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New Methodologies in Phosphate Pollution Control: using bio-sorbents derived from *Terminalia arjuna* and *Madhuca indica* plants

Y. Hanumantha Rao[1] and K. Ravindhranath[2]*

[1]Department of Chemistry, Andhra Loyola College (Autonomous), Vijayawada-520008, Andhra Pradesh, India
[2]Department of Chemistry, K. L. University, Green Fields, Vaddeswaram - 522 502, Guntur Dt., Andhra Pradesh, India

Abstract: The adsorption nature of bio-sorbents derived from *Terminalia arjuna* and *Madhuca Indica* plants towards Phosphate ions has been investigated by varying the various physicochemical parameters such as pH, time of equilibration, and sorbent dosage using simulated waters. The conditions have been optimized for the maximum removal of Phosphate from waters. The effect of commonly found co-ions in natural waters on the % of extraction of Phosphate has been studied. The methodologies developed have been successfully applied to industrial and natural lake sample.
Key Words: Phosphate, Pollution control, Bio-sorbents, *Terminalia arjuna* and *Madhuca Indica* plants.

Introduction

There is global consciousness of Phosphate pollution in natural water bodies and in fact, some countries banned the detergents having Phosphate component. About 65% of Phosphate pollution is contributed by run-offs from agricultural fields due to over utilization of Phosphate containing fertilizers; nearly 25% is from the effluents of detergent and fabric manufacturing industries and nearly 15% from domestic and municipal sewages[1-4].

Treatment methods based on chemical precipitation and active sludge process (biological) have been developed to remove Phosphates from waste waters and some patents also existing [1, 3-16].

The methods based on the sorption abilities of bio-adsorbents derived from waste materials of flora or fauna are proving to be potential alternatives to these traditional methods and stimulating the rapid expansion of research work in developing simple and economical methods in controlling the pollution. Our research group is working on this aspect of pollution research and some successful, economical and eco-friendly methodologies have been developed for some potential pollutants[17-22].

Iron coated natural and synthetic sorbents[12, 23] , biomass[24], pumic rocks[25], activated red mud [26-28], spent alum sludge[14,29] and wood fiber treated with carboxymethyl cellulose and ferrous chloride[30], have been probed for their abilities to remove Phosphate from waters. Further, sawdust and barks, and other agricultural residues like corncobs, have been explored for their inherent potentialities in the removal of Phosphates[31-33]. LuzE. De-Bastan and Yoav Bashan [34]have reviewed the new trends in the control of Phosphate pollution. **These methods have one or the other disadvantage and globally acceptable, simple, effective and economical method, is still eluding the researchers.**

In our preliminary investigations in identifying plants having affinity towards Phosphate ions, we noticed ***Terminalia arjuna*** and ***Madhuca indica*** plants. In the present work surface sorption nature of leaves, barks and their ashes towards the Phosphates have been thoroughly studied with respect to various physicochemical parameters such as pH, equilibration time, sorbent dosage and interfering ions and further, the developed methodologies have been applied to remove Phosphate from polluted waters.

Materials and Methods

A. Chemicals: All chemicals used were of analytical grade.

Stock solution of Phosphate of 500 ppm concentration was prepared by using potassium di-hydrogen Phosphate in double distilled water and was suitably diluted as per the need.

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

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

B. ADSORBENTS: The bio-materials of *Terminalia arjuna,* and *Madhuca indica*

plants have been found to have affinity towards Phosphate ions.

A: Terminalia arjuna **B: Madhuca Indica**

Fig No. 1: Plants showing affinity towards Phosphate ions

Terminalia arjuna is a tree of about 20-25 meters height with buttressed trunk belongs to the family of Combretaceae and of Terminalia genus. It grows on the banks of rivers in South and Central India and its leaves are fed to Antheraea paphia moth that produces the tassar silk and further, it is possesses traditional medicinal values and is used in the treatment of wounds, hemorrhages and some types of ulcers.

Madhuca Indica is a forest based tree belongs to the genus Mahuca and is found in the central parts of India and also sub mountainous parts of the Himalayan region. The seeds and flowers of the tree are used in the production of alcohol, syrups and vinegars and the non-edible oil obtained from the seed is used as an additive in the manufacturing of soaps and also being probed for its utility as bio-diesel.

C. Preparation Adsorbent: The leaves or barks of the plants were cut freshly, washed with tap water, then with distilled water and then sun dried. The dried materials were powdered to a fine mesh of size: <75 microns and activated at 105^{o} C in an oven and then employed in this study. Further, the leaves and barks of the said plants were burnt to ashes, meshed and also used in this work.

Adsorption experiment:

Batch system of extraction procedure was adopted[1, 2, 35]. Carefully 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 spectrophotometrically by "Molybdenum Blue" method[36].

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 10 min, removed and cooled rapidly. The flask was shaken and adjusted the volume. Blue color was developed. Optical Density was measured 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.

D. Effect of Interfering Ions: The synthetic mixtures of Phosphate and tenfold excess of common co-ions present in natural waters as has been listed in the Table No. 1, were prepared. With 500 ml of these simulated waters, extraction studies were made. The results were presented in the Table No. 1.

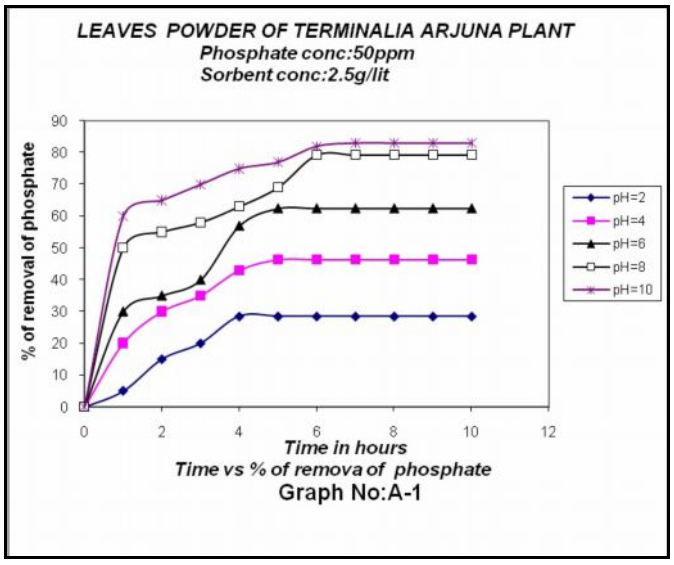
E. Applications of the Developed Bio-Sorbents:

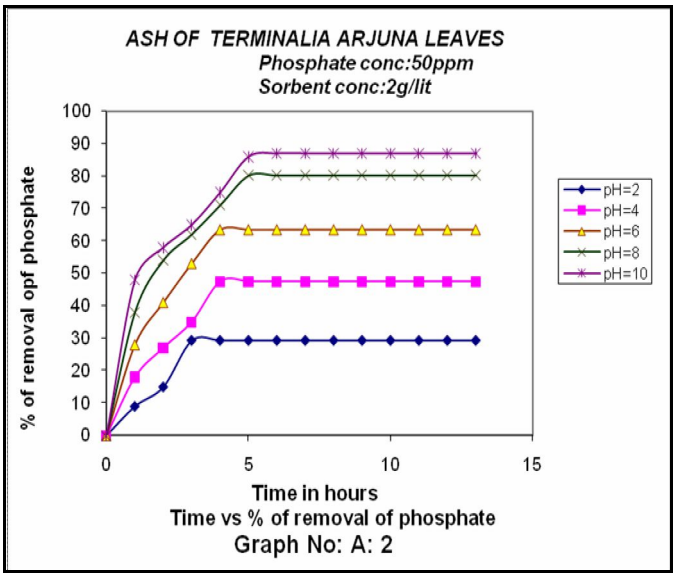
The new methodologies developed in this work have been applied for the removal of the Phosphate from polluted lakes in the Guntur District of Andhra Pradesh.

Then these samples were **subjected to extraction for the Phosphate ions using the bio-sorbents developed in this work at optimum conditions of extraction. The results obtained were presented in the Table 2.**

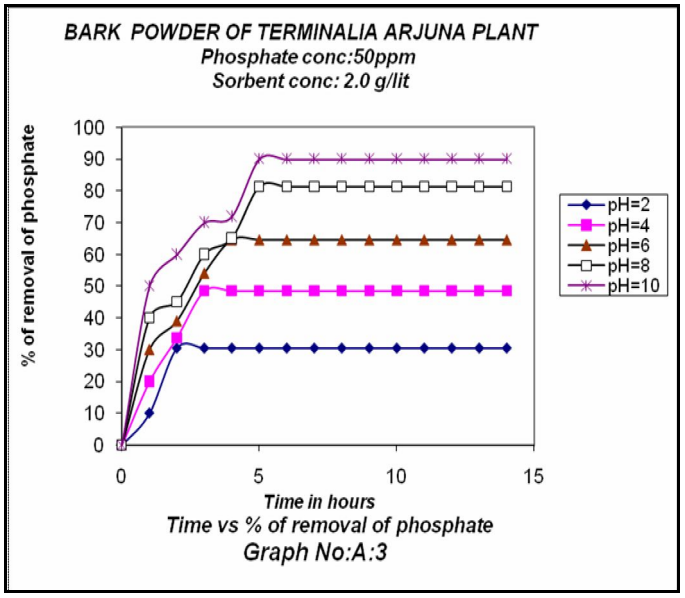
Results and Discussions

Using the sorbents derived from ***Terminalia arjuna*** and ***Madhuca Indica*** plants, the percentage removal of Phosphate is studied under various physicochemical parameters such as time of equilibration, pH, sorbent dosage and interfering ions and the obtained are presented in the Graph No: A: 1-8; B: 1&2; C: 1&2 and Table No.1 &2.

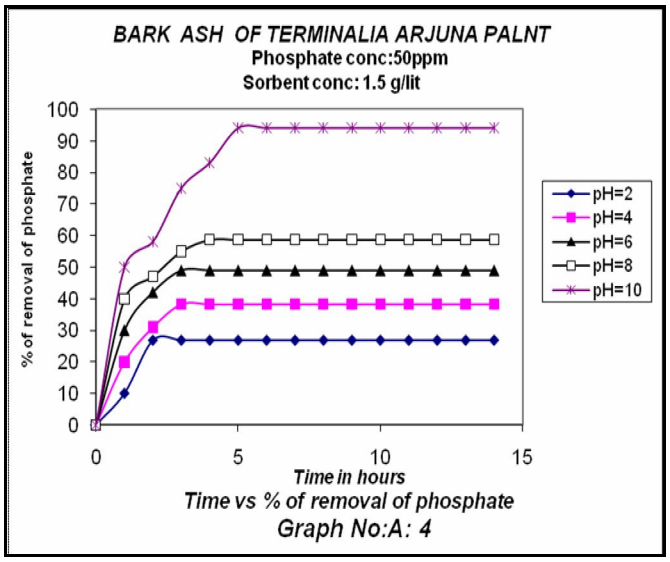




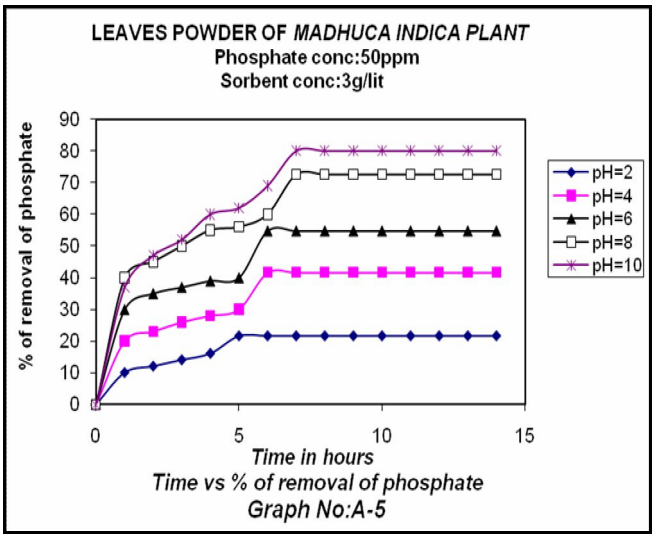
Time vs % of removal of phosphate
Graph No: A: 2



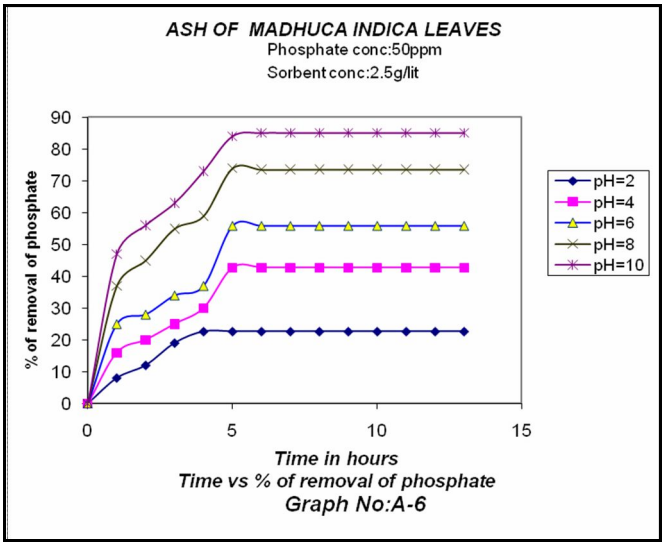
Time vs % of removal of phosphate
Graph No:A:3



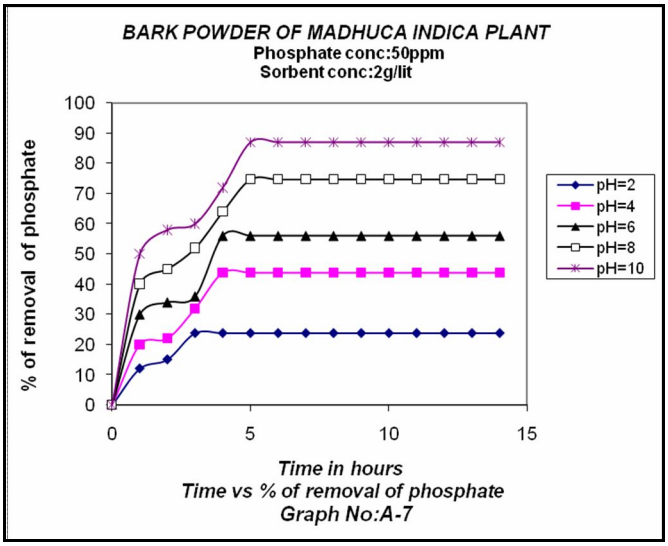
Time vs % of removal of phosphate
Graph No:A: 4



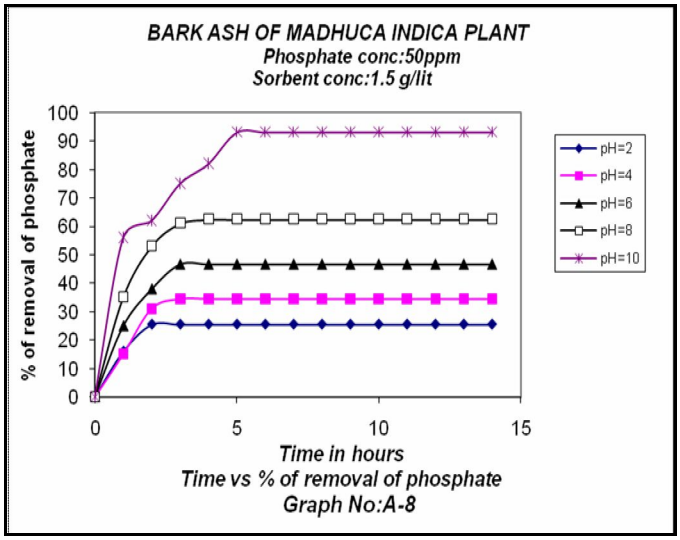
Time vs % of removal of phosphate
Graph No:A-5



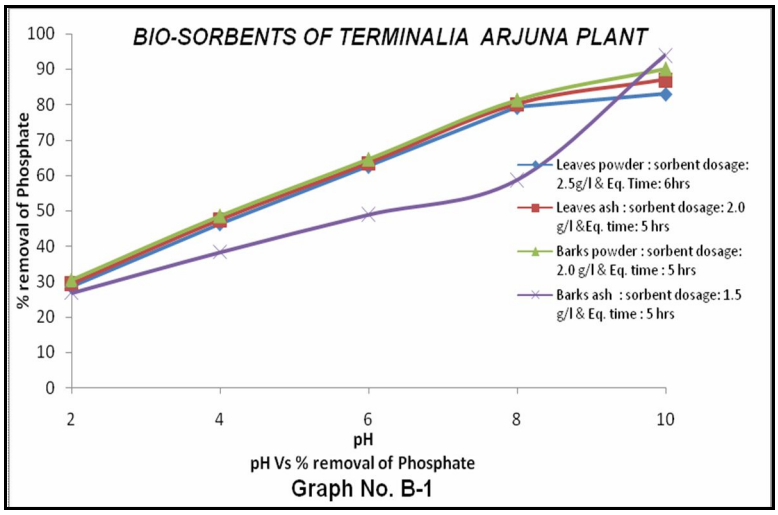
Time vs % of removal of phosphate
Graph No:A-6



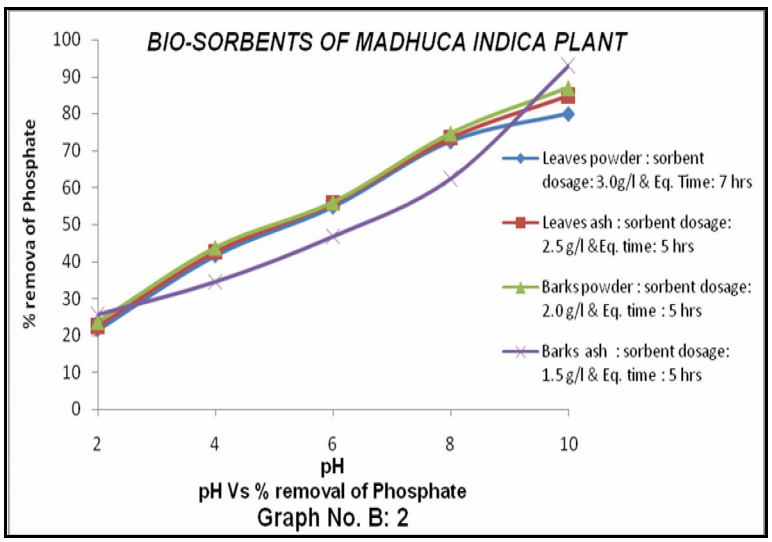
Time vs % of removal of phosphate
Graph No:A-7



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



pH Vs % removal of Phosphate
Graph No. B-1



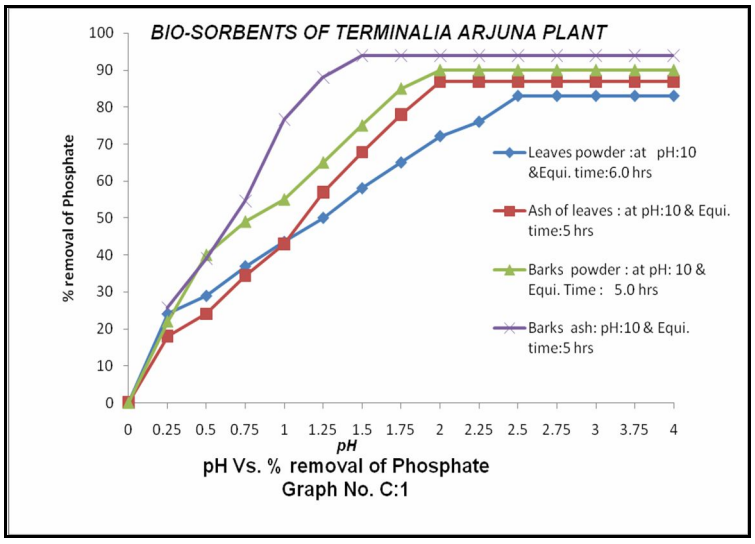
pH Vs % removal of Phosphate
Graph No. B: 2

Table No. 1: Effect of Interfering Ions on The Extractability of Phosphate

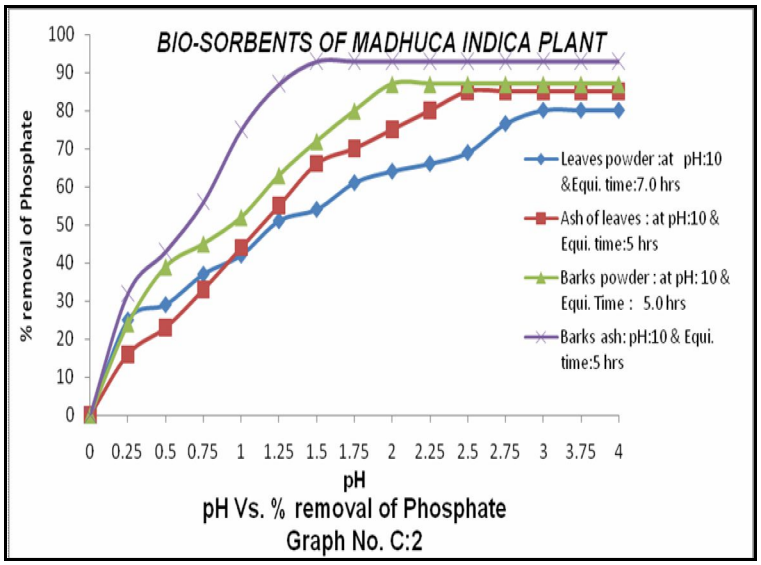
S. No	Adsorbent	Maximum Extractability at optimum conditions	Extractability of Phosphate in presence 500 ppm of interfering ions at optimum(pHs) in percentage										
			SO_4^{2-}	NO_3^-	Cl^-	F^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}	Fe^{2+}	Ni^{2+}
1	Leaves powder of Terminalia arjuna	83.0%;pH:10, Eq. time: 6.0 hrs, Sorbent Conc. 2.5 g/l	75.0	78.0	77.0	79.0	76.0	86.4	88.9	89.0.5	90.0	93.0.5	92.05
2	Leaves ash of Terminalia arjuna	87.0%;pH:10; Eq. time: 5.0hrs; Sorbent Conc. 2g/l	79.0	80.0	81.0	79.0	76.0	89.0	91.0	92.5	93.0	94.5	96.5
3	Barks powder of Terminalia arjuna	90.0%;pH:10, Eq. time: 5.0 hrs, Sorbent Conc. 2.0 g/l	82.5	83.7	84.5	89.0	83.5	91.0	93.4	95.0	93.0.6	95.0.5	91.0
4	Barks ash of Terminalia arjuna	94.0%;pH:10, Eq. time: 5.0hrs; Sorbent Conc. 1.5g/l	80.0	83.5	84.5	86.7	89.0	95.4	96.0	97.5	98.6	97.0	96.0
5	Leaves powder of Madhuca indica	80.0%;pH:10; Eq. time: 7.0 hrs, Sorbent Conc. 3.0 g/l	73.5	72.5	78.0	77.0	76.5	82.0	83.0	85.0	86.0	86.9	88.0
6	Leaves ash of Madhuca indica	85.0%;pH:10; Eq. time: 5.0hrs; Sorbent Conc. 2g/l	76.0	80.0	82.3	80.0	81.0	86.0	87.1	86.5	89.0	88.0	90.0
7	Barks powder of Madhuca indica	87.0%;pH:10; Eq. time: 5.0 hrs, Sorbent Conc. 2.0 g/l	79.0	82.0	81.0	83.0	83.6	90.0	91.0	92.0	93.0	93.5	94.0
8	Barks ash of Madhuca indica	93.0%; pH:10; Eq. time: 5.0hrs; Sorbent Conc. 1.5g/l	84.0	87.0	83.5	89.0	85.6	94.0	95.0	95.9	94.5	96.0	97.5

Table No. 2: Extractability of Phosphate in Different Industrial and Natural Samples using Bio-Sorbents

Samples	Phosphate concentration in the Sample	% of Maximum extractability							
		Terminalia arjuna				Madhuca indica			
		Leaves		Barks		Leaves		Barks	
		Powders	Ashes	Powders	Ashes	Powders	Ashes	Powders	Ashes
Detergent Industries Effluents									
1	16.5 ppm	82.0%	85.0%	87.0%	91.0%	79.0%	83.4%	86.5%	91.0%
2	20.4 ppm	80.0%	83.5%	85.5%	90.0%	78.0%	80.0%	82.5%	89.0%
3	24.2 ppm	77.0%	82.0%	84.0%	89.0%	77.0%	81.4%	82.5%	92.0%
4	34.1 ppm	76.0%	80.0%	82.0%	88.0%	76.0%	84.0%	85.5%	89.0%
Natural Lake Samples									
1	35.4 ppm	81.0%	81.0%	84.0%	90.0%	77.0%	82.0%	83.0%	89.0%
2	46.8 ppm	83.0%	82.0%	85.0%	92.0%	76.0%	81.5%	82.5%	88.0%
3	56.7 ppm	79.0%	79.0%	88.0%	93.0%	73.0%	82.6%	87.5%	86.0%
4	65.2 ppm	78.0%	81.0%	89.0%	92.8%	80.0%	79.0%	84.5%	85.5%



pH Vs. % removal of Phosphate
Graph No. C:1



pH Vs. % removal of Phosphate
Graph No. C:2

The following observations are significant:

1. All the sorbents are found to be pH sensitive. With increase in pH, the maximum extraction is increasing. The optimum pH is found to be 10. In the case of sorbents pertaining to ***Terminalia arjuna***, the maximum extraction at pH: 10, is found to be 83.0% with leaves power and 87.0% with their ashes; 90.0% with barks powders and 94.0% with their ashes (vide Graph No. B: 1). With the *Madhuca Indica* plant sorbents, the % removal at pH: 10, is found to be 80.0% with leaves powder and 85.0% with their ashes; 87.0%with barks powder and 93.0% with their ashes (vide Graph No. B:2)

2. % removal of Phosphates is dependent on the equilibration time i.e. the time that the sorbent is in contact with the waters during the process of agitation. More is the time of agitation, more is the % of removal initially but after certain time, the extraction remains constant (vide Graph No. A: 1-8). As for example, the % of extraction of Phosphate from simulated waters at pH:10 with leaves powers of *Terminalia arjuna* , is found to be : 60% at 1 hr of agitation, 65.0 at 2 hrs, 70.0% at 3 hrs, 75.0% at 4 hrs, 77.0% at 5 hrs, 83.0% at 6 hrs or more (vide Graph No. A: 1). The trend is the same with all other adsorbents (vide Graph No. A: 1-8). It may be inferred from the Graphs that the minimum time needed for the maximum possible extraction at optimum pH:10 is found to be 6.0 hrs with leaves powders and 5.0 hrs with leaves ashes or with barks powder or with barks ashes in the case of sorbents of *Terminalia arjuna.* With *Madhuca Indica* plant sorbents, the optimum time at pH is found to be: 7 hrs with leaves powders, 5.0 hrs with the ashes of leaves or with barks or with barks ashes (Vide Graph Nos. A: 1-4).

3. The extraction of Phosphate ions depends upon the sorbent concentration (vide Graph Nos. C: 1 &2). When the extraction is studied with the gradual increase in sorbent concentration at optimum pH: 10 and

at optimum equilibration times, the graphs increase up to certain dosage and from then onwards plateaus are obtained (vide Graph Nos. C:1 &2) The minimum sorbent concentration needed for the maximum removal of Phosphate is found to be: **2.5 g/l for leaves powder, 2.0 g/l for leaves ashes, 2.0 g/l for barks and 1.5 g/l for barks ashes in the case of *Terminalia arjuna* plant sorbents** (vide Graph No. C: 1). With the sorbents pertaining to ***Madhuca Indica* plant, the optimum sorbent dosage is found to be : 3.0 g/l for leaves, 2.5 g/l for leaves ash, 2.0 g/l for barks powder and 1.5 g/l for barks ash (vide Graph No. C: 2).**

4. **Effect of interfering ions**: The effect of tenfold excess of co-ions commonly found natural waters viz., Chlorides, Fluorides, Sulphates, Carbonates, Nitrates, Calcium, Magnesium, Cupper, Ferrous and Zinc on the % of extraction of Phosphate has been studied and obtained results are presented in the Table No.1. It may inferred from the table that :

a) The anions have affected, though marginally, % of the extraction. As for example, with barks powder of *Terminalia arjuna* as sorbent, the % of extraction is found to be 90.0% at optimum condition of extraction while in the presence of tenfold excess of SO_4^{2-}, NO_3^{2-}, Cl^-, F^- and CO_3^{2-}, the % of extraction is found to be 82.5%, 83.7%, 84.5%, 89.0% and 83.5% respectively (vide Table No. 1: item No. 3)

b) Cations have markedly enhanced the % of extraction. As for example, with the leaves powders of *Terminalia arjuna,* the % of extraction is 83.0% while in the presence of Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+} and Ni^{2+} ions, the % of extraction is enhanced to 86.4%, 88.9% 89.0%, 90.0%, 93.5% and 92.05% respectively (vide Table No.: 1: item No.1). The same trend was observed in the case of remaining adsorbents of interest. (Vide Table No.:1).

Applications:

The Applicability of the methodologies developed in this work was tested with respect to the real samples of diverse nature, which were collected from the sewages/effluents of detergent industries and also from polluted lakes. The results have been presented in the Table No: 2.

It is found that the sorbents developed in this work are remarkably successful in removing Phosphate in the samples studied at optimum conditions of pH, equilibration time and sorbent dosage. In the case of sorbents of *Terminalia arjuna*, the % removal of Phosphate is found to be in the range: 76.0% to 82.0% with thermally activated leaves powder and 80.0% to 85.0% with their ashes; 82.0 to 87.0% with bark powders (thermally activated) and 88.0 to 91.0% with their ashes (vide Table No.2). With the *Madhuca indica* plant sorbents, the % of extraction is found to be in the range: 76.0 to 79.0% with the powders of leaves and 80.0 to 84.0% with their ashes; 82.5% to 86.5% with bark powders and 89.0 to 91.0% with their ashes (vide Table No.2). In the case of natural lake samples, the % of maximum extraction is found to be in the range: 78.0% to 83.0% for leaves powder and 79.0% to 82.0% for their ashes; 85.0% to 89.0% with bark powder and 90.0% to 93.0% with their ashes (vide Table No. 2). With *Madhuca indica,* the % of extraction with natural lake samples is found to be in the range: 73.0% to 80.0% with powders of leaves and 79.0% to 82.6% with their ashes; 82.5% to 87.5% with the barks powders and 85.5% to 89.0% with their ashes (vide Table No. 2)

Discussions

For accounting each observation with theory, surface morphological studies adopting X-ray XPS, FTIR, SEM and EDS in addition to the classical elemental chemical analysis before and after the sorption of the Phosphate on the sorbent surface are needed and this aspect of research work is beyond the scope of the present work. However, the sorption characteristic may be understood roughly. The sorbents derived from leaves or barks have a number of OH-/-COOH groups on their surface and these groups being strong in the formation of hydrogen bonding are showing affinity with the increase in pH towards Phosphate ions which is a salt of tri-basic acid H_3PO_4 having pK values: 2.15; 7.20; 12.3.(Vogel,1961).

Further, the divalent or trivalent metal ions form salts with of HPO_4^{2-} which are sparingly soluble in water. Naturally occurring adsorbents chosen for study, **contain some impurities of metal ions like Mg, Ca, Fe, Al**. Hence, at high pH values, **the HPO_4^{2-} forms sparingly soluble salts with these cation impurities present in the powders of plant materials**. 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 co-ions are interesting. Anions are interfering to some extent while cations are increasing the % of extraction. Anions having negative charge will compete with the negatively charged Phosphate ions for sorption sites on the surface of the sorbent and hence, % of extraction is affected. Di- or trivalent cations that form precipitates with Phosphate which is trapped or occluded in the matrix of the sorbent and hence show enhanced or synergic extraction.

Conclusions

1. **Bio-sorbent derived from *Terminalia arjuna*** and ***Madhuca Indica*** plants have been investigated for their sorption abilities towards Phosphate ions from simulated waters by varying various physicochemical parameters such as pH, time of equilibration, and sorbent dosage. The effect of co-ions present normally in natural waters on the % of removal of Phosphate has been investigated keeping the concentrations of co-ions tenfold excess than the Phosphate concentration,
2. The extractions are found to be pH sensitive and the optimum pH is found to be 10.
3. The maximum removal of Phosphate is found to: 83.0%, 87.0%, 90.0% and 94.0% respectively with the sorbents derived from leaves, leaves ash, barks and barks ash of ***Terminalia arjuna*** plant at optimum conditions of extraction.
4. At optimum conditions of extraction as has been cited in the Table No. 1, the maximum % of extraction of Phosphate is found to be 80.0%, 85.0%, 87.0% and 93.0% respectively with leaves powder, leaves ash, barks powder and barks ash of ***Madhuca Indica*** **plant.**
5. The minimum dosage needed for the maximum removal of Phosphate is found less for leave or barks powders than with their ashes as adsorbents: in the case of ***Terminalia arjuna*** **plant : 2.5 g/l for leaves powder and 2.0 g/l for its ash;2.0 g/l for barks powder and 1.5 g/l for its ash; in the case of *Madhuca Indica*** plants: **3.0 g/l for leaves powder and 2.5 g/l for its ash; 2.0 g/l for barks powder and 1.5 g/l for its ash**.
6. Co-anions, namely Chlorides, Sulphates, Nitrates, Fluorides and Carbonates are found to have some effect on the % removal of at the optimum conditions as given in the Table No. 2. Divalent cations such as Ca^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+} Zn^{2+}, Fe^{2+} and Mg^{2+} ions are enhancing the % of removal of Phosphate from waters. This is an interesting point for further investigation.

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