molybdate reagent A :

2.5 g ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, was dissolved in 17.5 mL distilled water. Next, 28 mL of concentrated H_2SO_4 was added to 40 mL of distilled water and cooled to room temperature before adding to the ammonium molybdate solution. The solution mixture was diluted to a final volume of 100 mL [10].

2.7.3 Stannous chloride reagent B :
2.5 g of $SnCl_2 \cdot 2H_2O$ was dissolved in 100 mL of glycerol by heating in a water bath at 50°C and stirring to hasten dissolution. This reagent was stable and required neither preservatives nor special storage conditions.

2.7.4 Color development: By stannous Chloride method

General Scheme: 3

With thorough mixing after each addition, 4.0 mL of ammonium molybdate reagent A and 0.50 mL of stannous chloride reagent B were added to a sample. The rate of color development and intensity of the color depended on temperature of the final solution. Each 1°C increase caused about a 1% increase in color intensity [11]. Hence, the samples, standards, and reagents were strictly maintained within 2°C of one another in a temperature range between 20°C and 30°C. Measurements reported here were conducted at 22°C.

2.8.1 Color measurement:

The samples were filtered through 0.45 µm syringe filters and analyzed with a Shimadzu-1800 UV–Vis spectrophotometer using the stannous chloride method. The absorbance at 690 nm was recorded between 10 and 12 min after mixing the coloring reagents and the samples. The same specific time interval was followed for all determinations. A calibration curve and reagent blank were used to determine the sample concentration.

2.9 Sample characterization

2.9.1 Fourier transform infrared Ray (FTIR)

The infrared spectra of Rice hull ash and Sylhet sand were recorded on FTIR spectrometer the region of 4000 – 700 cm^{-1}. All sample had dried. A small portion of samples were taken into vial and oven dried at 95°C to confirmed their dryness. RHA and Sylhet sand is hard so it was grinded into a mortar with a pestle to get powder. RHA samples were not grinded because they were physically granule/powder in shape after completely drying. The powder was then placed in the path of IR beam for measurements.

2.9.2 Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS) analysis

The completely air-dried samples were put on a conducting carbon strip. The sample loaded strip was then mounted to a chamber that evacuated to ~ 10-3 to 10-4 torr and then a very thin platinum layer (~few nanometers thick) were sputtered on the sample to ensure the conductivity of the sample surface. The sample was then placed in the main SEM chamber to view its surface. The microscope was operated at an accelerating voltage of 5.0 kV. The system was computer interfaced and thus provides recording of the surface images in the computer file for its use as hard copy.

2.9.3 X-ray diffraction (XRD)

The crystallinity Rice hull ash (RHA) and Sylhet sand (SS) composite were analyzed by X-ray diffraction pattern in the powder state. The powder samples were pressed in a square aluminum sample holder (40 mm × 40 mm) with a 1 mm deep rectangular hole (20 mm x 15 mm) and pressed against an optical smooth glass plate. The upper surface of the sample was labeled in the plane with its sample holder. The sample holder was then placed in the diffracts meter.

2.10 Hach spectrophotometer

The DR6000 is a benchtop UV-VIS (190 -1100 nm), split beam spectrophotometer that delivers top performance for both routine laboratory tasks and demanding applications. It offers high speed wavelength scanning across the UV and Visible Spectrum, and comes with over 250 pre-programmed methods, which include the most common testing methods used today is shown in figure 2.7[12]. Color developing reagent was added with phosphate solution and allowed it to stand for until color developed, then TNT plus reagent vials was set on the spectrophotometer and the concentration was showed in the screen within a few second as mg/L unit.

Figure 2.7 Image of Hach spectrophotometer

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CHAPTER 3

Results and Discussion

3.1 Characterization of pure RHA & Sylhet sand

3.1.1 Functional group analysis using Fourier transform infrared (FTIR)

The IR spectra of RHA are shown in figure 3.1 The Infrared spectrum showed the structural composition of the RHA. The summarized results are presented in the table 3.7. From the IR spectrum, major spectra bands are observed at 3445 cm^{-1} (Si--OH stretch), 2800 cm^{-1} (-CH stretch), 1610 cm^{-1} (–C=O stretch), 788 cm^{-1}(Si-O stretch), 1055 cm^{-1} (Si-O-Si stretch) and at 670 cm^{-1} (Si-H stretch).[1]
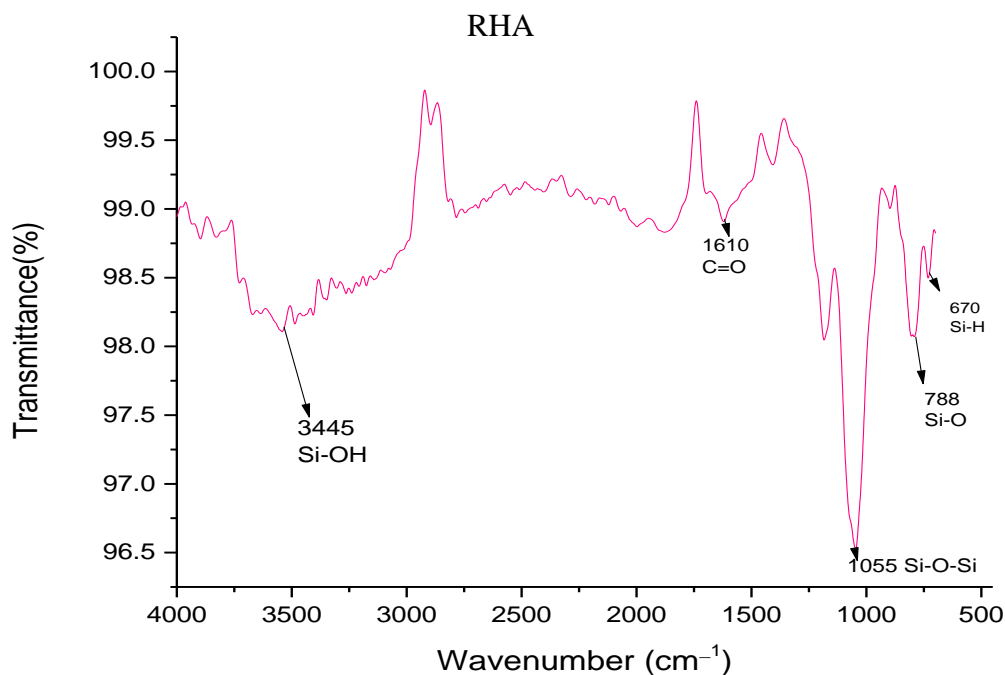
Figure 3.1 FTIR spectra of pure RHA

Table 3.1 Summarized FTIR spectra of RHA in the zone 4000 cm^{-1} to 400 cm^{-1}

RHA Wave no.(cm^{-1})	Region Wave no.(cm^{-1})	Functional Group
	3445	Si-OH
	1610	C=O
	1055	Si-O-Si
	788	Si-O
	670	Si-H

3.1.2 Functional group of Sylhet sand

The plane bending vibration due to the presence of Si-O bond is indicate by the presence of peaks 1085 cm^{-1} and 1033 cm^{-1} for sand in figure 3.2. Gibbsite like vibration is also found to 778 cm^{-1} & 694 cm^{-1}. The presence of plane bending vibration due to Zn=O bond corresponding to 1999 cm^{-1}, 3457 cm^{-1} (Si-OH stretch), 2929 cm^{-1} (C-H stretch), 576 cm^{-1} (Fe-O stretch) [2].
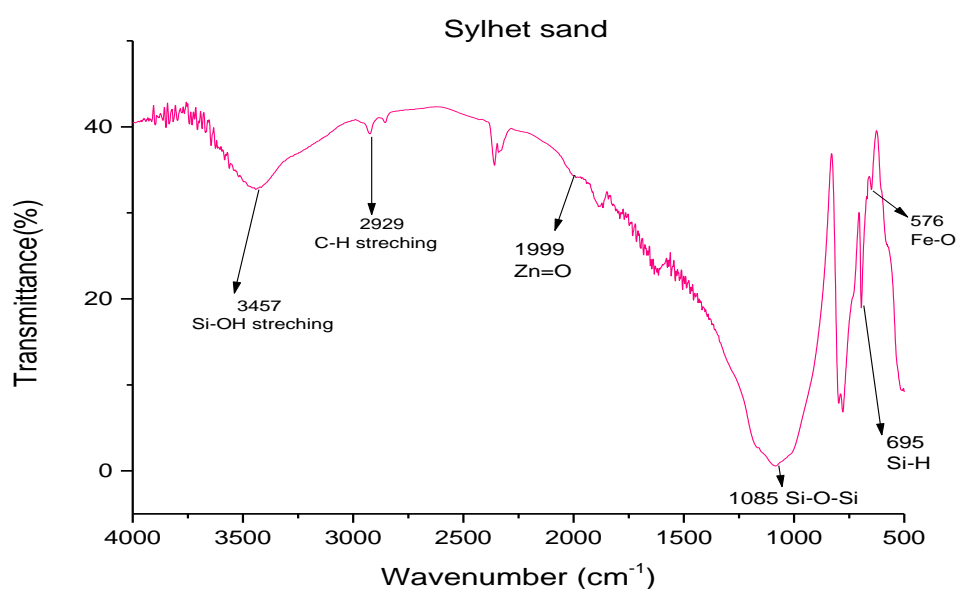

Figure 3.2 FTIR spectra of Sylhet sand

Table 3.2 Summarized FTIR spectra of Sylhet Sand in the zone 4000 cm^{-1} to 400 cm^{-1}

Sylhet Sand Wave no.(cm^{-1})	Region Wave no.(cm^{-1})	Functional Group
	3457	Si -OH
	2929	C-H
	1999	Zn=O
	1085	Si-O-Si
	695	Si-H
	576	Fe-O

3.1.3 X-ray diffraction analysis (XRD)

The XRD patterns of RHA and Sylhet sand are shown in Figure 3.9. Generally, Sylhet sand's powder exhibited a typical sharp peak at 26.28°, which corresponds to an interlay distance of 0.138 nm. The phase composition of the RHA was determined by the XRD analysis of the sample with Philips X-ray Diffractometer model operating with a Cu Kα radiation source (Kα=1.5406 AO). The samples were ground to a fine powder and loaded on a silicon low background sample holder over baseline adhesive. The XRD scans were recorded from 10 - 80° 2θ with 0.20° step-width and 5.1 s counting time for every step [3].

The rice hull samples were calcinated in a furnace for the temperatures such as 600°C and the XRD plot were observed. XRD analysis was observed for selected samples to identify differences in the formation of amorphous or crystalline silica. The intense broad peak observed for the RHA at 600°C samples indicates the amorphous nature of silica (Fig 3.3) [4].

Generally, dark ash exhibits higher carbon content (with the exception of those that may be darker due to soil chemistry or region). Lighter ash has achieved higher carbon burnout while those showing a pinkish tinge have higher crystalline (tridymite or cristobalite) content [5]. The complete white color of the ash shows the total amorphous structured silica. All the Sylhet sand samples shows the Crystalline nature. The sharp peak indicates at the (2θ) value 21°, 26.5° ,28° ,36° ,39.5° & 60° about the crystalline structure of Sylhet sand. (Fig. 3.5) [6].
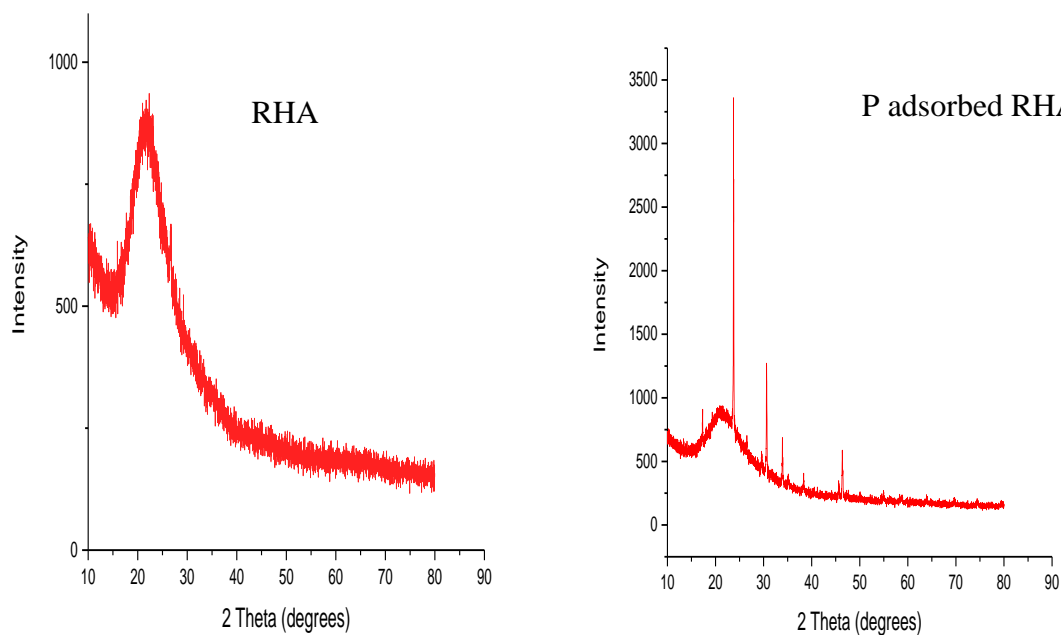

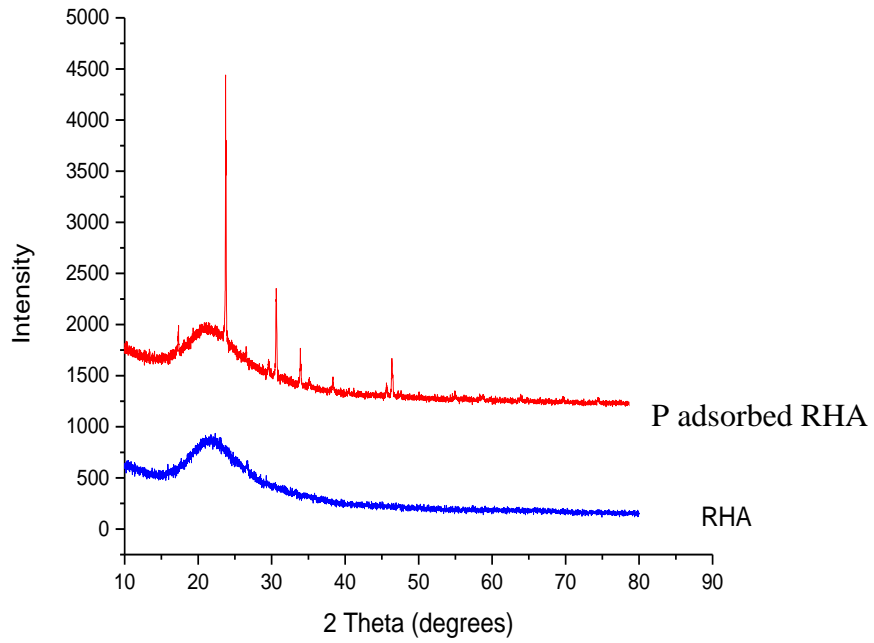**Figure 3.3** XRD spectra of RHA & P adsorbed RHA

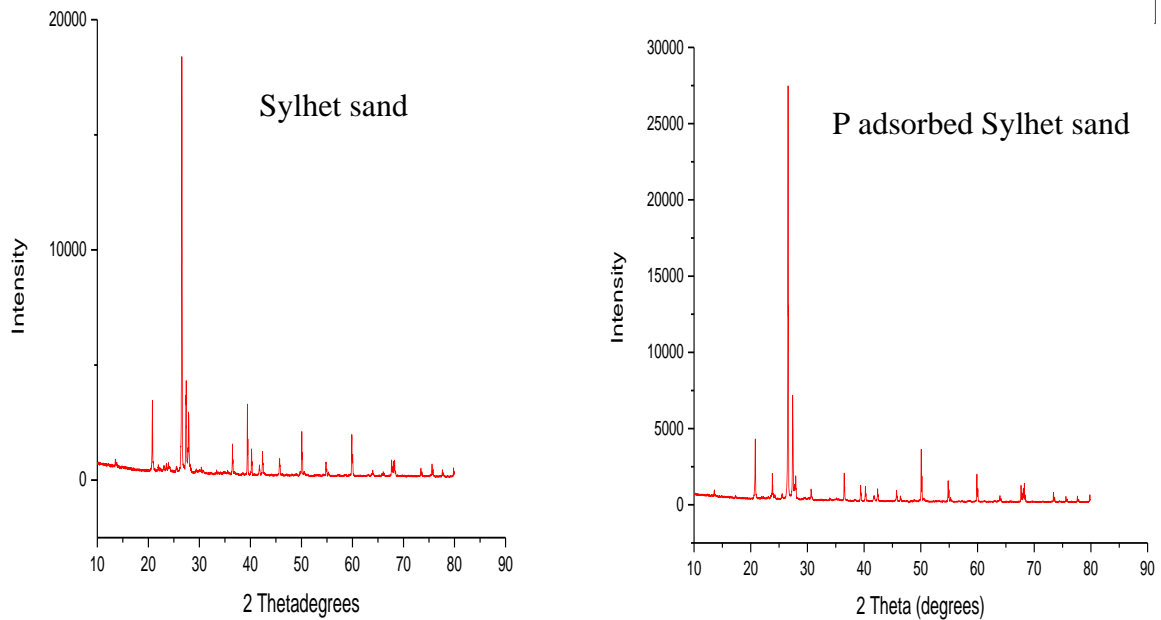**Figure 3.4** Compare of XRD spectra of RHA & P adsorbed RHA

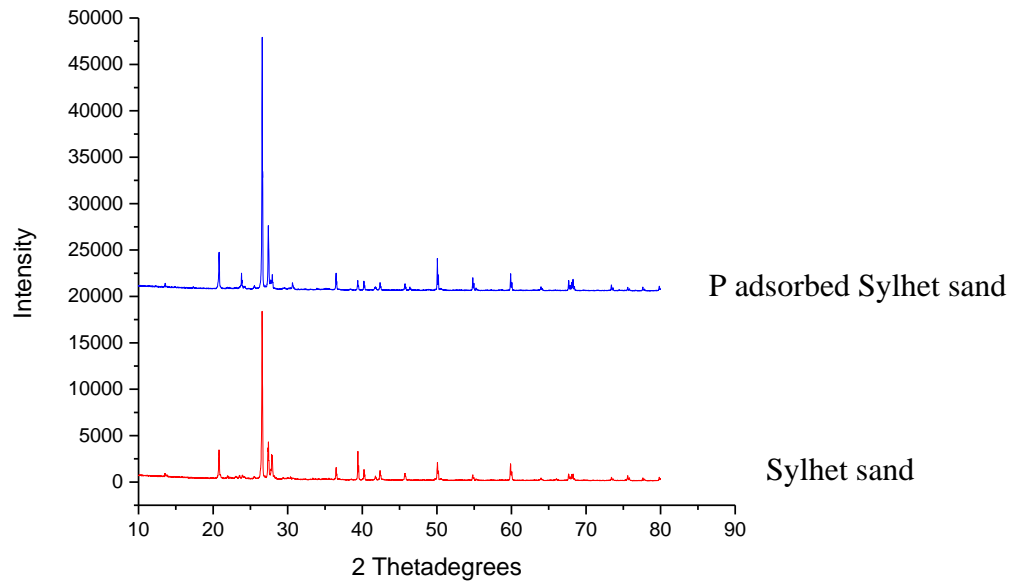**Figure 3.5** XRD spectra of Sylhet sand & P adsorbed Sylhet sand

Figure 3.6 Compare of XRD spectra of Sylhet sand & P adsorbed Sylhet sand

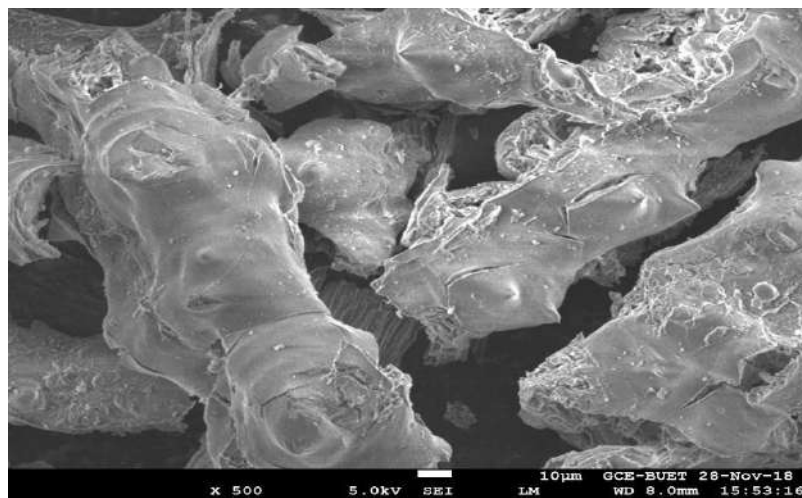## 3.2 Surface morphology study using Field Emission Scanning electron microscope (FE-SEM) SEM observations

Figure 3.7 SEM image of RHA resolution x500**.**

The SEM images (Figure 3.7) of RHA shows many residual pores. From SEM image it seems more porous which indicate about the adsorption capacity of RHA. These images indicate that the surface of RHA observed with a large of hole and network of SiO_2 component, silica is an active and highly porous material with a large internal surface area [7]. So, the rough surface of rice hull ash which increases the adsorption capacity.
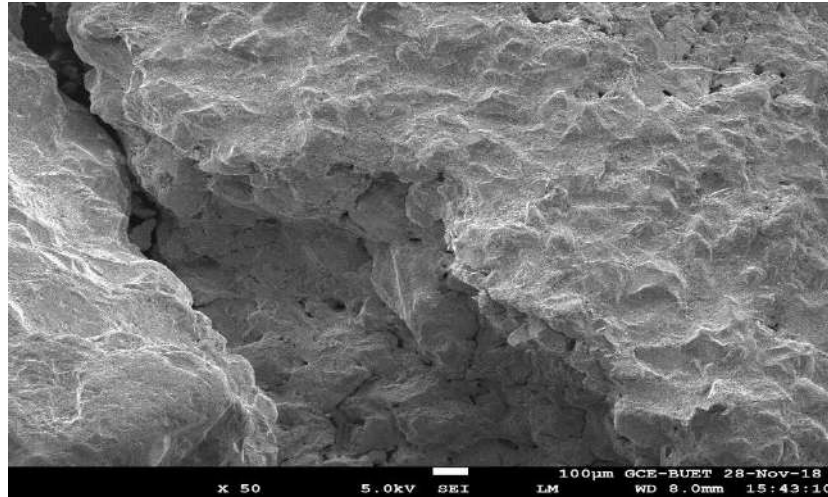
30

Figure 3.8 SEM image of Sylhet sand resolution x10

The SEM image of Sylhet sand (figure 3.8) is smoothly plane and seems not so porous as RHA.

3.2.1 Energy dispersive X-ray (EDX) spectra analysis

The EDX spectra of RHA and P adsorbed RHA is present in the figure 3.9 and 3.10. The EDX spectrum gives us the type and weight percent of each element present in the selected point in the SEM micrographs. From the figure 3.9, it is observed that the RHA contain carbon, oxygen, silicone, iron respectively. However, there is no peak of phosphorous was observed in this spectrum. But from the figure 3.10 spectra we see that there is a small Phosphorous peak is seen where P weight percentage is 5.28 which indicate that phosphate was adsorbed in RHA.

The EDX patterns are presented in figure 3.9 The peaks observed at 0.277, 0.525, 1.739, 2.013, and 6.398 keV, for K lines of C, O, Si, P and Fe respectively. Fig. 3.10 exhibits that the peaks appear at 0.277, 0.525, 1.739, 2.013 & 6.398 keV for K cell of C, O, Si, P & Fe. EDX indicates the presence of C, P, O, Si and Fe on RHA.[8]
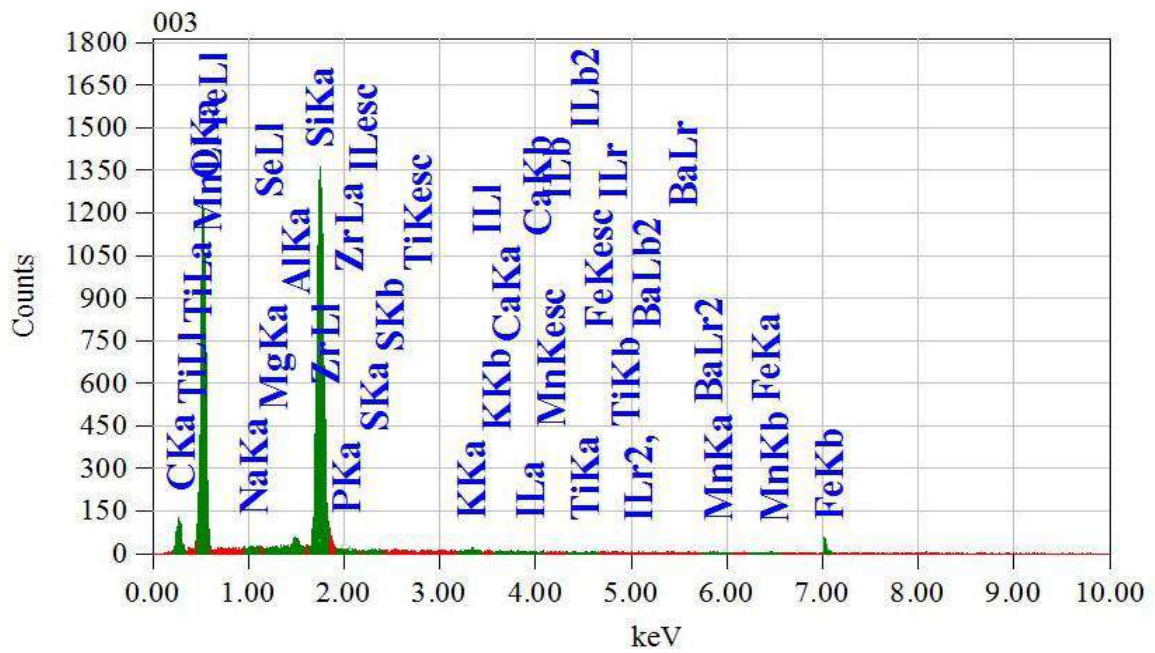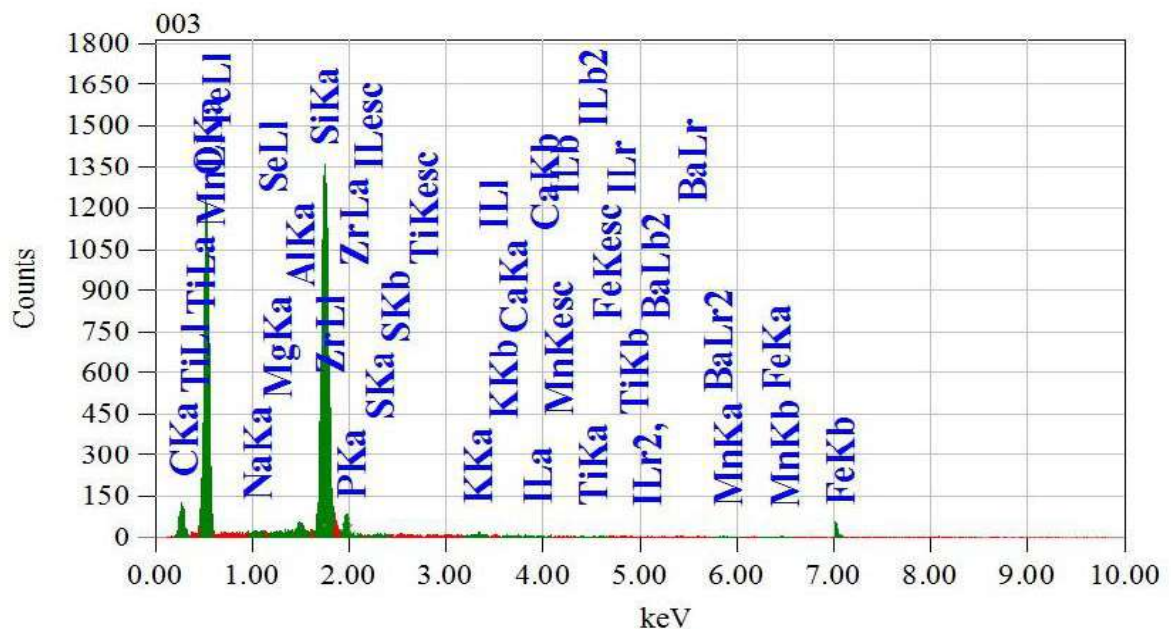
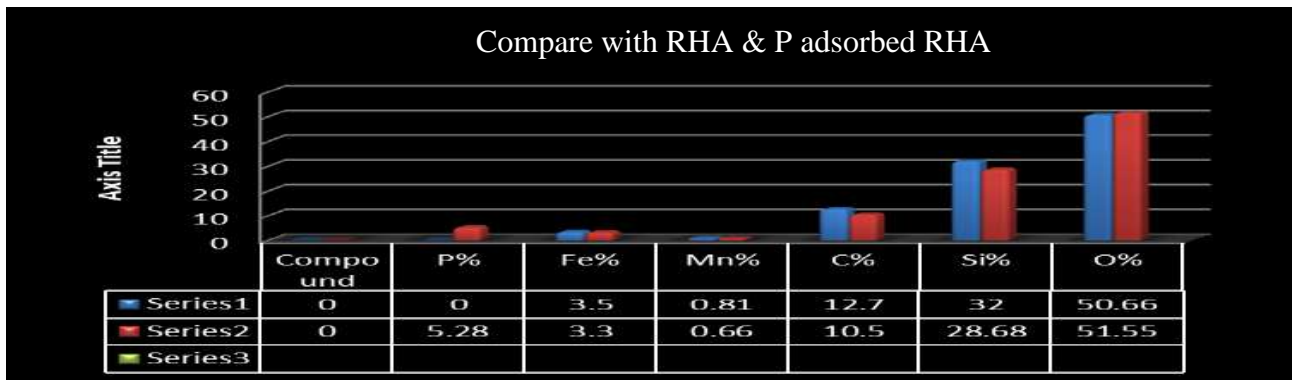**Figure 3.9** EDX spectra of RHA

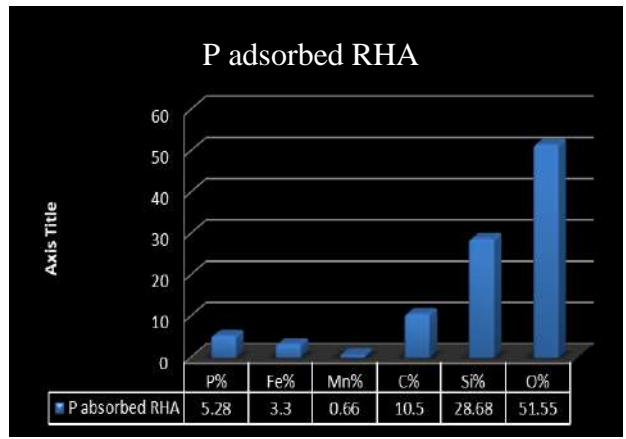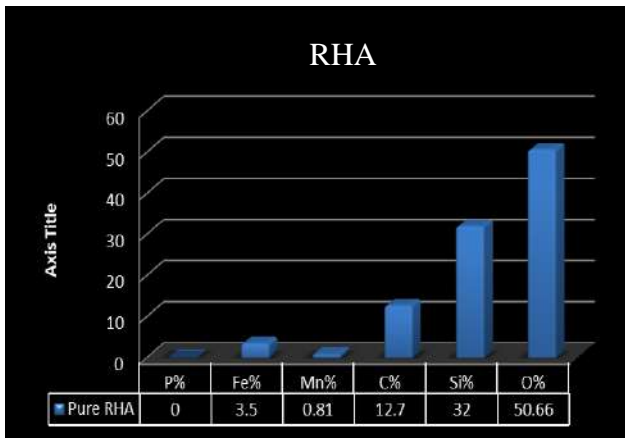**Figure 3.10** EDX spectra of P adsorbed RHA

Figure 3.11 Compare   EDX elemental percentage of RHA & P adsorbed RHA

Table 3.3 Normalized % mass elements in RHA & P adsorbed RHA

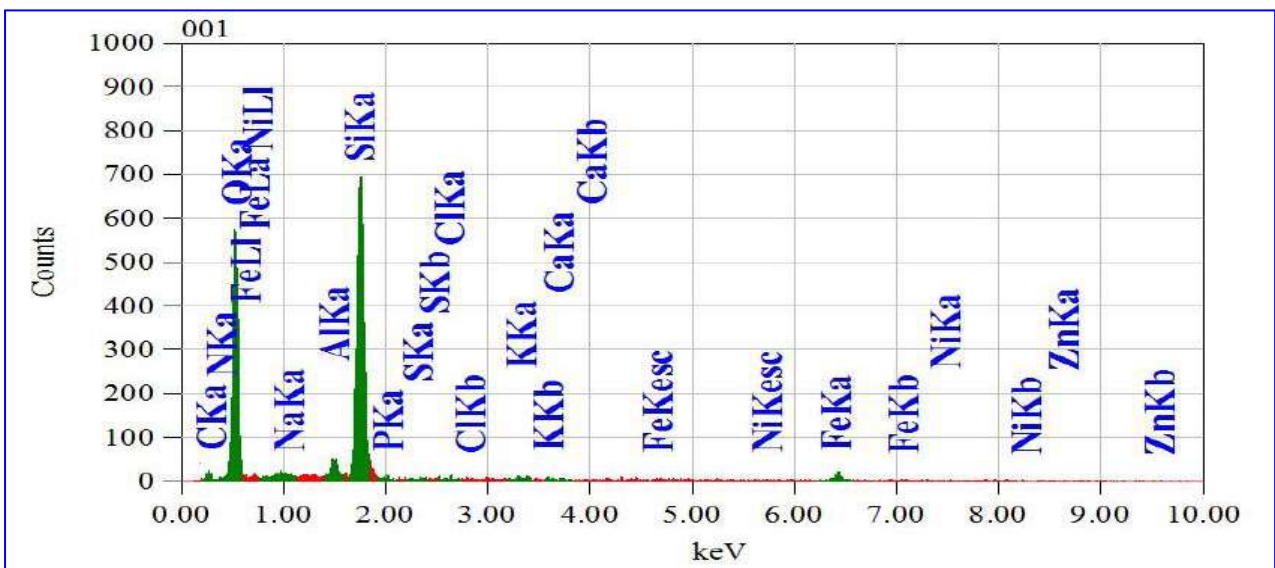| Compound	P%	Fe%	Mn%	C%	Si%	O%
RHA	0	3.5	0.81	12.70	32	50.66
P adsorbed RHA	5.28	3.3	0.66	10.5	28.68	51.55

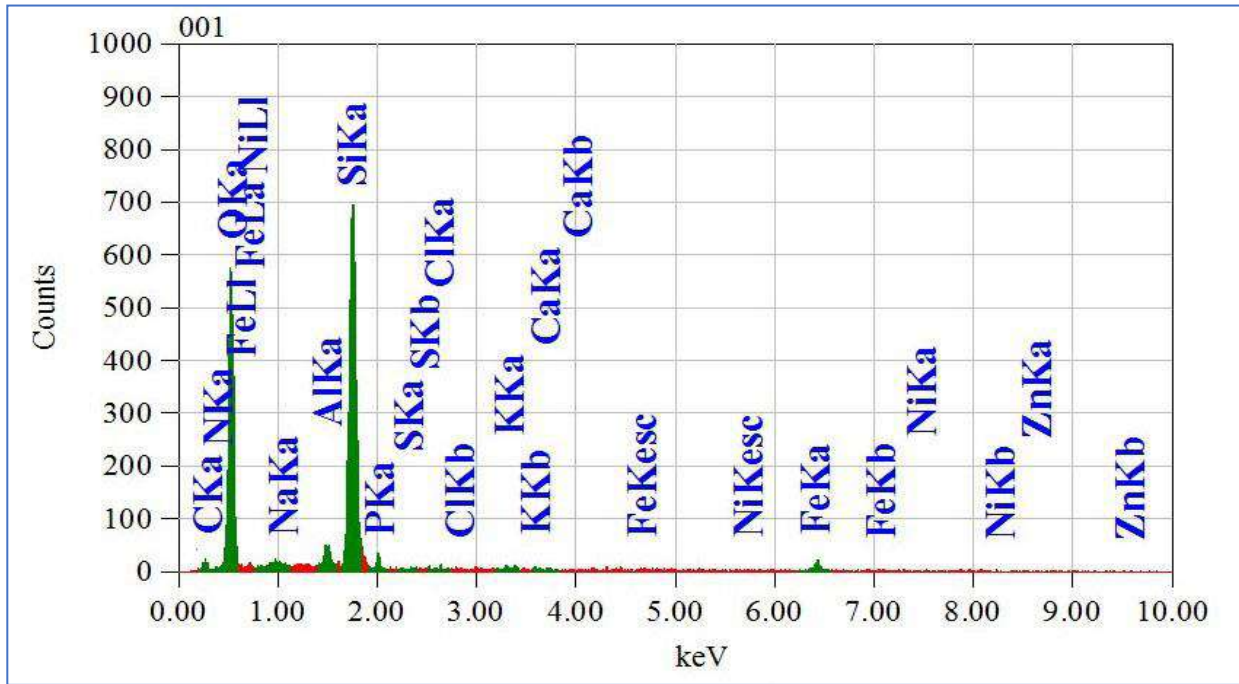**Figure 3.12** EDX spectra of Sylhet Sand

Figure 3.13 EDX spectra of P adsorbed Sylhet Sand

The EDX spectra of Sylhet sand and P adsorbed Sylhet sand are shown figure 3.12 and 3.13. The EDX spectra give us the type and weight percent of each element present in the selected point in the SEM micrographs. From the figure, it is observed that the pure sand contain carbon, oxygen, silicone, iron, Zinc and phosphorous respectively. However, there is no peak of phosphorous was observed in 3.12 spectrum. But from the 3.13 spectra we see that there is a small Phosphorous peak is seen where p weight percentage is 3.28 which indicate that phosphate was adsorbed in Sylhet sand. The amount of oxygen also increased. The EDX patterns are presented in Fig. 3.12. The peaks observed at 0.277, 0.525, 1.739, 2.013, 1.012 and 6.398 keV, for K lines of C, O, Si, P, Zn and Fe respectively. Fig. 3.13 exhibits that the peaks appear at 0.277, 0.525, 1.739, 2.013, 1.012 & 6.398 keV for K cell of C, O, Si, P & Fe. EDX indicates the presence of C, P, O, Si, Zn and Fe on Sylhet sand [9].
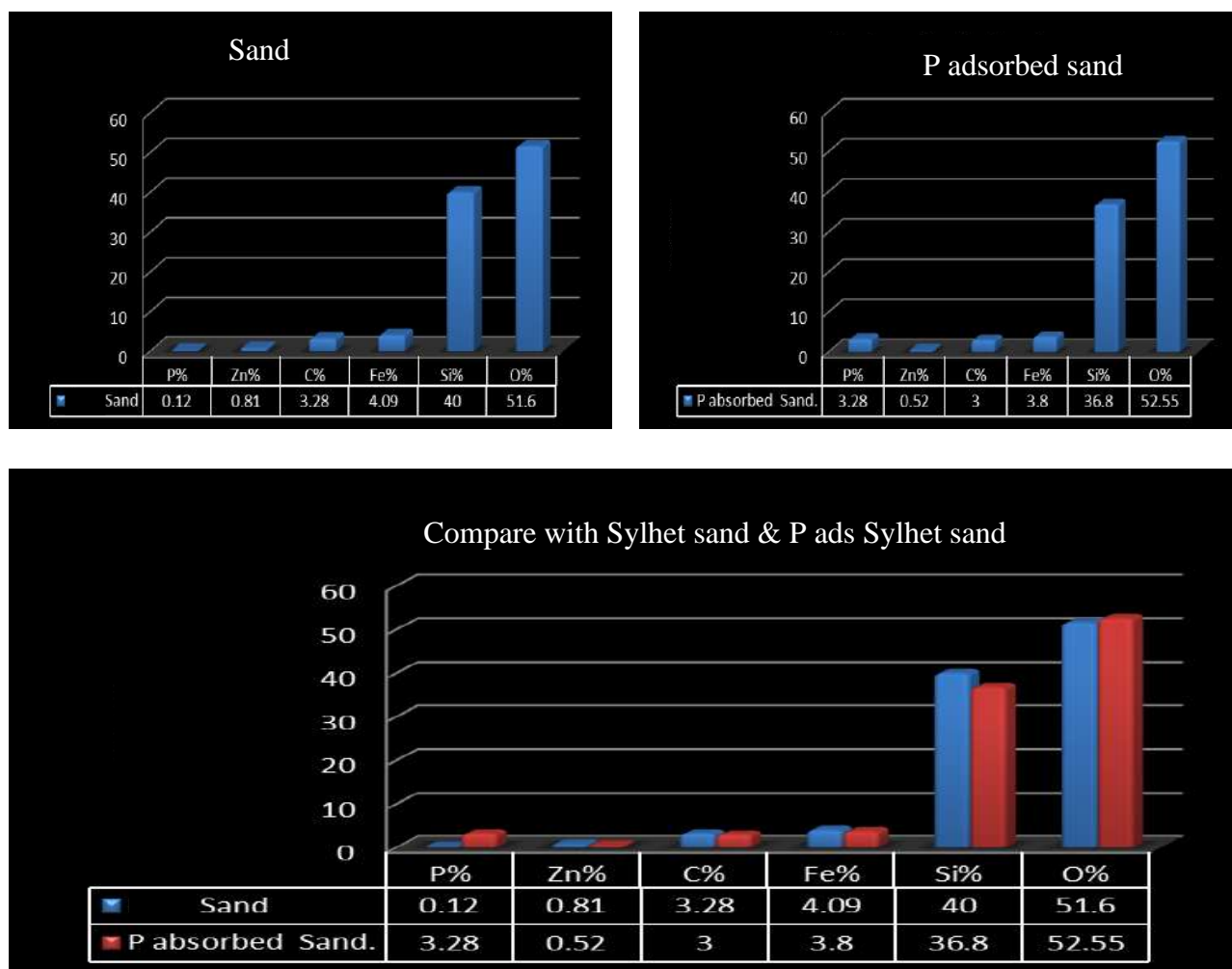
Figure 3.14 Compare EDX elemental percentage of Sand & P adsorbed Sand

Table 3.4 Normalized % mass elements in Sand & P adsorbed Sand

Compound	P%	Zn%	C%	Fe%	Si%	O%
Pure Sand	0.12	0.81	3.28	4.09	40	51.60
P adsorbed Sand.	3.28	0.52	3	3.8	36.8	52.55

3.3 Calibration of phosphorous solution by Stannous chloride method:

By dilution from stock solution 5ppm phosphorous solution was prepared. In several 25 ml volumetric flask 0.5mL, 1 mL, 2mL, 3mL, 4mL & 5 mL phosphorous solution was taken from 5ppm solution and then added 4ml molybdate reagent & 10 drop stannous chloride [10]. Among all the volumetric flask and diluted to 25 mL by adding distil water, thus 0.05ppm, 0.1ppm, 0.2ppm, 0.3ppm, 0.4ppm & 0.5ppm blue colored complex solution were prepared.

Figure 3.15 Phosphate with SnCl$_2$ reagent

After 10 min, but before 12 min, using the same specific interval for all determinations, absorbance was measured color photometrically at 690 nm which is shown in figure 3.16 [11]. Thus, a calibration curve was developed by concentration Vs absorbance which is seen in figure 3.17 and indicates a straight line because the R^2 value is 0.999.
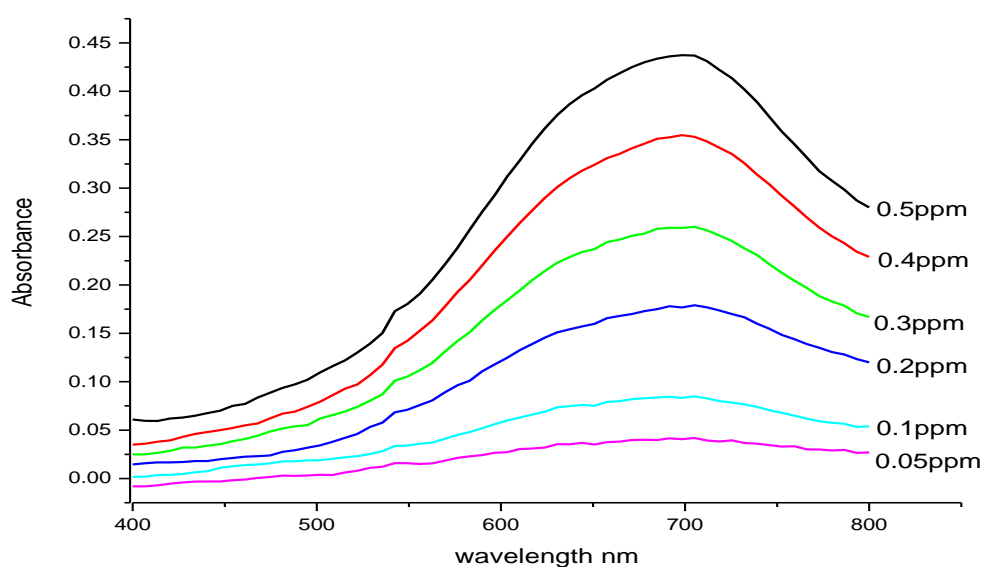

Figure 3.16 Spectra of phosphorous solution absorbance by Stannous chloride process
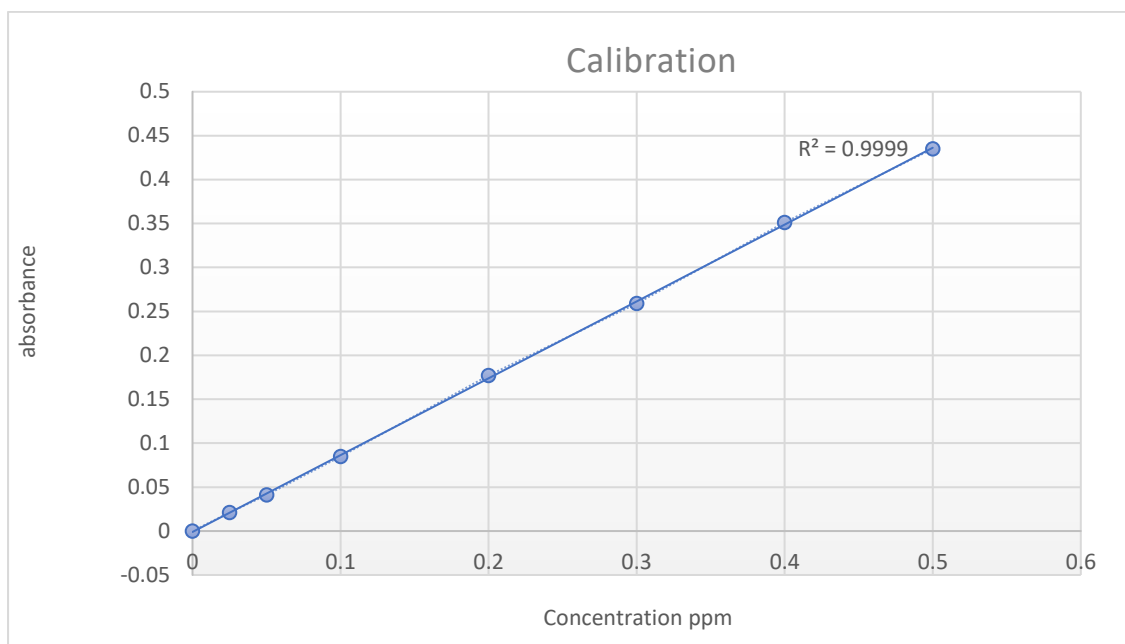
Figure 3.17 Calibration curve of phosphorous solution by stannous chloride process

Table 3.5 Absorbance by Stannous chloride process

Sample no	Wavelength (nm)	Absorbance	Concentration of P (mg/L)
1	690	0.023	0.025
2	690	0.041	0.05
3	690	0.085	0.1
4	690	0.177	0.2
5	690	0.259	0.3
6	690	0.351	0.4
7	690	0.435	0.5

3.4 Calibration of phosphate solution by vanadomolybdate process

By diluting stock solution 50 ppm solution was taken. In several 50 ml volumetric flask .5mL, 1 mL, 1.5mL, 2mL, 2.5 mL, 3mL, 3.5mL & 4 mL phosphorous solution was taken from 50ppm solution and then added 10ml vanadomolybdate reagent among all the volumetric flask and diluted to 50 mL by adding distil water, thus 0.5ppm, 1ppm,1.5 ppm, 2ppm ,2.5ppm, 3ppm, 3.5ppm & 4ppm solution were prepared. It took 10 minutes for developing phosphor vanadomolybdate yellow colored complex [12]. Then absorbance was measured by UV spectroscopy from 400nm to 600 nm wave length. Maximum absorbance was taken at 420 nm. Due to increasing the concentration the absorbance also increased. Thus, a calibration curve was developed by concentration Vs absorbance which are seen in figure 3.19 and indicate a straight line because the R^2 value is 0.9997.
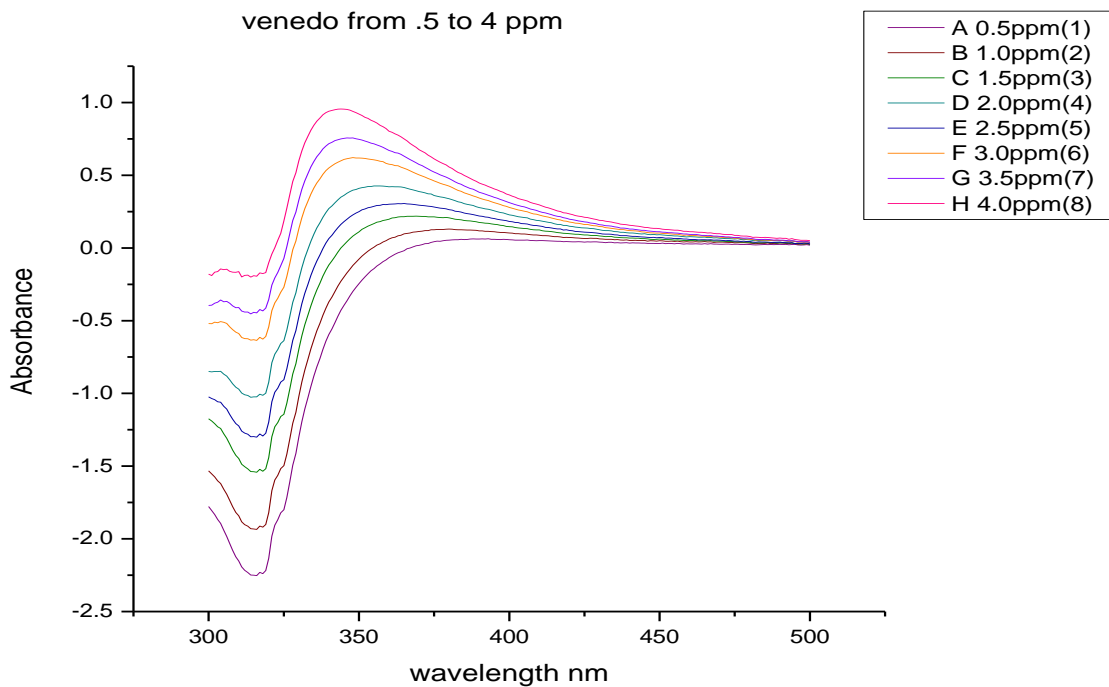
Figure 3.18 Spectra of absorbance by vanadomolybdate process
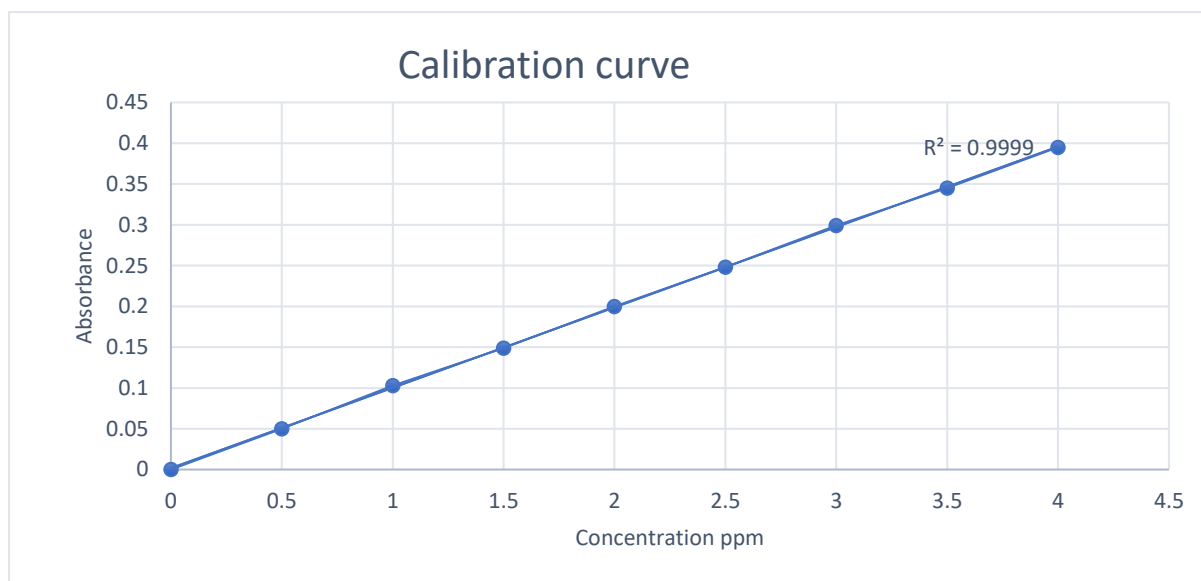
Figure 3.19 Calibration curve of phosphorous solution by vanadomolybdate

Table 3.6 Absorbance by vanadomolybdate

Sample no	Wavelength (nm)	Absorbance	Concentration of P (mg/L)
1	420	0.05	0.5
2	420	0.103	1.0
3	420	0.149	1.5
4	420	0.2	2.0
5	420	0.248	2.5
6	420	0.299	3.0
7	420	0.345	3.5
8	420	0.395	4.0

3.5 Removal of Phosphorous by RHA (Column method)

3.5.1 Removal of P 52.4% by RHA from 5 ppm stock solution.

Figure 3.20 Image of absorbance by RHA (5 ppm test solution)

Table 3.7 52.8% removal phosphorous by RHA

Sample no:	Wavelength (nm)	Absorbance	Concentration (mg/L)	Real concentration (mg/L)	Amount of P (mg)
1	690	0.351	0.4	5	0.25
2	690	0.166	0.189	2.3675	0.11818

Amount of Phosphorous in solution before adsorption w_i= 0.25 mg
Amount of Phosphorous in effluent $\qquad$ w_f = 0.11818 mg

Removal percentage = $\dfrac{W_i - w_f}{W_i} \times 100\%$

$$= \frac{0.25 - 0.118}{0.25} \times 100\%$$

$$= 52.8\%$$

About 5 ppm 50 mL phosphorous solution was passed through the syringe column in which column packing was done by 2g rice hull ash. The effluent was collected in a biker and filtered by 0.45 μm pore sized syringe filter and the absorbance was determined by UV spectroscopy using stannous chloride method. From the absorbance, concentration was determined by the difference of concentration removal percentage was calculated where about 52.4% removal was achieved in column experiment at PH 5, at figure 3.20.

3.5.2 Removal of P 78.5% by RHA from 1 ppm stock solution
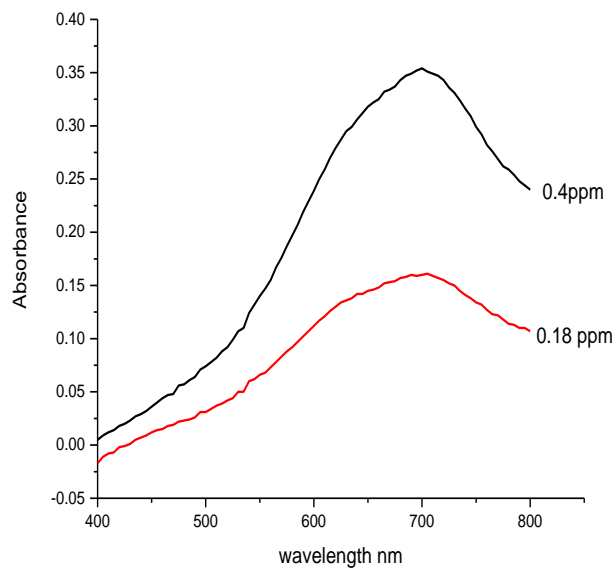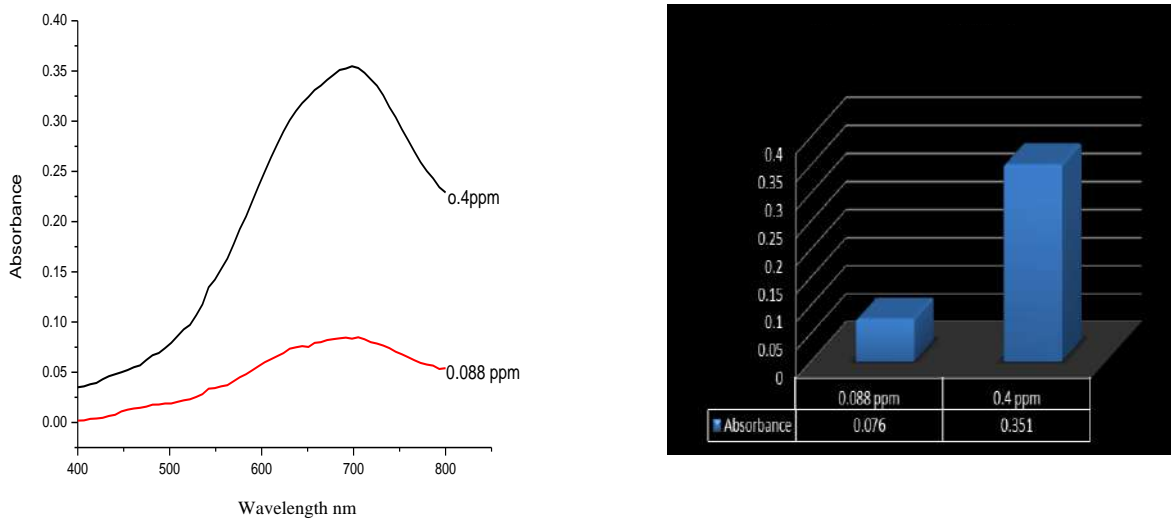

Figure 3.21 Image of absorbance by RHA (1 ppm test solution)

Table 3.8 78.5% removal phosphorous by RHA

Sample no:	Wavelength (nm)	Absorbance	Concentration (mg/L)	Real concentration (mg/L)	Amount of P (mg)
1	690	0.351	0.4	5	0.25
2	690	0.076	0.0866	0.2165	0.054

Amount of phosphorous in solution before adsorption w_i= 0.25 mg
Amount of phosphorous in effluent w_f = 0.054 mg

Removal percentage = $\dfrac{W_i - w_f}{W_i} \times 100\%$

$$= \frac{0.25 - 0.054}{0.25} \times 100\%$$

$$= 78.5\ \%$$

About 78.5% removal of phosphate was achieved by passing 5ppm 50 mL phosphate solution at PH 4.5 shown in figure 3.21. Before column packing adsorbent was treated by 1M $FeCl_3$ solution & kept overnight in oven to dry. Due to RHA was treated by Fe, the adsorption was increased.

3.6 Removal of phosphorous by Sylhet sand (batch method)

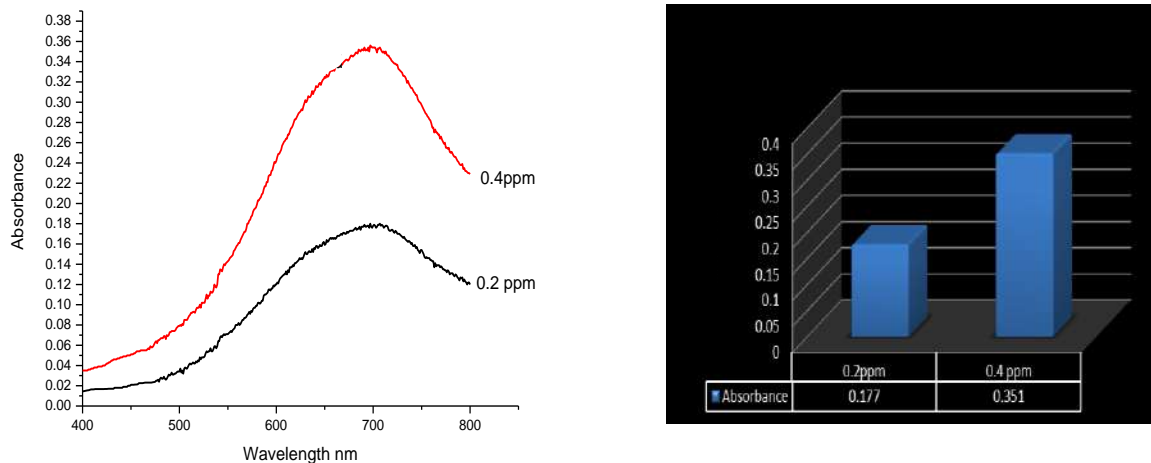### 3.6.1 Removal of P 49.6% by Sylhet sand from 5 ppm stock solution

Figure 3.22 image of absorbance by Sylhet sand (5ppm test solution)

Table 3.9 49.6% removal phosphorous by Sylhet sand

Sample no:	Wavelength (nm)	Absorbance	Concentration (mg/L)	Real Concentration (mg/L)	Amount of P (mg)
s1	690	0.351	0.4	5	0.25
2	690	0.177	0.2017	2.5213	0.126

Removal percentage = $\dfrac{W_i - w_f}{W_i} \times 100\%$

$$= \frac{0.25 - 0.126}{0.05} \times 100\%$$

$$= 49.6\ \%$$

At batch mood sorbent was Sylhet sand, batch mood was studied a several time as one, two and three hours respectively but the maximum adsorption was achieved for 3 hours in continuous shaking at 150 rpm by a shaker at pH 5. After adsorption the effluent was filtered by 45 μm filter and then absorbance was taken by UV-Vis spectrophotometer. From the difference of initial concentration and final concentration removal percentage was calculated. And about 49.6% P removal was achieved for 25mL 5 ppm phosphorous test solution.

3.7 Tanguar Haor sample

3.7.1 Removal of P 83.8% by RHA from Tanguar haor sample

After determining the sorbents on the 5 ppm synthetic solutions, sample from the Tanguar Haor was tested that contained 0.06 ppm phosphorous. It was collected on April 2017 flood events, that led to a hazardous algal bloom. Tanguar Haor sample were tested by both adsorbent RHA & Sylhet sand in batch mode.

For 1st experiment, 2.0 g of Fe-treated rice hull ash were mixed with 25 mL of the haor sample in 100-mL conical flasks. The flasks were installed on a rotary shaker for 3 hours and set to 150 rpm at 25^0C. The initial 0.06 ppm haor sample displayed an absorbance of 0.053 before the run and an absorbance of 0.009 afterwards. Removal efficiency of 83.8% was tested.
For the second experiment, 10.0 g of Sylhet sand were mixed with 25 mL of the haor sample for a 3-hour period on the rotary shaker at 25^0C. The sample was filtered and measured using the commercial Hach test kit. The before sample was 0.06 ppm and the after sample was 0.01 ppm. This represents an 83% removal efficiency, nicely comparable to the treated rice hull ash.
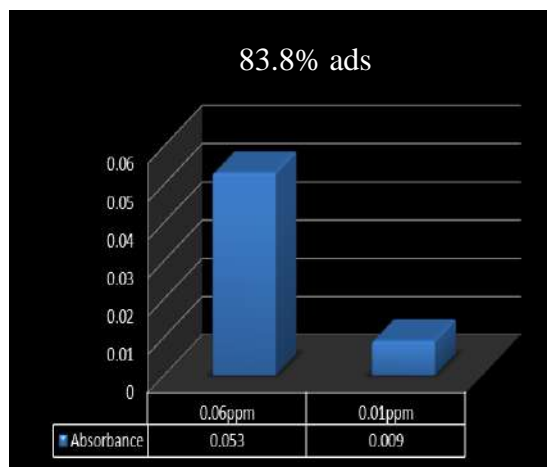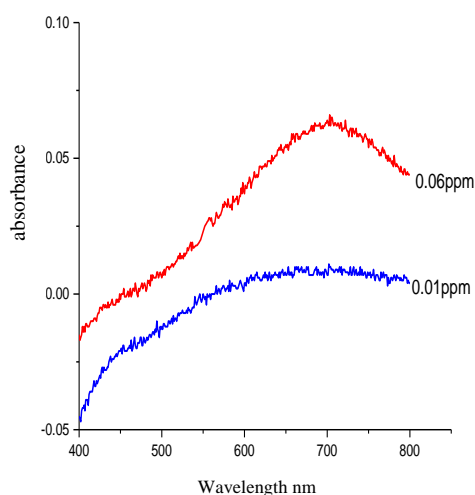
Figure 3.23 image of absorbance by RHA of Tanguar Haor sample

Table 3.10 About 83.8% removal phosphorous by RHA

Sample no:	Wavelength (nm)	Absorbance	Concentration (mg/L)	Amount of P (mg)
1	690	0.053	0.06	0.003
2	690	0.009	0.01	0.00048

Removal percentage = $\dfrac{W_i - w_f}{W_i} \times 100\%$

$= \dfrac{0.003 - 0.0005}{0.003} \times 100\%$

$= 83.8\ \%$

By the same process explained at before in batch mood adsorption was examined for Tanguar Haor sample. The initial concentration was measured 0.06 ppm by UV-Vis spectroscopy. The calculation shows that about 83.8 % removal was achieved for Tanguar Haor sample.

Recovery of Phosphate from sorbent:

3.8 Phosphate desorption and sorbent regeneration

When measured spectrophotometrically at 690 nm, the supernatant solutions indicated 42.9% of the phosphorous had desorbed from the RHA and 71.6% had desorbed from Sylhet sand is shown in figure 3.24.
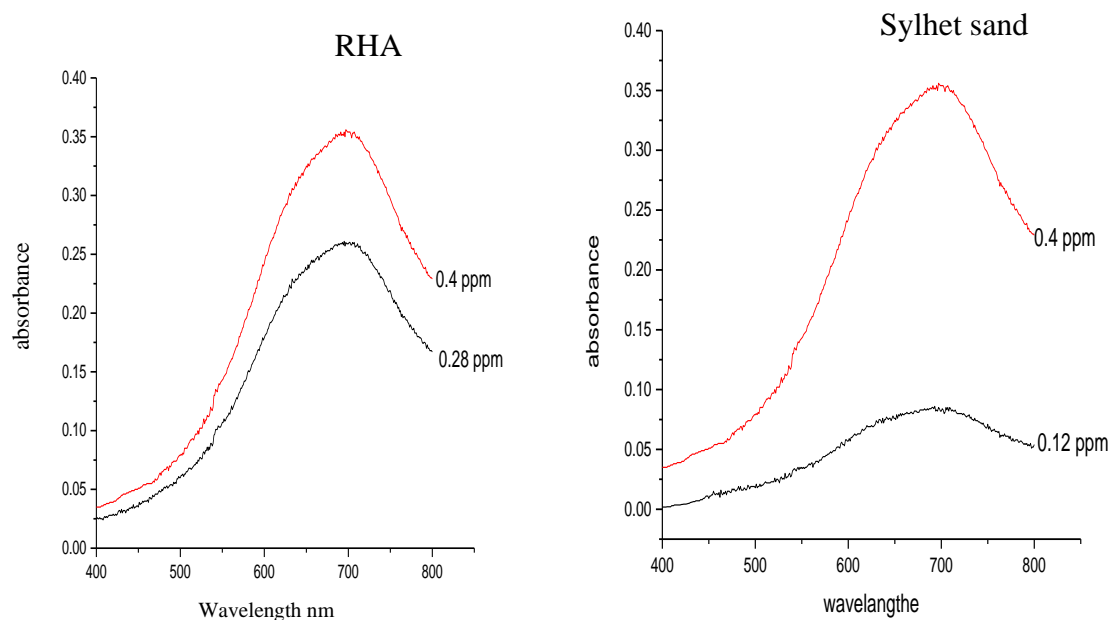

Figure: 3.24 Spectra of phosphate desorption from RHA(left) & Sylhet sand (right)

3.9 Phosphate recovery

Phosphate was recovered from the supernatant solution as $FePO_4$ by adding $FeCl_3$. For a 2.0 g sample of Fe-treated rice hull ash, 0.137 mg of phosphate (as P) was sorbed and 0.045 mg recovered, or 32.8%. For a 10.0 g sample of Sylhet sand, 0.125 mg of phosphate (as P) was sorbed and 0.093 mg recovered, or 74.4%.

3.10 Effect of contact time

10.0 g Sylhet sand was mixed with synthetic 25 mL of both 1-ppm and a 5-ppm test solution and installed in a rotary Shaker set to 150 rpm at 25^oC for contact time 1– 4.5 hours duration. Figure 3.25 indicate that, due to increasing the contact time, gradually removal percentages also increased. At the time duration 2 hours 45 minutes the peak reaches at highest means maximum removal obtained. After a while removal efficiency is decreasing due to desorption started. Beyond that, the removal efficiency dropped off to a fairly steady level of 38%. This suggests that the optimal sorption level is not achieved under equilibrium conditions [13]. There must be some kinetic impediment for desorption that requires the longer contact period.
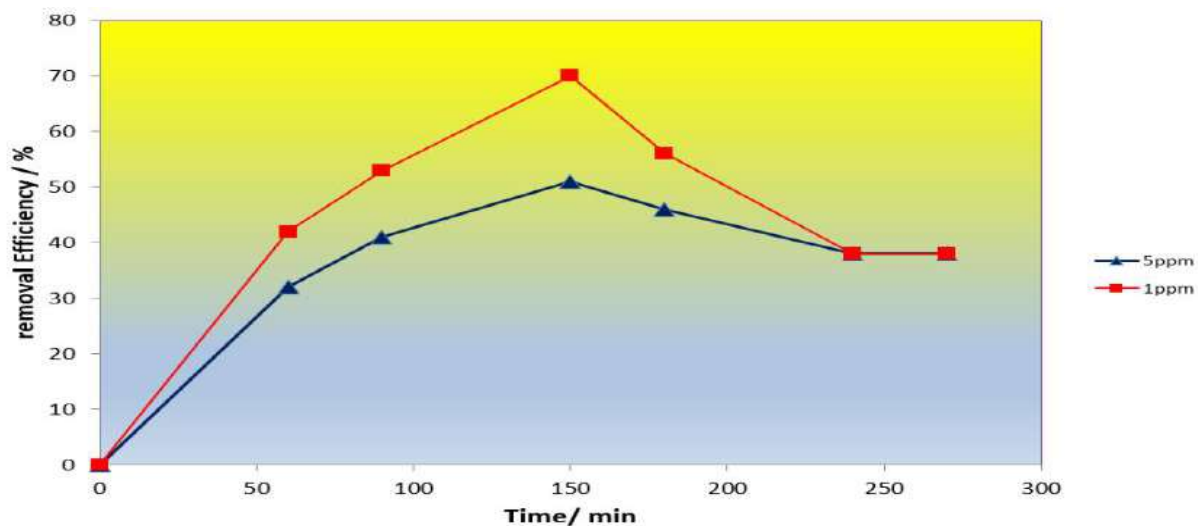

Figure 3.25 Removal efficiencies vs. time for Sylhet sand

3.11 Effect of pH

A set of experiments examined the effect of pH on removal efficiency with a second series of batch studies. Again, 25.0 mL of 5-ppm phosphate test solution was used but the pH was adjusted beforehand with HCl or NaOH to a range of 4.0 – 10.0. Then, 10.0 g samples of Sylhet sand were added and the flasks containing the mixture were installed on the rotary shaker for 3 hours as previously described. The percentage removal efficiencies are shown in Figure 3.26. The highest removal efficiencies were obtained at a pH range of 4.0– 5.0 and at contact times of 3 hours.
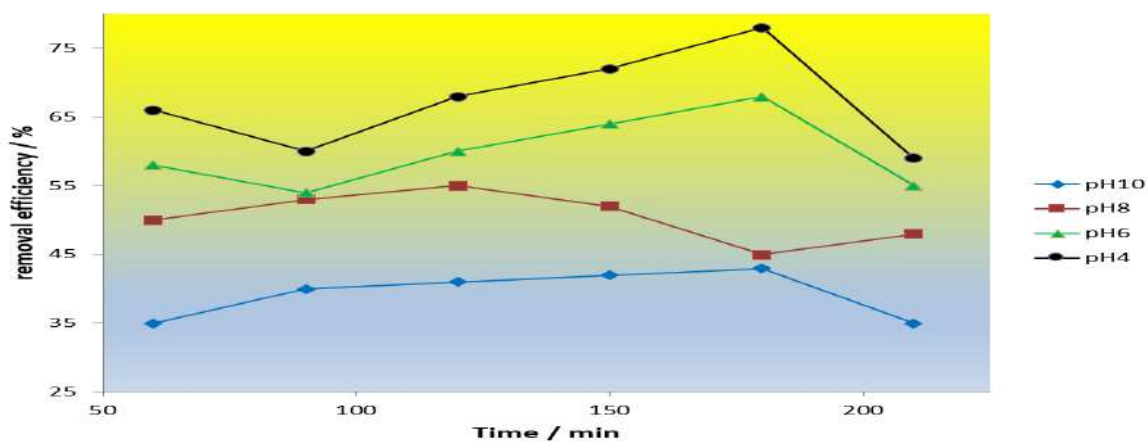

Figure 3.26 Effect of pH on phosphate removal efficiency.

The sorption studies indicated that a pH of 4 to 5 was optimal for phosphate removal. This is explained by noting that, at pH 5, the predominant phosphate species will be $H_2PO_4^-$ (Figure 3.27). The three acid dissociation constants (pi_{ka}) for the H_3PO_4 system are 2.148, 7.199 and 12.15, respectively [8]. If the pH is too much lower than 4, the species distribution shifts towards the uncharged H_3PO_4 form. With no charge, there is no attractive electrostatic attraction to make it attach to the surface. At higher pH, the increasing amount of OH^- in solution begins to compete with the phosphate species. Because Fe^{3+} was correlated with good removal efficiencies, the presence of higher OH^- with increasing pH will block access to these binding sites for $H_2PO_4^-$ ions. OH^- is a stronger complexing ligand than the dihydrogen phosphate. An indication of this is that subjecting the materials after they had surged phosphate to a solution of pH 7.0-8.0 was effective in causing the phosphate to desorb. Essentially, the OH^- was binding more tightly than $H_2PO_4^{2-}$ and considerably less labile once attached.
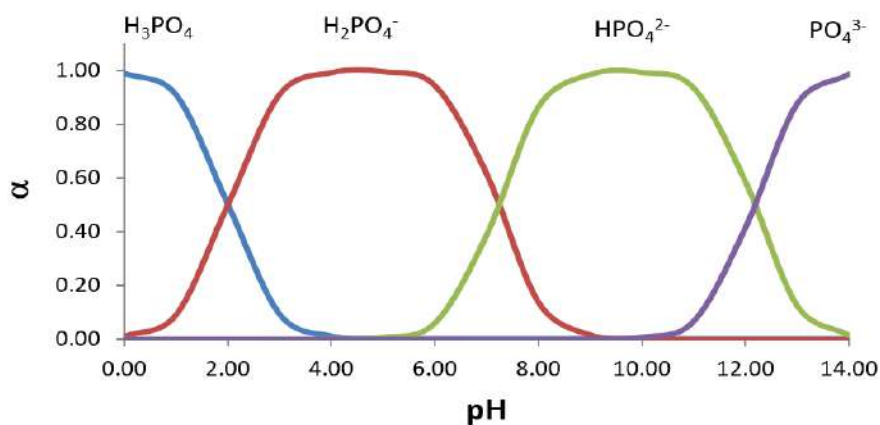
45

Figure 3.27 Species distribution diagram for the phosphoric acid system showing that $H_2PO_4^-$ is the predominant form at pH 5.

The optimal sorption time of three hours is interesting. This was observed in earlier studies on phosphate removal [14]. They, too, found that there was an initial higher sorption peak before settling in to a lower equilibrium level. They suggested the enhanced early adsorption could be due to phosphate levels in the solution that overwhelm the mass transfer process occurring between the sorbent surface and the bulk solution. Not only was this drop off in removal efficiency seen in the time studies of Figure 3.26, but also in the pH study of Figure 3.27.

3.12 Conclusion

Preliminary investigations have been performed on two potential materials for removing excess phosphates from agricultural runoff in Bangladesh. They offer cost effective means to develop methods that can prevent the occurrence of harmful algal blooms as experienced in the April 2017 floods of the haor regions. When tested on an actual haor sample from that incident, 83% of the phosphate was removed with a single exposure to either the Fe-treated rice hull ash or the Sylhet sand. Luckily, the PO_4^{3-} levels that created that algal bloom situation are far below the test solutions that challenged the capacity of the sorbent beds.

The overall removal capacities of the two sorbent materials was 2.37 µg / g rice hull ash and 0.475 µg / g Sylhet sand. This ratio of about 5 to 1 is reflected in the quantities of sorbents that were used in this series of experiments, i.e., 2.0 grams of rice hull ash vs. 10.0 g of Sylhet sand. While the rice hull ash has a higher capacity per gram, it requires a more elaborate preparation procedure. The availability of rice hull ash has a seasonal availability issue.

The ashing and calcining steps require the net input of an energy source. Finally, $FeCl_3$ for treatment adds an additional cost to this material. $FeCl_3$ of sufficient quality would probably have to be acquired from out of country sources. The Sylhet sand, on the other hand, is available in much larger quantities, has no seasonality to its acquisition and needs only to be washed prior to use. This makes it a more attractive option to pursue for development at this juncture. Given that Sylhet sand appears to offer the best opportunity for development, applications need to be designed with a batch mode in mind. The sand was too coarse and packed too loosely to allow for much contact time between the phosphate-containing solutions and the sorbent bed. Because the sorbent was so

It appears that the sorbents can be at least partially regenerated for future use and that the phosphate can be recaptured as an input for fertilizer production. Working out the details of how to best implement the application of these materials to a feasible control program and resource recovery system yet remains.

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