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Barks or stems and their ashes of some herbal plants as sorbents in removing phosphates from waste waters

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ABSTRACT

Exploring the use of bio-sorbents in controlling the phosphate pollution in waste waters is one of the main areas of present research on pollution control methods. In the present work, stems or barks and their ashes of Phyllanthus neruri, *Pongamia pinnata*, *Annona squamosa*. Cassia occidentalis are found to have strong affinity towards Phosphate ions. A thorough investigation has been made in optimizing the various physico-chemical parameters such as equilibration time, pH and sorption dosage for the maximum extraction of phosphates from waters. It is found that % of extraction of Phosphate increases with time and increase of pH for a fixed adsorbent. With stem powder of Phyllanthus neruri the maximum extractability is found to be 90%while with its ashes the extractability increases to 98.0% under the optimum experimental conditions of pH: 10 and after an equilibration period of 5 hrs. Similarly, under the experimental conditions pH:10 and optimum equilibration time of 5 hrs, the maximum extractability is found to 87.0% with *Pongamia pinnata* bark powder and 95.0% with its ashes; 98.0% with powder of stems of *Annona squamosa and 100% with its ashes;* 89.0% with powders of stems of Cassia occidentalis and 92.0% with its ashes. Anions like Chlorides, Sulphates, Nitrates, Fluorides and Carbonates marginally effected the % of maximum extraction at the optimum conditions of pH and equilibration time while cations viz., Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+} and Ni^{2+} ions at concentration of 500 ppm are synergizing the extraction of phosphate and thereby % of removal of Phosphate is increased further. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Phosphate;
Pollution control;
Bio-sorbents.

INTRODUCTION

Phosphorous pollution in natural waters is threatening our ecosystems and deteriorating the quality of our water supplies and moreover, it is spoiling the recreational and economical benefits of clean water bodies. The storm water runoff containing elevated levels of phosphorous can disrupt the balance of nutrients and lead to the proliferation of algae and aquatic weeds; such unrestrained growth often results in lowering the

dissolved oxygen contents which cause loss of aquatic life[10, 43]. This is especially true in urban and suburban environments where widespread fertilizer use and the accumulation of yard debris, often occur near impervious surfaces that channel nutrients to surrounding aquatic ecosystems and in the slow moving rivers or in surface waters. It is desirable to reduce the "total phosphorus" in municipal waste waters from below that of 2ppm.

The sources of phosphorus pollution include concentrated animal feeding operations (CAFOs), agricultural fertilizers, garden products, erosion and presence of common detergents and food residues in domestic sewages. So the Global awareness towards the Phosphate problem has come and different governments started issuing Phosphate Acts to control the pollution. Many countries, making law and legislation to control phosphate levels in environment and in fact, the Switzerland has banned the use of phosphates in industries and detergents.

The literature survey indicates that traditionally the phosphate is removed by chemical precipitation[2, 4, 5, 11, 27, 41]. Biological treatment methods coupled with active sludge processes are thoroughly being investigated in controlling the problem of Phosphate pollution and in fact a number of patents exist in this regard[3, 7, 8, 17, 23, 33-36]. Biomass, either in its native state, or chemically modified, has been suggested as an option to capture water pollutants and nutrients. Wood processing residues (e.g., sawdust, bark) and agricultural residues (e.g., corncobs) have been targeted because of their availability and low value[1, 6, 15, 28]. Studied the Phosphorus removal from aqueous solutions using iron coated natural and engineering sorbents. Use of aqueous plants like water hyacinth has been studied in controlling the pollution[9, 12, 13, 18, 20, 24-26, 30-32], studied the removal of Phosphorous using chemically modified lignocelluloses materias[14]. Reviewed recent advances in removing phosphorous from waste water and its future use as fertilizer[15]. Used cationized milled pine bark as an absorbent for oththophosphate anions. Activaed red mud has been used to remove phosphates from aqueous solutions[22, 29, 40, 42]. Studied the phosphate removal by refined aspen wood fiber treated with carboxymethyl cellulose and ferrous chloride[38]. Studied the simultaneous removal of metal ions Cu^{2+}, Fe^{3+}, and Cr^{3+} with anions SO_4^{2-} and HPO_4^{2-} using clinoptilolite.

Biomass appears to necessitate chemical modification and needs further dwelling in this novel aspect of research.

Bio-sorbent are proving to be potential source of developing methods to control pollutants in natural waters and these sorbent are endowed with natural inherent sorption capabilities and at times, they may need activation by some chemical treatment.

The present work endeavors to explore the sorption abilities of some of the waste materials of flora origin in effecting the phosphate removal from polluted water.

MATERIALS AND METHODS

Chemicals

All chemicals used were of analytical grade

Stock solution of Phosphate was prepared by dissolving 0.2197g of potassium di hydrogen phosphate in double distilled water and is made up to 1 lit. Its concentration is 500ppm. It is suitably diluted as per the need.

Sodium molybdate solution

12.5g of Sodium Molybdate was dissolved in 500ml of 10N. H_2SO_4.

Hydrazine sulphate solution

1.5gms of Hydrazine Sulphate solution was dissolved in 1lit of double distilled water.

Adsorbents

Diverse adsorbents of flora origin were used in this work. The methodology herewith presented is only for the bio-adsorbents showing interesting results. The plants Phyllanthus neruri, Pongamia pinnata, *Annona squamosa* and Cassia occidentalis were found to be sensitive to Phosphate ions concentrations.

Phyllanthus neruri is herb and is best known by the common names are Stonebreaker, Chanca Piedra, Seed-Under-Leaf and in telugu "Nela Usiri" It is a widespread tropical plant and is commonly found in coastal areas. It is a relative of the spurges, belonging to the leaf flower genus of Family Phyllanthaceae. *Pongamia pinnata is* one of the few nitrogen fixing plant to produce seeds containing 30-40% oil. Ac-

cording to Lewis (1988), this species may eventually be transferred to genus *Millettia*. It is often planted as an ornamental and shade tree. This species is commonly called pongam, karanga, or a derivation of these nams. *Annona squamosa is* a small well-branched tree or shrub that bears edible fruits called sugar-apple and belongs to species of the genus Annona, member of the family Annonaceae and grows at lower altitudes making it the most widely cultivated. Cassia occidentalis is a very leafy malodorous tropical weedy shrub whose seeds have been used as an adulterant for coffee belongs to Caesalpiniaceae (Gulmohar) family.

The stems or barks of Annona Squmosa, Ponganuia *pinnata,* Phyllanthus neruri and Cassia Occidentalis were cut or scrapped freshly. The obtained plant materials were washed with tap water and then with distilled water. Then the pieces of stems or barks were sun dried. Then dried stems were powdered to a fine mesh of size: less than 75 microns and thus obtained powders were activated at 105°C in a oven and were employed in this study. Further, these barks/stems were burnt to ashes and these ashes were also used in this work.

Adsorption experiment

The Batch system of extraction procedure was adopted[8, 19, 32]. Weighted quantities of adsorbents were taken into previously washed 1 lit/500 ml stopper bottles containing 500ml/250ml of potassium di-hydrogen phosphate solution of predetermined concentrations. The various initial pH values of the suspensions were adjusted with dil. HCl or dil . NaOH solution using pH meter. The samples were shaken vigorously in mechanical shakers and were allowed to be in equilibrium for the desired time. After the equilibration period, an aliquot of the sample was taken for Phosphate determination. Phosphate was determined spectro photometrically by "Molybdenum Blue" method[39].

Estimation of phosphate

An aliquot amount of Phosphate sample was taken in a 50ml volumetric flask. To it 5 ml each of molybdate solution and hydrazine sulphate solution were added successively and the solution was then diluted to the volume and mixed well. The flask was immersed in a boiling water bath for 10min, removed and cooled rapidly. The flask was shaken and adjusted the volume. Blue color was developed. Optical Density was mea-

TABLE 1 : Effect of interfering Ions on the Extractability of PHOSPHATE

S.No	Adsorbent	Maximum Extractability at optimum conditions	Extractability of phosphate in presence 500ppm of interfering ions at optimum conditions pH and equilibration time									
			SO_4^{2-}	NO_3^-	Cl^-	F^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}	Fe^{2+}	Ni^{2+}
1	Stem Powder of Phyllanthus Neruri	90.0% pH:10, 5.0 hrs	86.5% pH:10, 4.5 hrs	88.5% pH:10, 4..0hrs	84.7% pH:10, 2.0 hrs	85.6% pH:10, 2.5 hrs	88.4% pH:10, 4 .0hrs	92.5% pH:10, 4.5 hrs	91.5% pH:10, 3 .0hrs	94.5% pH:10, 2 .5hrs	95.0% pH:10, 2.5hrs	97.0% pH:10; 2.0 hrs	96.0% pH:10, 2.5 hrs
2	Bark Powder of Pongamia Pirnnata	87.0% pH:10, 5.0hrs	83.6% pH:10, 2 .5hrs	83.9% pH:10, 5.0hrs	81.6% pH:10, 3.5 hrs	82.1% pH:10, 4.5 hrs	86.3 % pH:10, 2.5 hrs	91.3% pH:10, 2.5 hrs	92.2% pH:10, 2 .5hrs	94.5% pH:10, 3.0 hrs	95.8% pH:10, 3.0 hrs	97.3% pH:10; 2.0 hrs	96.0% pH:10, 3.0hrs
3	Bark Powder of Annona Squamosa	98.0% pH:10, 5 .0hrs	89.1% pH:10, 4.5hrs	89.4% pH:10, 1.5 hrs	90.1% pH:10, 4.0hrs	91.8 % pH:10, 2.0 hrs	94.5 % pH:10, 3 .0hrs	99.2 % pH:10, 2.0 hrs	99.1% pH:10, 4.5 hrs	100% pH:10 3.5hrs	100% pH:10, 2.0hrs	100% pH:10; 2.0 hrs	100% pH:10, 2.0hrs
4	Stem Powder of Cassia Occidentalis	89.0% pH:10, 5.0 hrs	85.4 % pH:10, 2.0 hrs	83.2 % pH:10, 3.0 hrs	84.1% pH:10, 2.5 hrs	85.0 % pH:10, 3.0 hrs	85.6 % pH:10, 2.0hrs	93.8 % pH:10, 3 .0hrs	92.2% pH:10, 2.0hrs	96.2% pH:10, 2.0hrs	97.8 % pH:10, 2.5 hrs	97.3% pH:10; 2.0 hrs	96.2% pH:10, 3.5 hrs
5	Stem Ash of Phyllanthus Neruri	98.0% pH:10, 5.0 hrs	92.5 % pH:10, 2.5 hrs	93.5 % pH:10, 2.0 hrs	94.2% pH:10, 3.5 hrs	95.8 % pH:10, 2.5 hrs	96.6% pH:10, 2.0 hrs	98.5 % pH:10, 3.5 hrs	99.0% pH:10, 2.0 hrs	100 % pH:10, 2.0hrs	100 % pH:10, 2.5 hrs	100% pH:10; 2.0 hrs	100% pH:10, 3.5 hrs
6	Bark Ash of Pongamia Pinnata	95.0% pH:10, 5 .0hrs	93.1% pH:10, 3.5 hrs	94.2% pH:10, 3.0 hrs	95.7% pH:10, 2.5 hrs	96.9% pH:10, 1.5 hrs	96.0% pH:10, 2.5 hrs	97.3% pH:10, 3.0 hrs	99.7% pH:10, 2.5 hrs	99.1% pH:10, 2.5 hrs	99.2% pH:10, 2.0hrs	97.3% pH:10; 2.0 hrs	98.4% pH:10, 3.0rs
7	Bark Ash of Annona Squamosa	100.0% pH:10, 4.0hrs	96.3% pH:10, 3.0 hrs	96.4% pH:10, 2.0 hrs	97.0% pH:10, 2.5 hrs	98.5% pH:10, 3.5 hrs	98.0% pH:10, 3.0 hrs	100.0% pH:10, 1.5 hrs	100.0% pH:10, 1.5 hrs	100.0% pH:10, 2.0hrs	100.0% pH:10, 3.5 hrs	100% pH:10; 2.0 hrs	100% pH:10, 3.0hrs
6	Stem Ash of Cassia Occidentalis	92.0% pH:10, 5.0 hrs	88.0 % pH:10, 2.0 hrs	89.0% pH:10, 1.5 hrs	89.1% pH:10, 2.0 hrs	90.4 % pH:10, 3.5 hrs	91.2% pH:10, 1.5 hrs	93.8 % pH:10, 2.5 hrs	94.6 % pH:10, 3.5 hrs	100% pH:10, 2.0 hrs	100 % pH:10, 2.5 hrs	100% pH:10; 2.0 hrs	100% pH:10, 2.0 hrs

sured at 830nm against a reagent blank using U.V and Visible Spectrophotometer (Systornics make). Thus obtained O.D Value was referred to standard Graph (drawn between O.D and Concentration) prepared with known amounts of Phosphate by adopting method of Least Squares to find concentration of Phosphate in unknown solutions.

Effect of Interfering Ions

The interfering ions chosen for study were the common ions present in natural waters, viz. Sulphate, fluoride, Chloride, Nitrate, Carbonate, Calcium, Magnesium, Copper, Zinc, Ferrous and Nickel. The synthetic mixtures of Phosphate and of the interfering ions were so made that the concentration of the interfering ion was maintained at 500ppm. 500 ml of these solutions were taken in stopper bottles and then correctly weighted optimum quantities of the promising adsorbents (as decided by the Graph Nos.: A, B and C) were added. Optimum pH was adjusted with dil. HCl or dil. NaOH using pH meter. The samples were shaken in shaking machines for desired optimum periods and then small portions of the samples were taken out, filtered and analyzed for Phosphate. % of extraction was calculated from the data obtained. The results were presented in the TABLE: 1.

RESULTS AND DISCUSSIONS

The percentage removal of Phosphate was studied under various parameters such as time of equilibration, pH and interfering ions with the four plant materials and their ashes. The interesting results obtained are presented in the Graph No: A: 1-8; B: 1-4; C: 1-4 and TABLE No.:1.

The following observations are significant:

Effect of equilibration time

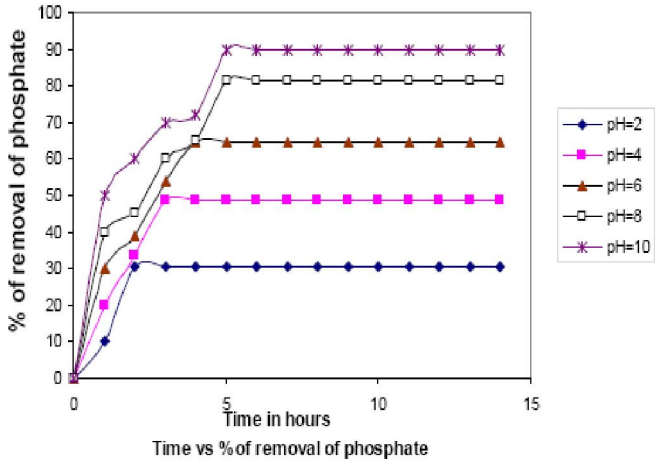
With the powders of barks/stems, percent of extractability increases with time for a fixed adsorbent at a fixed pH and after certain duration, the extractability remains constant, i.e. an equilibrium state has been reached. In other words, there will not be any further adsorption after certain time of equilibration time (vide Graph Nos. A: 1-8). As for example, the minimum time to be allowed for maximum extraction are 2hrs at pH:2; 3hrs at pH:4; 4 hrs at pH:6 and 8; 5hrs at pH:10 for bark powders of Annona squamosa and same is the trend in other bark/stem powders also. With the bark ashes of Annona squamosa, the minimum time needed for attaining the equilibrium states was found to be 2 hrs at pH:2; 3 hrs at pH:4 and 6; 4 hrs at pH:8 and 10. The same trend was noted in other ashes also. It may be noted that the equilibrium state was reached quickly in the case ashes of barks than with bark powders.

Effect of pH

As pH increases, the maximum extractability of Phosphate at optimum equilibration times, is increasing for a fixed adsorbent concentration (vide Graph Nos:B:1-4). As for example, in the case of Phyllanthus neruri, the maximum extractability is found to be 30.4% at pH:2; 48.5% at pH:4; 64.5 % at pH:6; 81.2% at pH:8 and90.0% at pH:10 after an equilibration period of 5 hrs. In the case of Pongamia Pinnata, the maximum extractability is found to be 23.7% at pH:2 ; 43.8% at pH:4; 56.1% at pH:6; 74.7% at pH:8 and 87.0% at pH:10 after 5hrs. In the case of Annona Squmosa, the maxamimum extractability is found to be 24.1% at pH:2; 35.9% at pH:4; 58.6% at pH:6; 67.7% at pH:8 and 98.0% at pH:10 after 5 hrs. In the case of Cassia Occidentalis the maximum extractability is found to be 22.1% at pH:2; 33.5% at pH:4 ;54.1 % at pH:6; 66.5% at pH:8 and 89.0% at pH:10 after 5hrs.

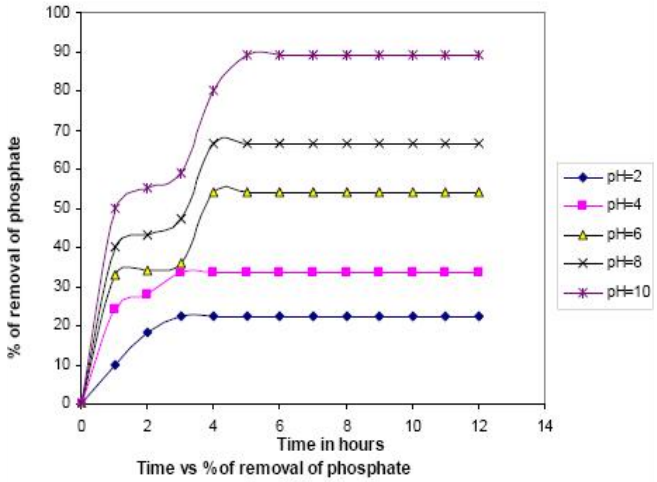
In case of ashes of braks or stems, the % of extraction of phosphate was found to more than with bark or stem powders. With the sashes of stems of Phyllanthus neruri, the maximum extractability is found to be 32.5% at pH:2; 50.7% at pH:4; 67.6 % at pH:6; 84.3% at pH:8 and 98.0% at pH:10 after an equilibration period of 5 hrs. In the case of Pongamia Pinnata, the maximum extractability is found to be 25.8% at pH:2 ; 46.9% at pH:4; 59.2% at pH:6; 75.8% at pH:8 and 95.0% at pH:10 after 5hrs. In the case of Annona Squmosa, the maxamimum extractability is found to be 24.2% at pH:2; 36.4% at pH:4; 59.7% at pH:6; 69.8% at pH:8 and 100.0% at pH:10 after 4 hrs. In the case of Cassia Occidentalis the maximum extractability is found to be 224.2% at pH:2; 35.6% at pH:4 ;54.2 % at pH:6; 67.7% at pH:8 and 92.0% at pH:10 after 5hrs.

STEM POWDER OF PHYLLANTHUS NERURI
Phosphate conc:50ppm
Sorbent conc:1.5g/lit



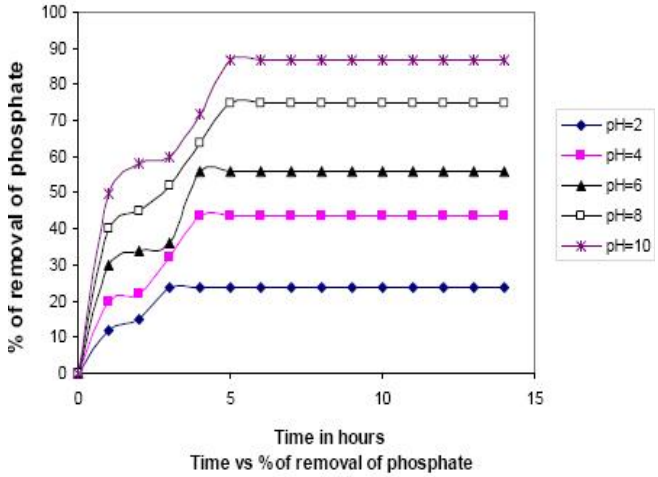
Time vs %of removal of phosphate
Graph No:A-1

STEM POWDER OF CASSIA OCCIDENTALIS
Phosphate conc:50ppm
Sorbent conc:2.0g/lit



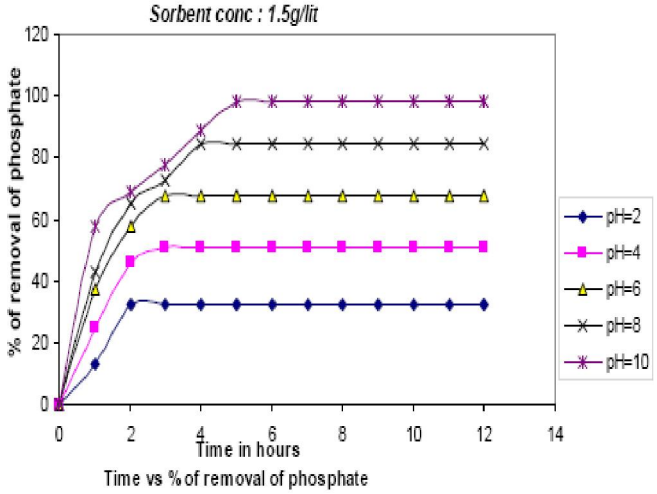
Time vs %of removal of phosphate
Graph No:A-4

BARK POWDER OF PONGAMIA PINNATA
Phosphate conc:50ppm
Sorbent conc:2g/lit



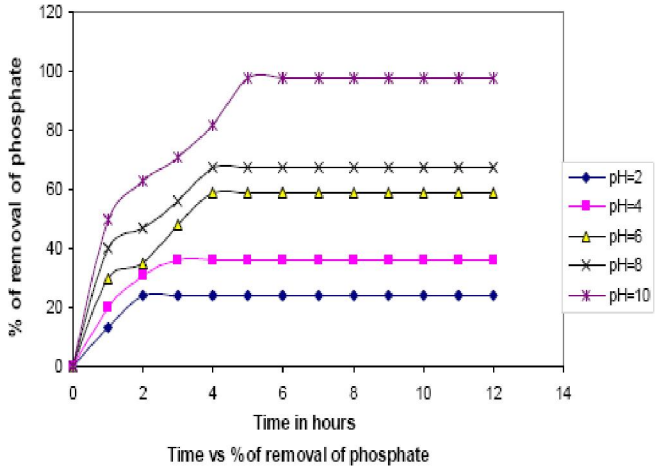
Time vs %of removal of phosphate
Graph No:A-2

STEM ASH OF PHYLLANTHUS NERURI
Phosphate conc : 50ppm
Sorbent conc : 1.5g/lit



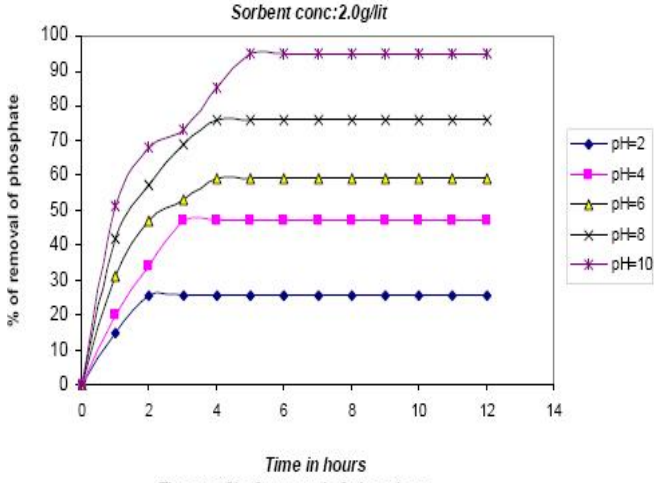
Time vs %of removal of phosphate
Graph No:A-5

BARK POWDER OF ANNONA SQUAMOSA
Phosphate conc:50ppm
Sorbent conc:1.5g/lit



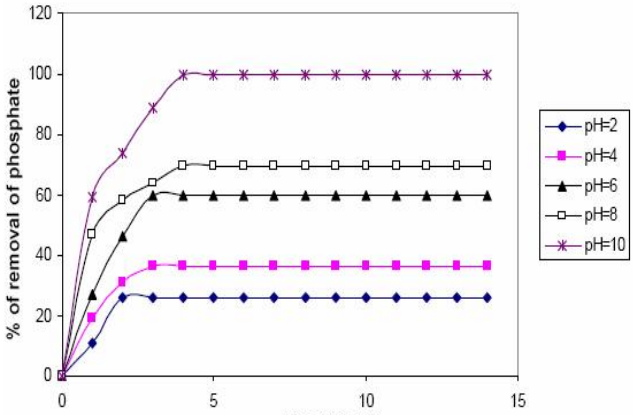
Time vs %of removal of phosphate
Graph No:A-3

BARK ASH OF PONGANUIA PIRMATA
Phosphate conc:50ppm
Sorbent conc:2.0g/lit



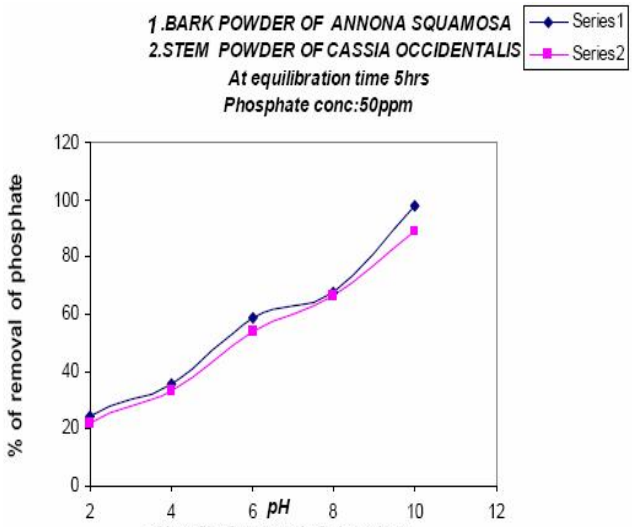
Time vs % of removal of phosphate
Graph No:A-6

BARK ASH OF ANNONA SQUAMOSA
Phosphate conc:50ppm
Sorbent conc:1g/lit



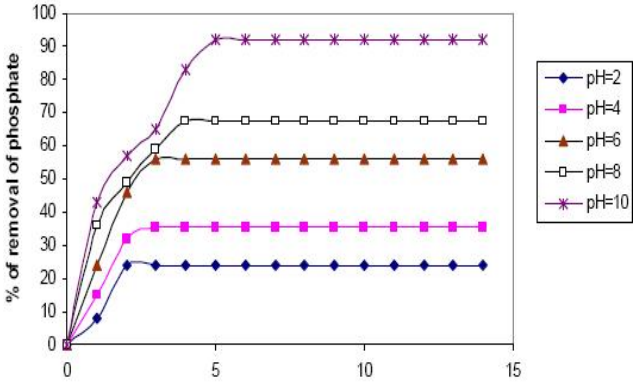
Time vs % of removal of phosphate
Graph No:A-7

1.BARK POWDER OF ANNONA SQUAMOSA
2.STEM POWDER OF CASSIA OCCIDENTALIS
At equilibration time 5hrs
Phosphate conc:50ppm



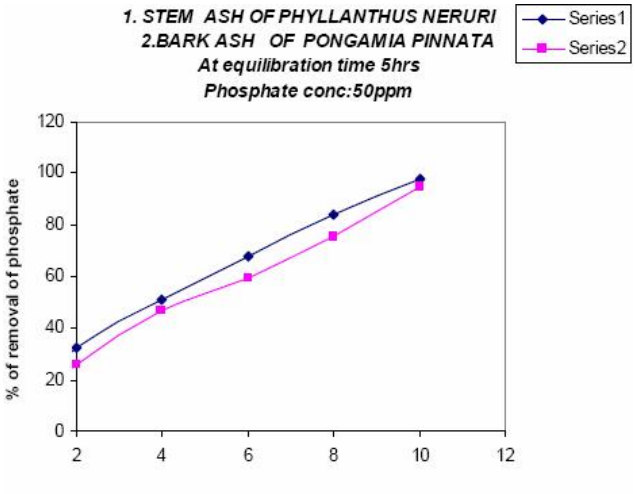
pH vs % of removal of phosphate
Graph No:B-2

STEM ASH OF CASSIA OCCIDENTALIS
Phosphate conc:50ppm
Sorbent conc:2.0g/lit



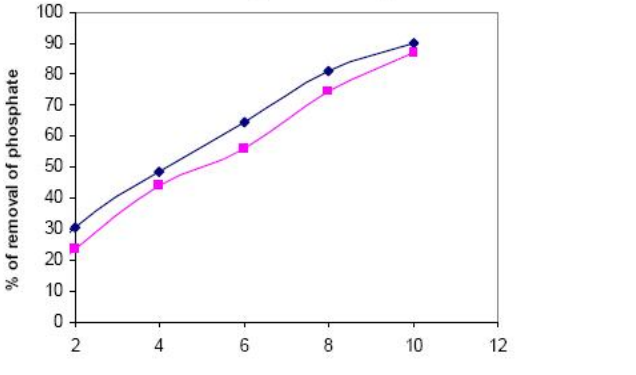
Time vs % of removal of phosphate
Graph No:A-8

1. STEM ASH OF PHYLLANTHUS NERURI
2.BARK ASH OF PONGAMIA PINNATA
At equilibration time 5hrs
Phosphate conc:50ppm



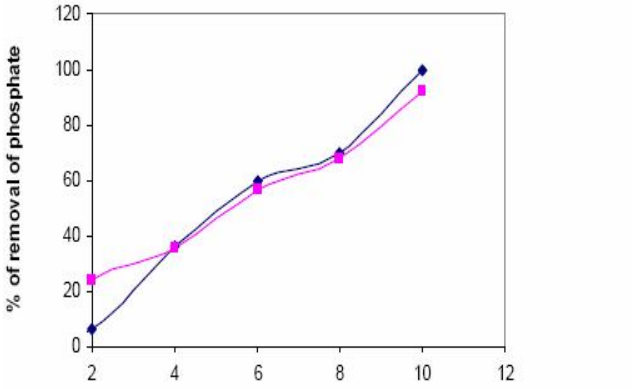
pH vs % of removal of phosphate
Graph No:B-3

1. STEM POWDER OF PHYLLANTHUS NERURI
2.BARK POWDER OF PONGAMIA PINNATA
At equilibration time 5hrs
Phosphate conc:50ppm

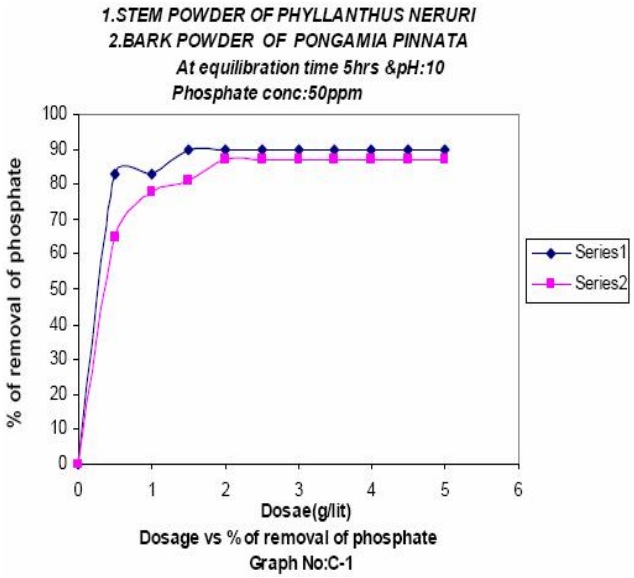


pH vs % of removal of phosphate
Graph No:B-1

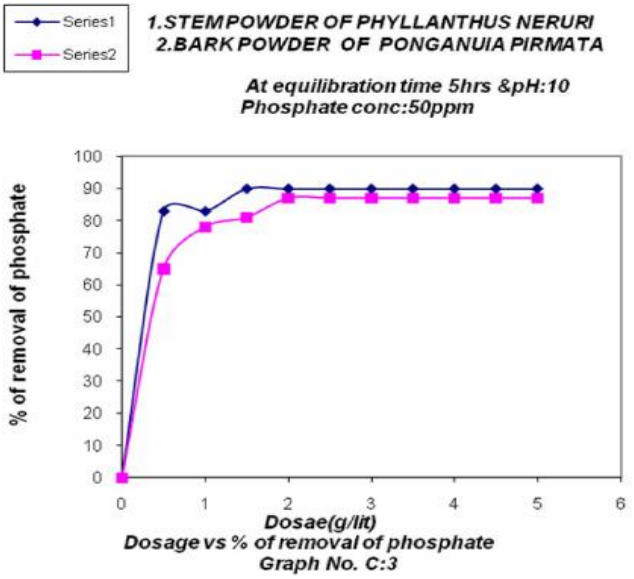
1.BARK ASH OF ANNONA SQUAMOSA (4 hrs)
2.STEM ASHOF CASSIA OCCIDENTALIS (5hrs)
Phosphate conc:50ppm



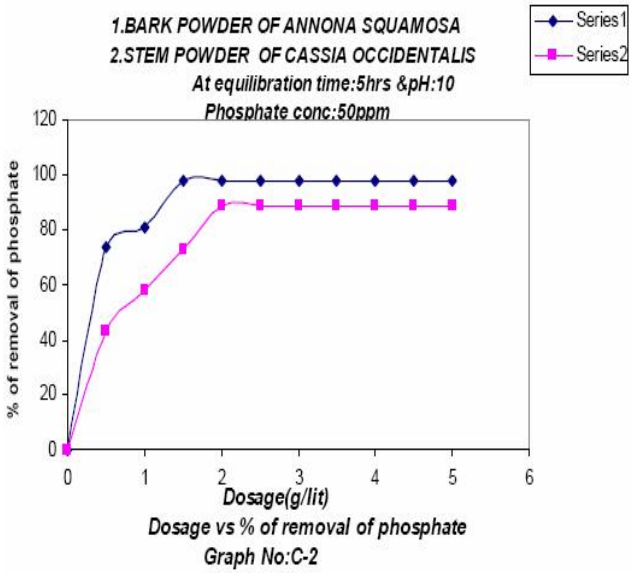
pH vs % of removal of phosphate
Graph No:B-4



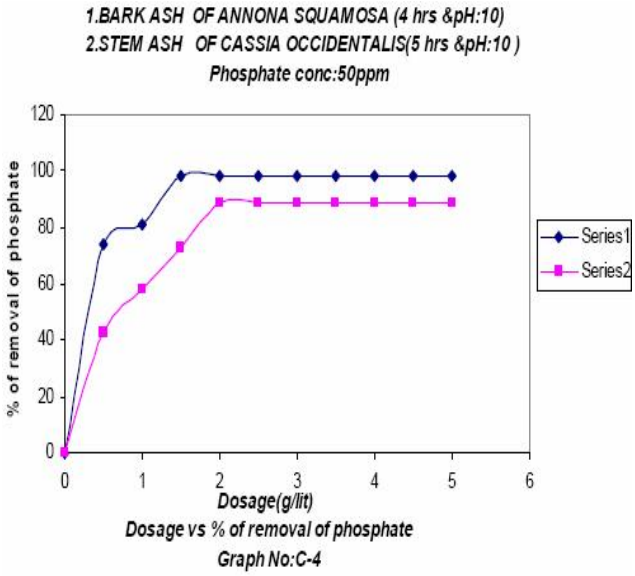
Dosage vs % of removal of phosphate
Graph No:C-1



Dosage vs % of removal of phosphate
Graph No. C:3



Dosage vs % of removal of phosphate
Graph No:C-2



Dosage vs % of removal of phosphate
Graph No:C-4

When percentage removal was studied with respect to adsorbent dosage at fixed optimum pH: 10 and at optimum equilibration times, the Graphs increase up to certain dosage and from then onwards a plateaus are obtained. The optimum dosage is found to be 1.5grms/ lit for powders of stems of PHYLLANTHUS NERURI and barks of ANONA SQUAMOSA; 2.0grams/lit for bark powders of PONGAMIA PINNATA and stem powders of CASSIA OCCIDENTALIS, (vide Graph Nos.:C:1 and 2).

With ashes, the optimum dosage is found to be 1.5 g/lit for barks/stems of ANONA SQUAMOSA and PHYLLANTHUS NERURI; 2.0grams/lit for PONGAMIA PINNATA and CASSIA OCCIDENTALIS (vide Graph Nos. : C: 3 and 4).

Effect of Interfering ions

The extractability of phosphate ions in presence of 500 ppm of the common ions found in natural waters, namely Chlorides, Fluorides, Sulphates, Carbonates, Nitrates, Calcium, Magnesium, Cupper, Ferrous and Zinc ions has been studied with these successful adsorbents at optimum conditions of extractability. The results are presented in the TABLE:1. The following observations are significant:

1. The extractability is marginally affected in the presence of 500 ppm of anions chosen for study viz., Chlorides, Sulphates, Nitrates, Fluorides and Carbonates at the optimum conditions of pH and time of equilibration. time. (Vide TABLE Nos: 1)

2. In the presence of cations, remarkable synergetic effect is seen in enhancing the maximum extractability of phosphates by the stem or bark powders and their ashes. As for example, with Bark powders of Phyllanthus neruri, % of extraction is 90.0% at pH:10 after 5 hrs of equilibration time. But in the presence of Ca^{2+},Mg^{2+}, Cu^{2+}, Zn^{2+}, $Fe^{2+}$and Ni^{2+}, the % of extraction of phosphate is enhanced to 92.5%, 91.5%, 94.5%, 95%, 97.0% and 96.0% respectively with varying equilibration times less than 5 hrs. (vide TABLE No.1: item No.1). It is to be noted that the equilibration time for the maximum removal of phosphate is also attained quickly in the presence of the said cations than without the cations. The same trend was observed in the case of remaining stem or bark powerds of interest. (vide TABLE No.: 1).
3. With the bark or stems ashes as sorbents, the presence of the subject cations markedly increased the % of extraction of phosphate. As for example the extractability of phosphate is 98.0%at pH:10 with the ashes of stems of Phyllanthus neruri but in the presence of of Ca^{2+},Mg^{2+}, Cu^{2+}, Zn^{2+}, $Fe^{2+}$and Ni^{2+} % of extraction of phosphate is enhance to 98.5%, 99.0%, 100%, 100%, 100% and 100 % respectively (vide TABLE No. 1: item No.5). The same trend was observed in the case of remaining adsorbents of interest. (vide TABLE No.: 1).

DISCUSSIONS

With the available data it is not possible to account theoretical grounds for the each observation and it needs further deep thorough study with regard to surface characteristics of the sorbents, their sorption nature with respect to the adsorbates using more sophisticated instruments and methodologies and it is beyond the aims of this work . However from the available data it can be inferred that phosphate is showing more affinity towards the sorbents choosen for study with higer pH values . H_3PO_4 is a tribasic acid with pK_1=2.15; pK_2:7.20;pK_3: 12.3 yielding three series of salts, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 when it is neutralized with an acid. The acid vs. base titration curve shows three steps with two inflexions at pH4.5 and 9.5; the first inflexion, correspond to the formation of NaH_2PO_4 and second corresponding to Na_2HPO_4 and the third inflexion point is at pH: 12.35 which cannot be detected directly by means of a colored indicator.

The barks or stems being a lingo celluloses' materials have the functional groups OH-/COOH and their ashes, being the oxides of some heavy metal ions and silica, contain surface "–O-" From the pK values of phosphoric acid and the nature of the functional groups it is supposed that the sorbents have affinity towards the phosphates at higher pH values. This is reflected in the increase in % of extractability with increase in pH.

Further, naturally occurring adsorbents chosen for study contain traces of metal ions like Mg, Ca, Fe, Cu. The divalent metal ions form salts with of HPO_4^{2-} which are sparingly soluble in water. Hence, at high pH values, the HPO_4^{2-} forms sparingly soluble salts with these cation impurities present in the powders of leaves and barks. Most of these precipitates are gelatinous in nature and are being trapped in the matrixes of the bio-adsorbents and thus resulting in the increase of % removal of Phosphate. This is more so in the case of ashes, which are oxides of some metal ions.

The decrease in the rate of adsorption with the progress in the equilibration time may be due to the more availability of adsorption sites initially and are progressively used up with time due to the formation of adsorbate film on the sites of adsorbent and thus resulting in decrease in capability of the adsorbent.

The observations made with respect to the foreign ions are also conforming as per the expected nature of extraction. % of extractability is marginally affected in the presence anions chosen for study viz., Chlorides, Sulphates, Nitrates, Fluorides and Carbonates. With Cations, the % extraction of Phosphate is increased. This kind of synergic effect may be due to the formation of sparingly soluble gelatinous precipitates metal phosphates which are trapped or occulted in the matrix of the sorbents.

CONCLUSIONS

1. The importance of bio-adsorbents : stems or barks of *Phyllanthus neruri*, *Pongamia pinnata*, *Annona squamosa* and *Cassia* occidentalis and their ashes in controlling Phosphate in polluted waters is brought to the lime light.

2. % of extractability of Phosphate increases with time and pH for a fixed adsorbent. With bark powder of Phyllanthus neruri the maximum extractability is found to be 90% while with its ashes the extractability increases to 98.0% under the optimum experimental conditions of pH: 10 and after an equilibration period of 5 hrs. Similarly, under the experimental conditions pH: 10 and optimum equilibration time of 5 hrs, the maximum extractability is found to 87.0% for *Pongamia pinnata* bark powder and 95.0% with its ashes; 98.0% for powder of stems of *Annona squamosa and 100% with its ashes;* 89.0% with powders of stems of Cassia occidentalis and 92.0% with its ashes.
3. The minimum dosage sorbent and minimum time of equilibration needed for the maximum removal of phosphate is found be less for stems/barks ashes than for stems/barks powders.
4. **Inteference**: Anions like Chlorides, Sulphates, Nitrates, Fluorides and Carbonates marginally affected the % of extraction at the optimum conditions cited in the TABLE:1. while cations viz., Ca^{2+},Mg^{2+}, Cu^{2+}, Zn^{2+}, $Fe^{2+}$and Ni^{2+} ions at concentration of 500 ppm are synergizing the extraction of phosphate and thereby % of removal of Phosphate is increased.

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