INTERNATIONAL JOURNAL OF APPLIED BIOLOGY AND PHARMACEUTICAL TECHNOLOGY

Volume: 2: Issue-4: Oct - Dec -2011 IJABPT *ISSN 0976-4550*

REMOVAL OF PHOSPHATES FROM POLLUTED WATERS USING BIO-ADSOSRBENTS

M.Divya Jyothi[1], K. Rohini Kiran[2] and K. Ravindhranath[3]*

[3] Professor and Head, Department of Engg. Chemistry and Post Graduate Chemistry, Bapatla Engineering College (Autonomous), BAPATLA-422101, Guntur Dt., A.P.

*Author for correspondence: Email: ravindhranath.sita@yahoo.co.in

ABSTRACT: Increasing interest is being envisaged by environmental researchers in controlling the phosphates pollution in natural waters by evoking the surface sorption characteristics of bio-waste materials of flora origin. In the present work, a thorough investigation has been made to find powders of leaves or their ashes of different classes of plants, having the affinity towards phosphate ions. 10 plant leaves and their ashes have been found to have sensitivity towards Phosphate ion. Investigations have been made in optimizing the various physico-chemical parameters such as equilibration time, pH and sorption dosage for the maximum removal of phosphates. The % of removal is found to be increasing with the increase in pH and equilibration time. The ashes of leaves shows more sorption towards phosphates than powders of leaves.79% to 90% removal of phosphate from polluted waters are found at optimum conditions with the sorbents investigated in this work. The interference of foreign ions on the % of extraction of phosphate reveals that some divalent cations are found be synergizing the extraction and thereby % of removal of Phosphate is increased even in the presence of 500 ppm of the said ions.

Key Words: Phosphate, Pollution control, Bio-sorbents

INDTRODUCTION

Phosphorous is essential to sustain life and is required by all living cells. Phosphates has the ability to promote the growth of plant life and hence it used is widely used as fertilizer (Gerard Kiely, 1998; Metcalf & 2003). When excess of phosphate from agricultural run-off enters into lakes and rivers, a process known as Eutrophication occurs and thereby rendering the water sources unhealthy, incapable of supporting plant and animal life and thus lake dies (Ames et. Al, 1970; Batchelor et al., 1987). Surface run offs contributes to an extent of 65% of Phosphate pollution. Industrial wastes from detergent manufacturing and fabric treatment add to about 25% and domestic and municipal sewages accounts to about 15%. There is a growing awareness towards the phosphate pollution throughout the world and some countries made legislation and introduced phosphate control acts and in fact the Switzerland banned the use of phosphate in detergent.

The literature survey indicates that traditionally the phosphate is removed by chemical precipitation (Ames et al., 1970; Batchelor et al., 1987; Brattebo et al., 1986; Huang, 1977; Yee, 1966; Sona Saxena and S.F.D,Souza, 2004). 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 patens exist in this regard (Kioussis et al., 1999; Unnithan et al., 2002; Gerad Kiely, 1998; Baker, M.J. et al.,1998; Huang, SH and Chiswell, B, 2000;United States Patent 7285215;4183808;365555 and 6881346). Presently increasing interest is being envisaged in exploring the use of Biomasses or wastes in controlling the pollution either in their native state or chemically modified by evoking their surface sorption phenomenon. Studies have shown that iron adsorbed on synthetic filtration media (Unnithan et al., 2002) or biomass (Han et al., 2003) can impart a capacity to remove phosphates from water. Shiao,S.J and Akashi, 1997, investigated the Phosphate removal from aqueous solutions from activated red mud. K Huang, S.H and Chiswell, B (2000) studied the Phosphate removal from waste water using spent alum sludge; Inglezakis, V.J. et al (2003) studied the simultaneous removal of metals Cu^{2+} , Fe^{3+} and Cr^{3+} with anions SO_4^{2-} and HPO_4^{2-}using Clinoptlolite; Onar A.N.Balkaya N and Akyurz, T(1996) investigated the phosphate removal efficiencies of 13 natural pumic rock samples obtained from different regions Turkey.

Thomas L. Eberhardt et. Al(2006) studied the phosphate removal by refined aspen wood fiber treated with carboxymethyl cellulose and ferrous chloride. Promising result have been found with wood processing residues like sawdust, bark etc and some other agricultural residues like corncobs (Shukla et al., 2002; Tshabalaka et al., 2004; Vaughan et all., 2001).Boujelben et. Al 2008 studied the phosphorus removal from aqueous solutions using iron coated natural and engineering sorbents. LuzE. De-Bastan and Yoav Bashan,(2004) discussed in their review article on the recent advances in removing phosphorous from waste water and its future use as fertilizer. Xin Feng Zhu et. al (2011) studied the removal of phosphate from aqueous solutions by using Red Mud.

Immense is the potentiality of bio-processes and they can go along with other chemical processes hand in hand and my prove to be economical and more viable in agricultural counties like India in controlling the pollutants.

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

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

1. **Stock solution of Phosphate** was prepared by dissolving 0.2197g of potassium di hydrogen phosphate in double distilled water and was made up to 1 lit. Its concentration is 500ppm. It was suitably diluted as per the need.
2. **Sodium Molybdate solution**: 12.5g of Sodium Molybdate was dissolved in 500ml of 10N. H_2SO_4.
3. **Hydrazine Sulphate solution**: 1.5gms of Hydrazine Sulphate solution was dissolved in 1lit of double distilled water.

(B) Adsorbents: Diverse adsorbents of flora origin were used in this work. The methodology herewith presented is only for the bio-adsorbents showing interesting results.

a) **Leaves powders: The leaves of** Phyllanthus nerui**,** ,Pongenuia Pirmata,Datura Metal Nerium Odorum, Annona Squmosa, Cassia Occidentalis, Ficus Religiosa, Cassia Auriculate, Calotropis Zygantia, Punica Granthusm were used. The leaves were freshly cut from trees, washed with tap water and then with distilled water. The leaves then sun dried. The dried leaves were powdered to a fine mesh of size: less than 75 microns and thus obtained powders were used for study.

b) **Leaves Ashes: The leaves of** Phyllanthus neruri**,** Ponganuia Pirmata,Datura Metal Nerium Odorum, Annona Squmosa, Cassia Occidentalis, Ficus Religiosa, Cassia Auriculata, Calotropis Zygantia, Punica Granthusm were freshly cut from trees, washed with tap water and then with distilled water. The leaves then sun dried. The dried leaves were burnt to ashes. Thus obtained ashes were used for study.

(C) Adsorption experiment. :

Batch system of extraction procedure was adopted(Gerard Kiely, 1998; Metcalf and Eddy, 2003 and Trivedy, R.K., 1995). 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 (Vogel-1961).

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 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 interfering ions chosen for study were the common ions present in natural waters, viz. Sulphate, fluoride, Chloride, Nitrate, Carbonate, Calcium, Magnesium, Copper, Ferrous and Zinc. 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 stoppard 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: 1a&b.

RESULTS AND DISCUSSIONS

The percentage removal of Phosphate is studied under various parameters viz., time of equilibration, pH , sorbent dosage and interfering ions with various adsorbents of flora origin. Some of the interesting results obtained are presented in the Graph No: A: 1-20; B: 1-10; C: 1-10 and Table No.1A & B

A: POWDERS OF LEAVES: (vide Graph Nos. A:1-10;B:1-5;C:1-5):

The leaves powders of Phyllanthus neruri**,** ,Ponganuia Pirmata,Datura Metal Nerium Odorum, Annona Squmosa, Cassia Occidentalis, Ficus Religiosa, Cassia Auriculata, Calotropis Zygantia, Punica Granthusm have been found to have affinity towards Phosphate ions. The following observations are significant:

1. **Effect of equilibration time**: In these leaves powders, 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:1-10). As for example, the minimum time to be allowed for maximum extraction are 4hrs at pH:2; 5hrs at pH:4; and 6 hrs at pH: 6 &8 and 7hrs at pH:10 for powders of leaves of Phyllanthus nerui and same is the trend in other leaves powders also.
2. **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: :A:1-10;B:1-5). As for example, in the case of Phyllanthus neruri, the maximum extractability is found to be 29.3% at pH: 2; 46.4% at pH: 4; 62.4% at pH: 6; 79.1% at pH: 8 and 82.0% at pH: 10 after an equilibration period of 7 hrs.In the case of Ponganuia Pirmata, the maximum extractability is found to be: 21.5% at pH:2 ; 41.6% at pH:4; 54.8% at pH:6; 70.6% at pH:8; and 79.0% at pH:10 after 7hrs. In the case of Datura Metal the maximum extractability after 7hrs is found to be : 20.1% at pH:2; 37.5% at pH:4; 50.4% at pH:6; 623.4 % at pH:8 and 80.0% at pH:10. Nerium Odorum extracted to an extent of 201.5% at pH:2 ; 33.4% at pH:4; 55.2% at pH:6; 62.5% at pH:8 and 83.0% at pH:10 after 7hrs. In the case of Annona Squmosa, the maxamimum extractability is found to be 21.8% at pH:2; 31.7% at pH:4; 55.4% at pH:6; 65.5% at pH:8 and 88.0% at pH:10 after 6 hrs. In the case of Cassia Occidentalis the maximum extractability is found to be 20.4% at pH:2; 30.4% at pH:4 ;51.8% at pH:6; 62.3% at pH:8 and 80.0% at pH:10 after 7hrs .Ficus Religiosa is found to be 19.7% at pH:2; 29.4% at pH:4; 46.5% at pH:6; 52.5% at pH:8 and 80.0% at pH:10 after 7 hrs. Cassia Auriculata is found to extract 21.3% at pH:2; 35.6% at pH:4 ; 43.9% at pH:6; 54.3% at pH:8 and 88.0% at pH:10 after 6 hrs. Calotropis Zygantia is found to extract 21.8% at pH:2; 31.9% at pH:4; 44.7% at pH:6; 53.4% at pH:8 and 80.0% at pH:10 after 7hrs. Punica Granthusm is found to extract 19.5% at pH:2; 27.8% at pH:4; 39.8% at pH:6; 54.8% at pH:8 and 82.0% at pH:10 after 7 hrs.

3. In these leaf powders, the % of extractability of Phosphate **increases with time** and **pH** (vide Graph Nos. A: 1-10; B: 1-5) for a fixed adsorbent. The maximum extractability is 82% percent at pH: 10 and after an equilibration period of 7 hrs. for PHYLLANTHUS NERURI; 79% at pH:10 after an equilibration period of 7hrs for PONGANUIA PIRMATA; 80% at pH:10 after an equilibration period of 7 hrs for DATURA METAL ; 83% at pH:10 after an equilibration period of 7 hrs for NERIUM ODORUM; 88% at pH:10 after an equilibration period of 6 hrs for ANNONA SQUAMOSA ; 80% at pH:10 after an equilibration period 7hrs for CASSIA OCCIDENTALIS;, and 80% at pH:10 after an equilibration period of 7hrs for FICUS RELIGIOSA; 88.0% at pH:10 after an equilibration period of 6 hrs for CASSIA AURICULATA; 80.0% at pH:10 after an equilibration period 7hrs for CALOTROPIS ZYGANTIA and 82.0% at pH:10 after an equilibration period of 7hrs for PUNICA GRANTHUSM.
4. When percentage removal is 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 plateaus are obtained (vide Graph Nos.:C:1-5). The optimum dosage is found to be 2g/lit for leaves powders of ANONA SQUAMOSA and CASSIA AURICULATA, 2.5grms/lit for leaves powders of PHYLLANTHUS NERURI, NERIUM ODORUM, PUNICA GRANTHUSM,3grams/lit for PONGANUIA PIRMATA, CASSIA OCCIDENTALIS, FICUS RELIGIOSA, DATURA METAL and CALOTROPIS ZYGANTIA.

B: ASHES OF LEAVES: (vide Graph Nos. A: 11-20; B: 6-10; C: 6-10):

The leaves ashes of Phyllanthus neruri**,** ,Ponganuia Pirmata, Datura Metal Nerium Odorum, Annona Squmosa, Cassia Occidentalis, Ficus Religiosa, Cassia Auriculata, Calotropis Zygantia, Punica Granthusm have been found to have affinity towards Phosphate ions. The following observations are significant :

1. **Effect of equilibration time**: In these leaves ashes as in the case of leave powders, 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:11-20). As for example, the minimum time to be allowed for maximum extraction are 4hrs at pH:2; 5hrs at pH:4; and 6 hrs at pH:8 and at pH:10 for ashes of leaves of Ponganuia Pirmata and same is the trend in other leaves ashes also.

2. **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:A:11-20;B:6-10). As for example, in the case of ashes of Phyllanthus neruri, the maximum extractability is found to be 29.3% at pH:2; 47.4% at pH:4; 63.4 % at pH:6; 80.0% at pH:8 and 86.0% at pH:10 after an equilibration period of 6 hrs. In the case of Ponganuia Pirmata, the maximum extractability is found to be 21.3% at pH:2 ; 42.7% at pH:4; 55.1% at pH:6; 73.0% at pH:8 and 83.0% at pH:10 after 6hrs. In the case of Datura Metal the maximum extractability after 6hrs is found to be 21.3% at pH:2; 36.6% at pH:4; 53.4% at pH:6; 64.4 %at pH:8 and 85.0% at pH:10. Nerium Odorum extracted to an extent of 22.6% at pH:2 ; 35.4% at pH:4; 56.3% at pH:6; 65.6% at pH:8 and 86.0% at pH:10 after 6hrs. In the case of Annona Squmosa, the maxamimum extractability is found to be 22.5% at pH:2; 34.8% at pH:4; 57.5% at pH:6; 66.6% at pH:8 and 90.0% at pH:10 after 5 hrs. In the case of Cassia Occidentalis the maximum extractability is found to be 20.5% at pH:2; 29.3% at pH:4 ;50.0 % at pH:6; 62.4% at pH:8 and 82.0% at pH:10 after 6hrs .Ficus Religiosa is found to be 20.8% at pH:2; 30.5% at pH:4; 50.6% at pH:6; 54.5% at pH:8 and 83.0% at pH:10 after 6 hrs. Cassia Auriculata is found to extract 22.4% at pH:2; 38.7% at pH:4 ; 48.9% at pH:6; 57.3% at pH:8 and 89.0% at pH:10 after 5 hrs. Calotropis Zygantia is found to extract 21.8% at pH:2; 33.9% at pH:4; 43.7% at pH:6; 52.4% at pH:8 and 83.0% at pH:10 after 6hrs. Punica Granthusm is found to extract 20.6% at pH:2; 28.8% at pH:4; 39.8% at pH:6; 57.0% at pH:8 and 83.0% at pH:10 after 6 hrs.

3. In these leaves ashes the % of extractability of Phosphate **increases with time** and **pH** (vide Graph Nos.A:11-20; B: 6-10) for a fixed adsorbent. The maximum extractability is 86% percent at pH: 10 and after an equilibration period of 6 hrs. for PHYLLANTHUS NERURI, 83% at pH:10 after an equilibration period of 6 hrs for PONGANUIA PIRMATA, 85% at pH:10 after an equilibration period of 6 hrs for DATURA METAL 85% at pH:10 after an equilibration period of 6 hrs for NERIUM ODORUM, 90% at pH:10 after an equilibration period of 5 hrs for ANNONA SQUAMOSA , 82% at pH:10 after an equilibration period 6hrs for CASSIA OCCIDENTALIS , and 83% at pH:10 after an equilibration period of 6hrs for FICUS RELIGIOSA,. 89% at pH:10 after an equilibration period of 5 hrs for CASSIA AURICULATA , 85% at pH:10 after an equilibration period 6hrs for CALOTROPIS ZYGANTIA , and 83% at pH:10 after an equilibration period of 6hrs for PUNICA GRANTHUSM.

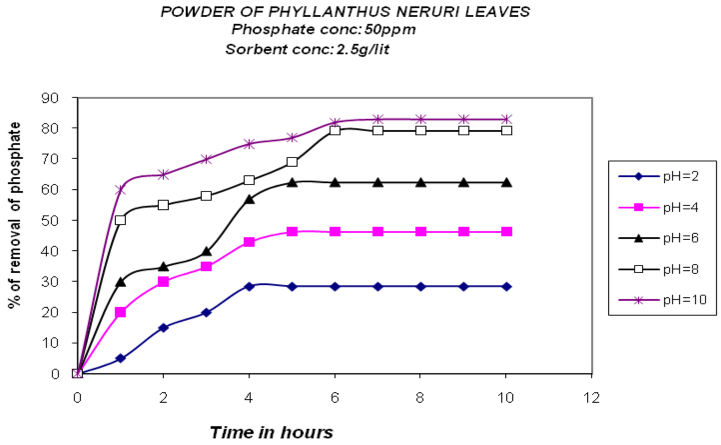
4. When percentage removal is studied with respect to adsorbent dosage at fixed optimum pH: 10 and at optimum equilibration times, the graphs increase up to certain dosage and from then onwards a plateaus are obtained. The optimum dosage is found to be 1.5g/lit for leaves ashes of ANONA SQUAMOSA and CASSIA AURICULATA; 2.0grms/lit for PHYLLANTHUS NERURI, NERIUM ODORUM, FICUS RELIGIOSA, DATURA METAL and CALOTROPIS ZYGANTIA; 2.5grams/lit for PUNICA GRANTHUSM, PONGANUIA PIRMATA, CASSIA OCCIDENTALIS, (vide Graph Nos.:C:6-10).

Table 1:A: Effect of interfering Ions on the Extractability of PHOSPHATE with powders of leaves

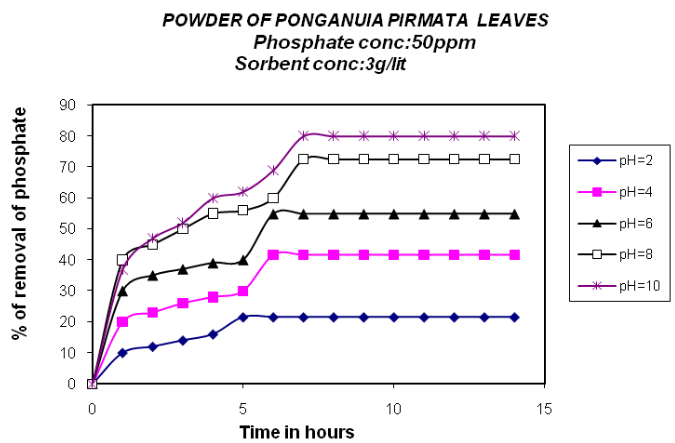
S.No	Adsorbent	Maximum Extractability at optimum conditions	*Extractability of phosphate in presence 500ppm of interfering ions at optimum(pHs)*										
			SO_4^{2-}	NO_3^-	Cl^-	F^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}	Fe^{2+}	Ni+
1	Powder of Phyllanthus Neruri leaves	82.0% pH:10, 7.0 hrs	77.1% pH:10, 1.5hrs	76.7% pH:10, 1.5 hrs	78.6% p H:10, 4hrs	79.4% p H:10, 4 .0hrs	79.7% pH:10, 2.5 hrs	86.4% H:10, 3.5 hrs	88.9% pH:10, 3.0 hrs	87.5% pH:10, 4 .0hrs	88.6% pH:10, 4.5 hrs	84.5% pH:10, 4.0 hrs	87.5% pH:10, 4.5 hrs
2	Powder of Ponganuia Pirmata leaves	79.0% pH:10, 7 . 0hrs	76.2% pH:10, 1.5 hrs	75.8% p H:10, 2.5hrs	77.9% pH:10, 2.0 hrs	78.8% pH:10, 2 .5hrs	78.1% p H:10, 3.0 hrs	81.5% H:10, 1.5 hrs	86.2% pH:10, 5.0hrs	88.3% pH:10, 3.5hrs	89.7% pH:10, 3 .0hrs	89.7% pH:10, 4.5hrs	87.3% pH:10, 3.0hrs
3	Powder of Datura Metal leaves	80.0% pH:10, 7.0hrs	75.2% pH:10, 2.5hrs	74.5% pH:10, 3.5 hrs	78.2% H:10, 1.0 hrs	79.7% pH:10, 3 .5hrs	80.2% pH:10, 4 .5hrs	85.3% pH:10, 2.5hrs	89.3% pH:10, 2.5hrs	87.2% pH:10, 2.5hrs	88.9% pH:10 4.5hrs	87.8% pH:10, 5 .0hrs	88.1% pH:10, 3 .5hrs
4	Powder of Nerium Odorum leaves	83.0% pH:10, 7.0hrs	79.3% pH:10, 4 .0hrs	78.6% pH:10, 4.0hrs	82.3% pH:10, 3.5 hrs	83.4% pH:10, 4 .0hrs	83.5% pH:10, 3 .0hrs	87.5% pH:10, 3.5hrs	86.2% pH:10, 3 .0hrs	88.8% pH:10, 1.5hrs	87.8% pH:10, 2.5 hrs	84.2% pH:10, 4 .0hrs	89.8% pH:10, 2 .0hrs
5	Powder of Annona Squamosa leaves	88.0% pH:10, 6.0hrs	82.5% pH:10, 4 .0hrs	79.4% pH:10, 4.5 hrs	84.6% pH:10, 4.5 hrs	85.2% pH:10, 3.0 hrs	86.8% pH:10, 4.0 hrs	87.4% pH:10, 2.5 hrs	86.8% pH:10, 4.0 hrs	89.7% pH:10, 4.5 hrs	88.2% pH:10, 3 .0hrs	87.3% pH:10, 3.0hrs	88.7% pH:10, 2.0hrs
6	Powder of Cassia Occidentalis leaves	80.0% pH:10, 7.0hrs	76.6% pH:10, 2.0hrs	75.1% pH:10, 3.5hrs	79.5% pH:10, 2.5 hrs	80.5% pH:10, 5 .0hrs	80.4% pH:10, 1.5 hrs	89.7% pH:10, 4.5 hrs	87.3% pH:10, 2 .0hrs	83.2% pH:10, 3.5hrs	85.7% pH:10, 4.5 hrs	84.3% pH:10, 3.0 hrs	86.2% pH:10, 3.5 hrs
7	Powder of Ficus Religiosa leaves	80.0% pH:10, 7.0 hrs	77.5% pH:10, 1.5 hr	76.2% pH:10, 2 .0hrs	79.4% pH:10, 3 .0hrs	79.6% pH:10, 5.0 hrs	79.6% pH:10, 2.5hrs	84.3% pH:10, 5.0 hrs	86.2% pH:10, 4.5hrs	84.8% pH:10, 4.0hrs	85.8% pH:10, 5 .5hrs	88.8% pH:10, 4.0hrs	84.8% pH:10, 4.5hrs
8	Powder of Cassia Auriculata leaves	88.0% pH:10, 6 .0hrs	80.6% pH:10, 5.0hrs	80.2% pH:10, 4 .5hrs	82.8% pH:10, 4.5 hrs	83.9% pH:10, 2 .5hrs	84.6% pH:10, 1.5 hrs	91.8% pH:10, 3.5 hrs	93.8% pH:10, 3 .0hrs	92.1% pH:10, 2.0hrs	93.4% pH:10, 4 .5hrs	91.8% pH:10, 41.5hrs	92.1% pH:10, 4 .0hrs
9	Powder of Calotropis Zygantia leaves	80.0% pH:10, 7.0 hrs	77.2% pH:10, 2.5hrs	77.3% pH:10, 5.0 hrs	80.4% H:10, 5.0 hrs	80.5% pH:10, 3.5 hrs	81.3% pH:10, 2.0hrs	82.4% pH:10, 4 .0hrs	85.7% pH:10, 2.0hrs	83.2% pH:10, 5.0hrs	85.2% pH:10, 5 .0hrs	87.8% pH:10, 4 .0hrs	86.2% pH:10, 2 .0hrs
10	Powder of Punica Granthusm leaves	82.0% pH:10, 7.0 hrs	79.5% pH:10, 3.0 hrs	78.6% pH:10, 4.5 hrs	81.4% pH:10, 6 .0hrs	82.1% pH:10, 2.0 hrs	82.8% pH:10, 4 .0hrs	84.8% pH:10, 2 .0hrs	87.8% pH:10, 2 .0hrs	84.5% pH:10 2.5hrs	86.7% pH:10, 2.0hrs	88.7% pH:10, 4.5hrs	86.5% pH:10, 5.0hrs

Table 1:B: Effect of interfering Ions on the Extractability of PHOSPHATE with ashes of leaves

S.No	*Adsorbent*	*Maximum Extractability at optimum conditions*	*Extractability of Phosphate in presence 500ppm of interfering ions at optimum(pHs)*										
			SO_4^{2-}	NO_3^{-}	Cl^{-}	F^{-}	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}	Fe^{2+}	Ni^{2+}
1	Ash of Phyllanthus Neruri leaves	86.0% pH:10, 6.0hrs	82.1% pH:10, 1.5 hr	83.9% pH:10, 1.5 hr	84.3% pH:10, 2.5 hrs	85.7% pH:10, 3 hrs	86.2% pH:10, 3 hrs	87.4% pH:10, 2 hrs	88.8% pH:10, 2.0 hrs	94.8% pH:10, 1.5 hrs	95.2% pH:10, 4.5 hrs	94.5% pH:10, 2.0 hrs	93.5% pH:10 4.0 hrs
2	Ash of Ponganuia Pirmata lleaves	83.0% pH:10, 6.0 hrs	83.4% pH:10, 2 .0hrs	84.2% pH:10, 3.0 hrs	83.5% pH:10, 2.0 hrs	84.1% pH:10, 2.5 hrs	84.9% pH:10, 2 hrs	86.5% pH:10, 3 hrs	85.9% pH:10, 3 .0hrs	95.8% pH:10, 2.5 hrs	96.3% pH:10, 3 .0hrs	94.7% pH:10, 1.5hrs	94.7% pH:10, 1.5hrs
3	Ash of Datura Metal leaves	85.0% pH:10, 6 .0hrs	83.5% pH:10, 2.5 hrs	84.6% pH:10, 4.0 hrs	85.9% pH:10, 2.5 hrs	85.2% pH:10, 3.5 hrs	85.1% pH:10, 13hrs	87.5% pH:10, 4 hrs	88.3% pH:10, 2.0 hrs	96.1% pH:10, 3.5 hrs	97.3% pH:10, 2 .5hrs	97.8% pH:10, 2 .0hrs	94.8% pH:10, 2.0hrs
4	Ash of Nerium Odorum leaves	85.0% pH:10, 6.0 hrs	84.6% pH:10, 3 .0hrs	82.4% pH:10, 2.5 hrs	83.7% pH:10, 1.5 hrs	84.6% pH:10, 1.5hrs	85.2% pH:10, 1 hrs	87.8% pH:10, 4 hrs	88.3% pH:10, 2.0hrs	95.8% pH:10, 1.5 hrs	96.9% pH:10, 2.5 hrs	94.2% pH:10, 3 .0hrs	94.2% pH:10, 4.0hrs
5	Ash of Annona Squamosa leaves	90.0% pH:10, 5 .0hrs	79.2% pH:10, 4.0hrs	84.1% pH:10, 1.5 hrs	85.1% pH:10, 1.0 hr	86.1% pH:10, 2 .0hrs	87.4% pH:10, 3 .0hrs	92.7% pH:10, 3.0 hrs	93.3% pH:10, 3.5 hrs	98.2% pH:10, 3.0 hrs	98.3% pH:10, 3.5 hrs	93.3% pH:10, 3.0hrs	96.3% pH:10, 5.0hrs
6	Ash of Cassia Occidentalis leaves	82.0% pH:10, 6.0hrs	79.2% pH:10, 1.5 hrs	80.6% pH:10, 2 hrs	81.0% pH:10, 3.5 hrs	82.3% pH:10, 3.0 hrs	83.4% pH:10, 4.5 hrs	84.7% pH:10, 3 .5hrs	85.9% pH:10, 3 .0hrs	87.3% pH:10, 2.5 hrs	88.3% pH:10, 4.5 hrs	89.3% pH:10, 2.0 hrs	88.0% pH:10, 3.0 hrs
7	Ash of Ficus Religiosa leaves	83.0% pH:10, 6 . 0hrs	78.6% pH:10, 3.5 hrs	80.3% pH:10, 5.0 hrs	81.6% pH:10, 2 .5hrs	83.5% pH:10, 2.5 hrs	84.6% pH:10, 2 .0hrs	84.7% pH:10, 4.0 hrs	85.2% pH:10, 2.5 hrs	86.8% pH:10, 1.5 hrs	94.6% pH:10, 2 .0hrs	94.8% pH:10, 2.0hrs	92.8% pH:10, 4.0hrs
8	Ash of Cassia Auriculata leaves	89.0% pH:10, 5.0 hrs	87.2% pH:10, 3.0 hrs	87.4% pH:10, 2hrs	88.9% pH:10, 2.5 hrs	88.9% pH:10, 3.5 hrs	89.7% pH:10, 3 .5hrs	92.2% pH:10, 2.5 hrs	93.4% pH:10, 3 .5hrs	95.8% pH:10, 2.5 hrs	97.3% pH:10, 2.5 hrs	93.8% pH:10, 1.5hrs	95.8% pH:10, 1.5hrs
9	Ash of Calotropis Zygantia leaves	85.0% pH:10, 6 .0hrs	82.1% pH:10, 1.51.hrs	83.9% pH:10, 3.0 hrs	84.1% pH:10, 4.0 hrs	84.1% pH:10, 1.5hrs	85.2% pH:10, 2.5 hrs	88.1% pH:10, 4.0 hrs	89.9% pH:10, 1.5 hrs	93.8% pH:10, 3 .0hrs	96.5% pH:10, 3.5 hrs	94.8% pH:10, 2 .0hrs	92.8% pH:10, 2.0hrs
10	Ash of Punica Granthusm leaves	83.0% pH:10, 6.0 hrs	80.6% pH:10, 2.5 hrs	81.4% pH:10, 2.00hrs	82.5% pH:10, 3.5 hrs	83.0% pH:10, 2 .0hrs	83.1% pH:10, 3.5 hrs	88.5% pH:10, 3 .0hrs	87.5% H:10, 2.5 hrs	90.7% pH:10, 2.0 hrs	91.3% pH:10, 3 .5hrs	92.7% pH:10, 4.5hrs	93.7% pH:10, 4.5hrs

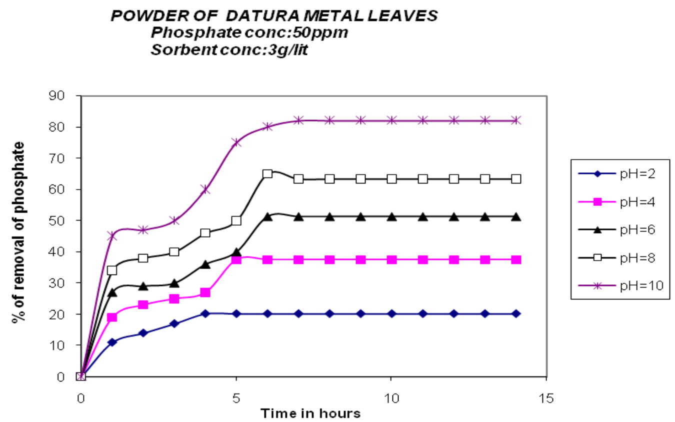

POWDER OF PHYLLANTHUS NERURI LEAVES
Phosphate conc:50ppm
Sorbent conc:2.5g/lit

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



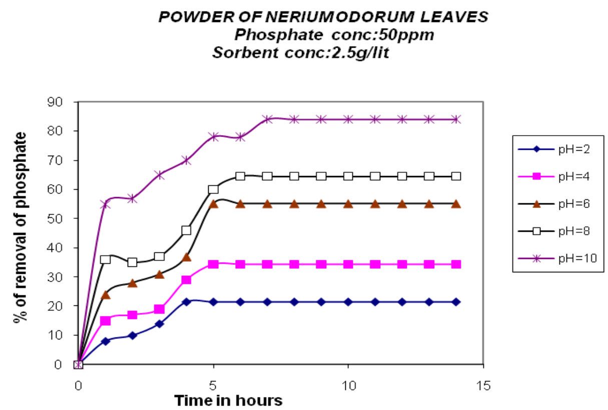
POWDER OF PONGANUIA PIRMATA LEAVES
Phosphate conc:50ppm
Sorbent conc:3g/lit

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



POWDER OF DATURA METAL LEAVES
Phosphate conc:50ppm
Sorbent conc:3g/lit

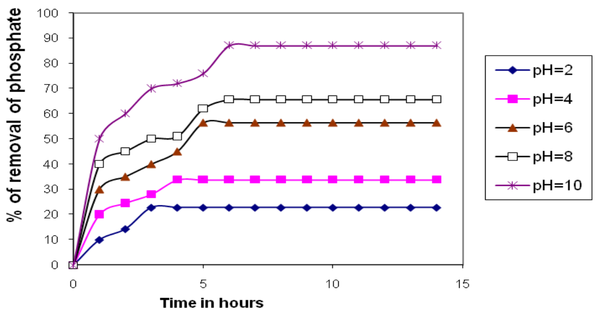
Time vs % of removal of phosphate
Graph No:A-3



POWDER OF NERIUMODORUM LEAVES
Phosphate conc:50ppm
Sorbent conc:2.5g/lit

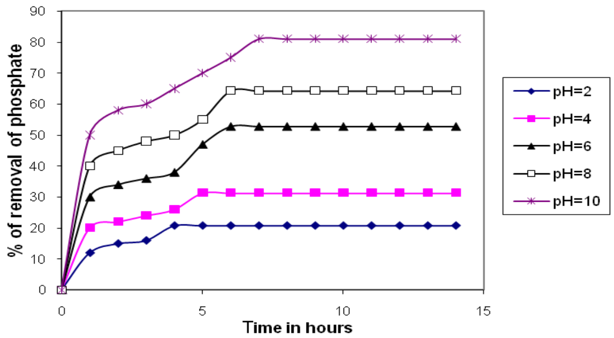
Time vs % of removal of phosphate
Graph No:A-4

POWDER OF ANNONA SQUAMOSA LEAVES
Phosphate conc:50ppm
Sorbent conc:2g/lit



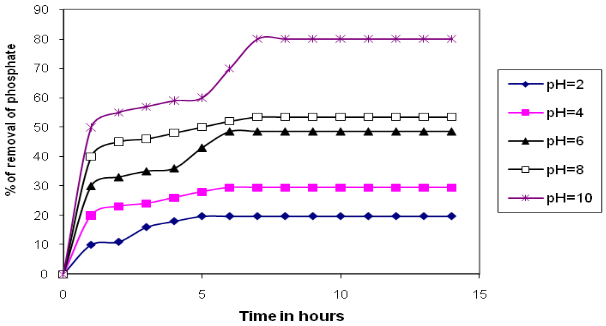
Time vs % of removal of phosphate
Graph No:A-5

POWDER OF CASSIA OCCIDENTALIS LEAVES
Phosphate conc:50ppm
Sorbent conc:3g/lit

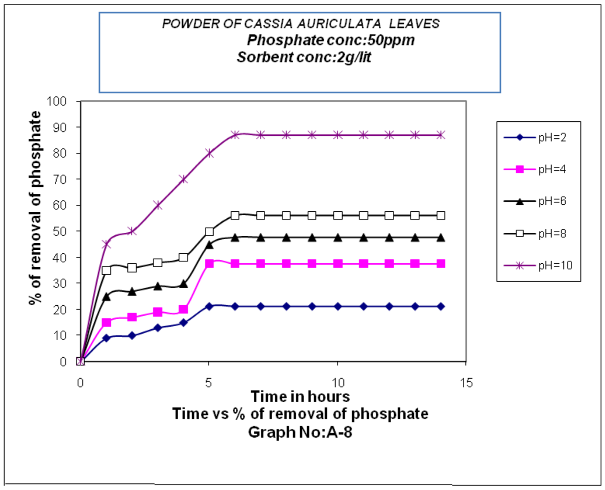


Time vs % of removal of phosphate
Graph No:A-6

POWDER OF FICUS RELIGIOSA LEAVES
Phosphate conc:50ppm
Sorbent conc:3g/lit

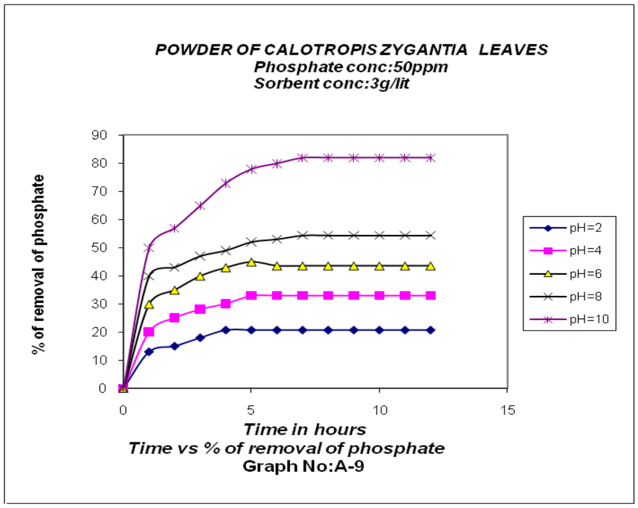


Time vs % of removal of phosphate
Graph No:A-7



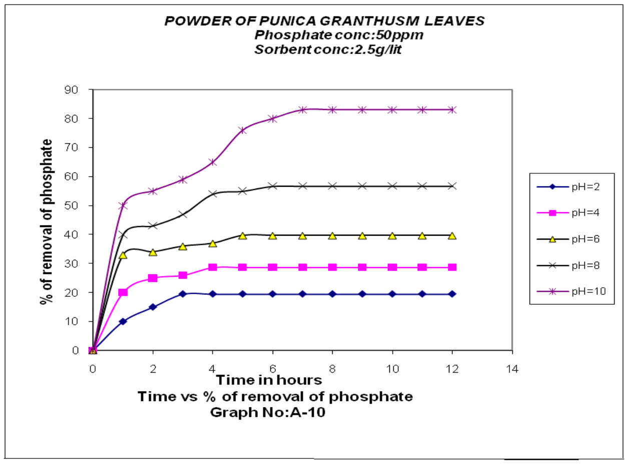
POWDER OF CASSIA AURICULATA LEAVES
Phosphate conc:50ppm
Sorbent conc:2g/lit

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



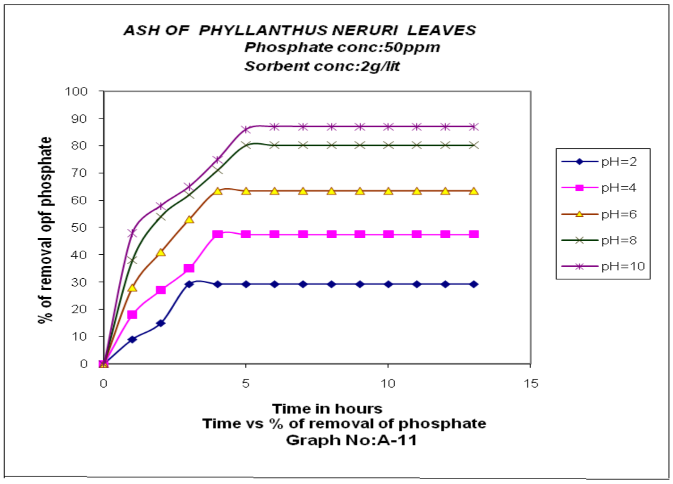
POWDER OF CALOTROPIS ZYGANTIA LEAVES
Phosphate conc:50ppm
Sorbent conc:3g/lit

Time vs % of removal of phosphate
Graph No:A-9



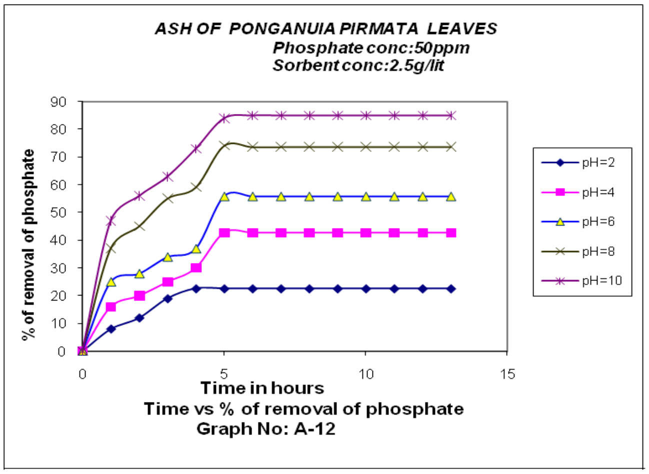
POWDER OF PUNICA GRANTHUSM LEAVES
Phosphate conc:50ppm
Sorbent conc:2.5g/lit

Time vs % of removal of phosphate
Graph No:A-10



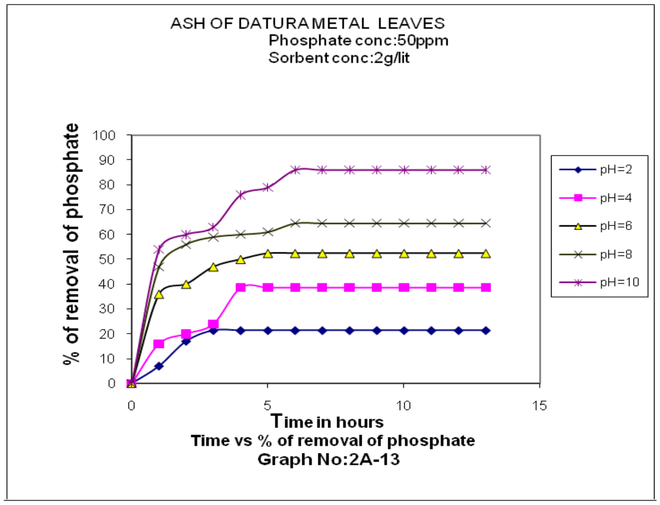
ASH OF PHYLLANTHUS NERURI LEAVES
Phosphate conc:50ppm
Sorbent conc:2g/lit

Time vs % of removal of phosphate
Graph No:A-11



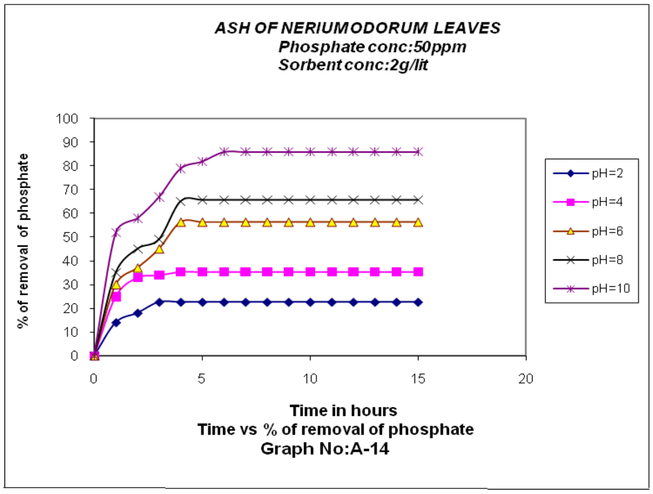
ASH OF PONGANUIA PIRMATA LEAVES
Phosphate conc:50ppm
Sorbent conc:2.5g/lit

Time vs % of removal of phosphate
Graph No: A-12

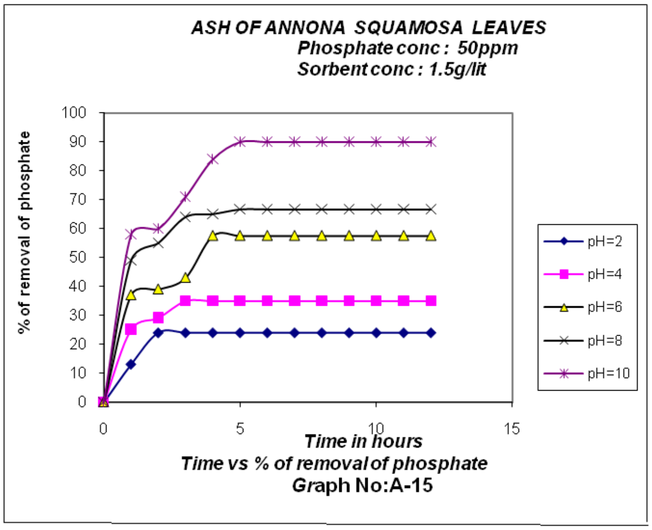


ASH OF DATURA METAL LEAVES
Phosphate conc:50ppm
Sorbent conc:2g/lit

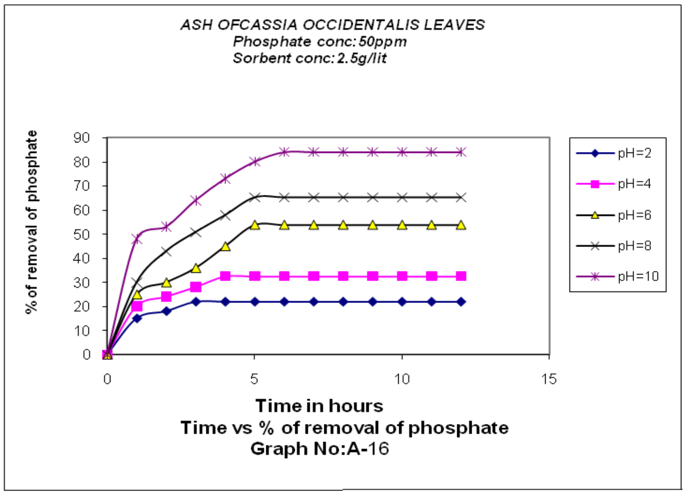
Time vs % of removal of phosphate
Graph No:2A-13



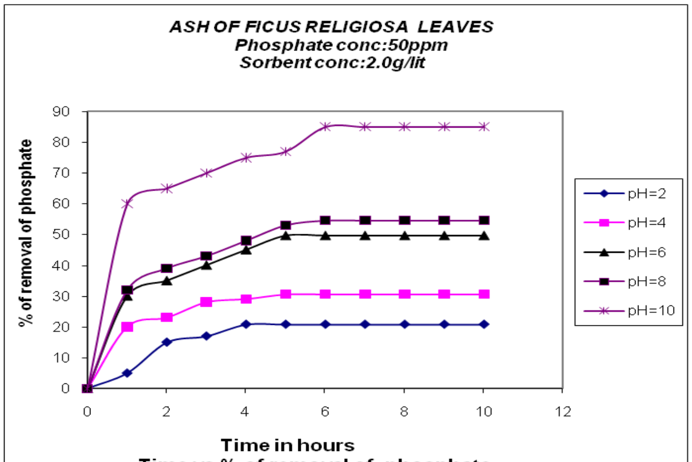
Time vs % of removal of phosphate
Graph No:A-14



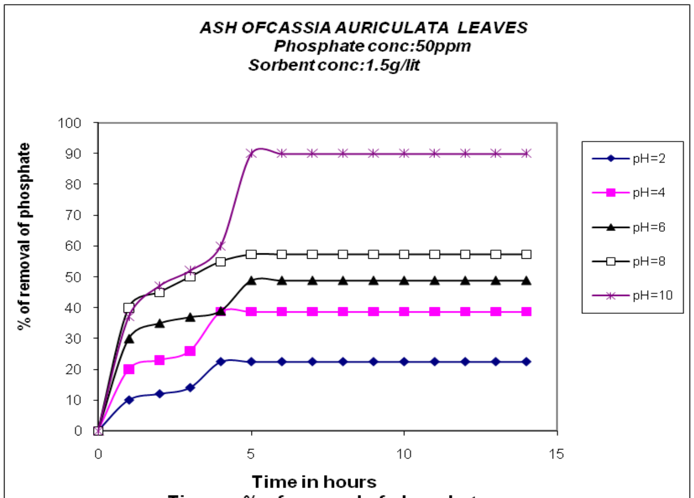
Time vs % of removal of phosphate
Graph No:A-15



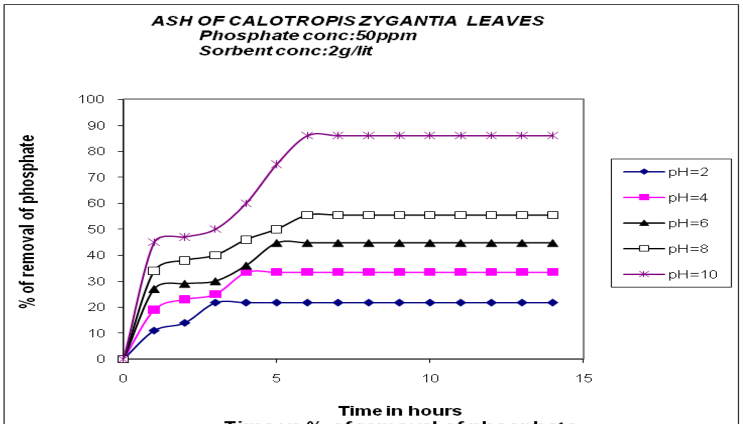
Time vs % of removal of phosphate
Graph No:A-16



Time vs % of removal of phosphate
Graph No:A-17

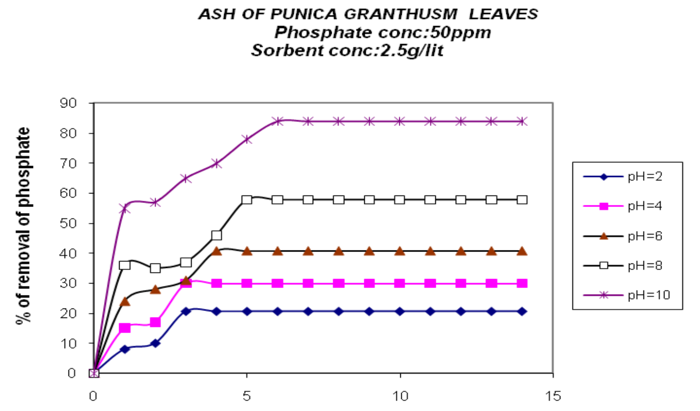


Time vs % of removal of phosphate
Graph No:A-18



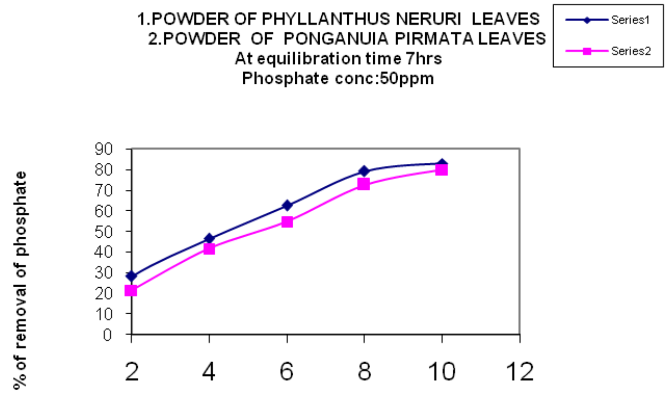
Time vs % of removal of phosphate
Graph No:A-19

ASH OF PUNICA GRANTHUSM LEAVES
Phosphate conc:50ppm
Sorbent conc:2.5g/lit



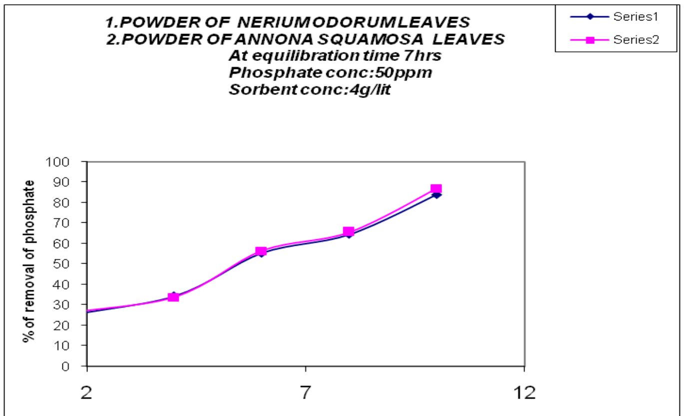
Time in hours
Time vs % of removal of phosphate
Graph No:A-20

1.POWDER OF PHYLLANTHUS NERURI LEAVES
2.POWDER OF PONGANUIA PIRMATA LEAVES
At equilibration time 7hrs
Phosphate conc:50ppm

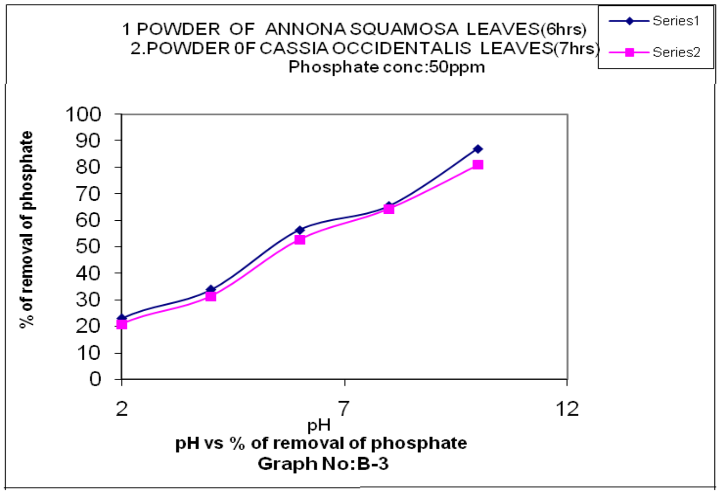


pH
pH vs % of removal of phosphate
Graph No:B-1

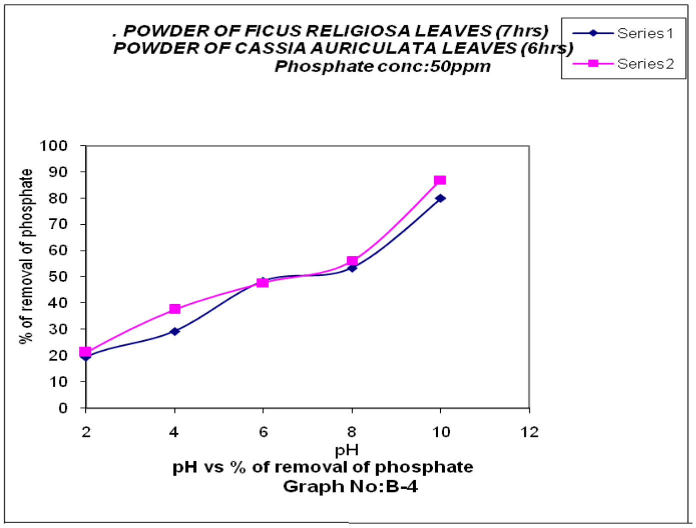
1.POWDER OF NERIUMODORUMLEAVES
2.POWDER OF ANNONA SQUAMOSA LEAVES
At equilibration time 7hrs
Phosphate conc:50ppm
Sorbent conc:4g/lit



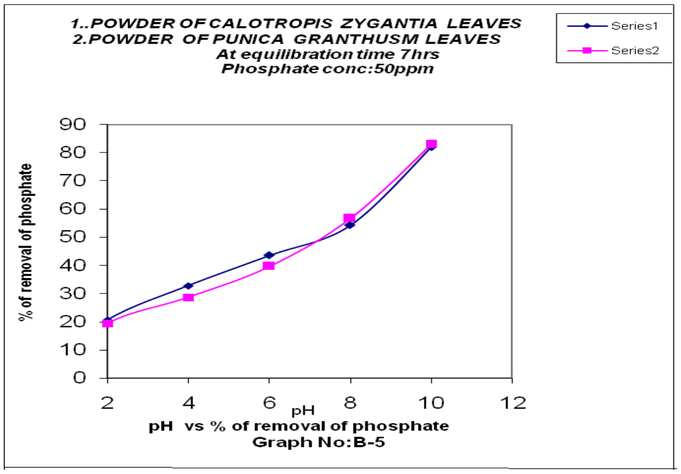
pH
pH vs % of removal of phosphate
Graph No:B-2



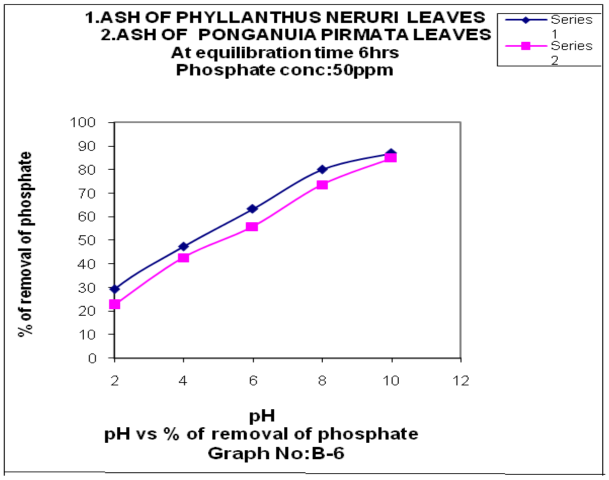
pH vs % of removal of phosphate
Graph No:B-3

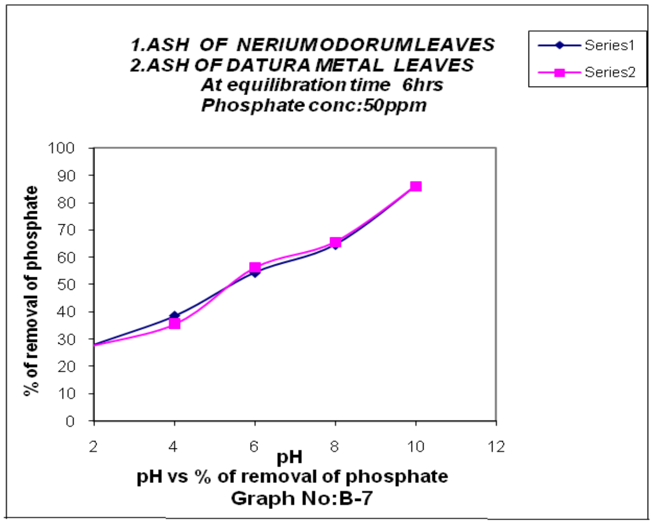


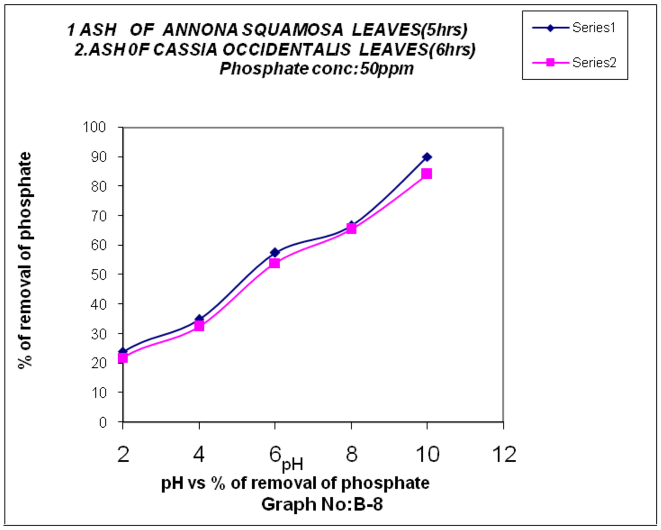
pH vs % of removal of phosphate
Graph No:B-4

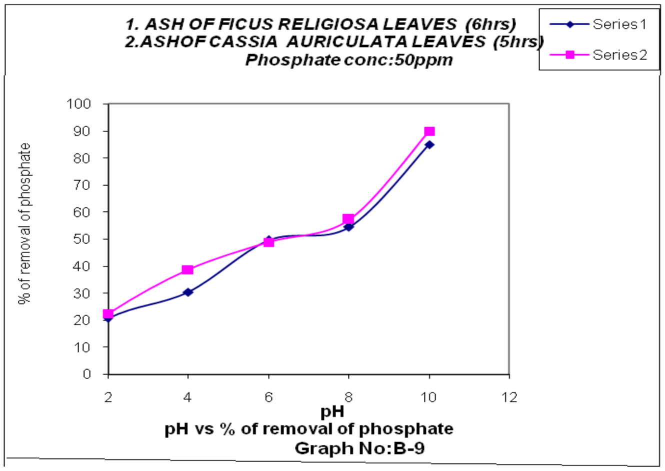


pH vs % of removal of phosphate
Graph No:B-5

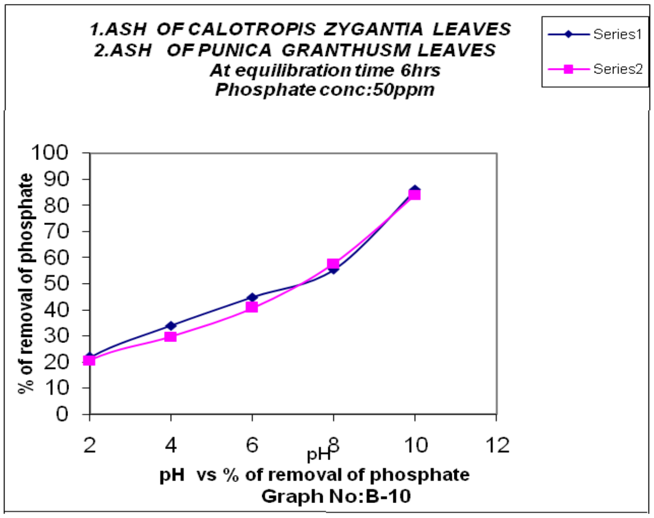

1.ASH OF PHYLLANTHUS NERURI LEAVES
2.ASH OF PONGANUIA PIRMATA LEAVES
At equilibration time 6hrs
Phosphate conc:50ppm
Series 1
Series 2
% of removal of phosphate
100
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
12
pH
pH vs % of removal of phosphate
Graph No:B-6


1.ASH OF NERIUMODORUMLEAVES
2.ASH OF DATURA METAL LEAVES
At equilibration time 6hrs
Phosphate conc:50ppm
Series1
Series2
% of removal of phosphate
100
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
12
pH
pH vs % of removal of phosphate
Graph No:B-7

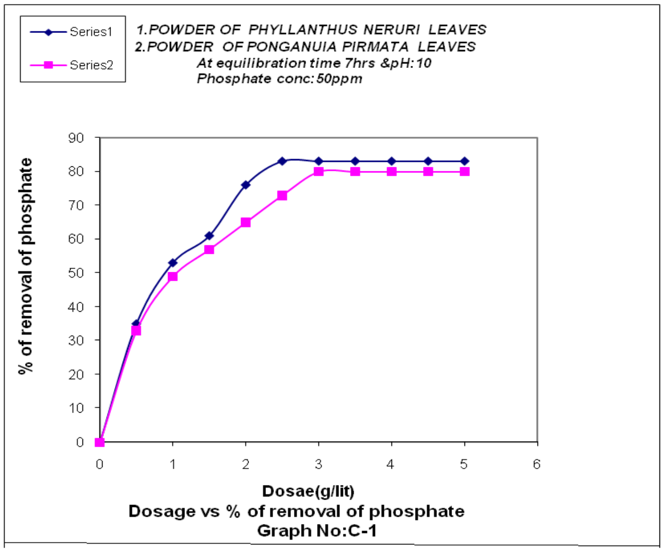

1 ASH OF ANNONA SQUAMOSA LEAVES(5hrs)
2.ASH 0F CASSIA OCCIDENTALIS LEAVES(6hrs)
Phosphate conc:50ppm
Series1
Series2
% of removal of phosphate
100
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
12
pH
pH vs % of removal of phosphate
Graph No:B-8



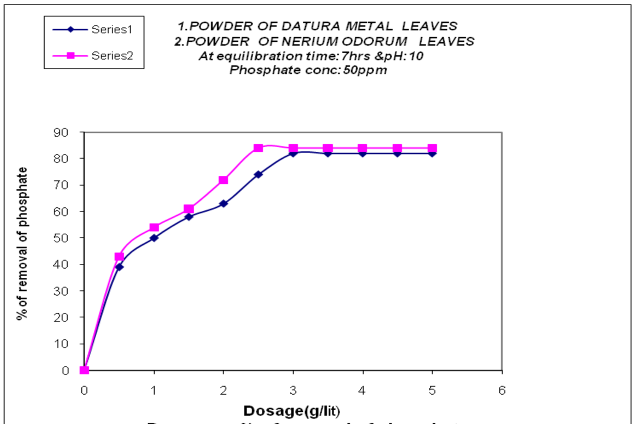
pH vs % of removal of phosphate
Graph No:B-9



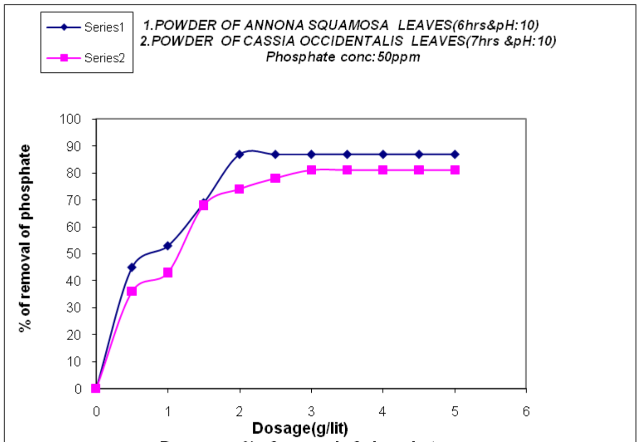
pH vs % of removal of phosphate
Graph No:B-10



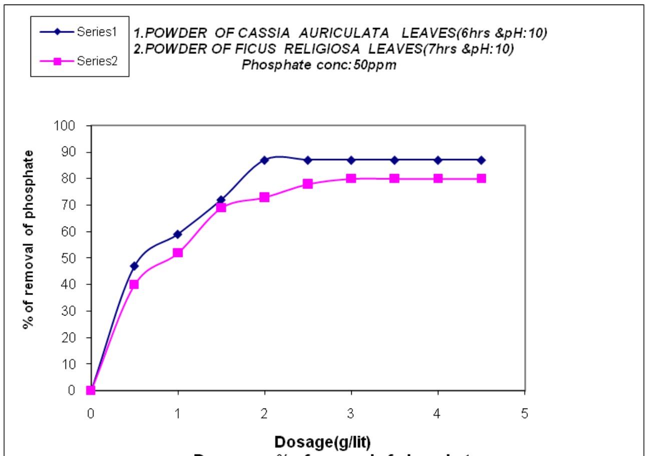
Dosage vs % of removal of phosphate
Graph No:C-1



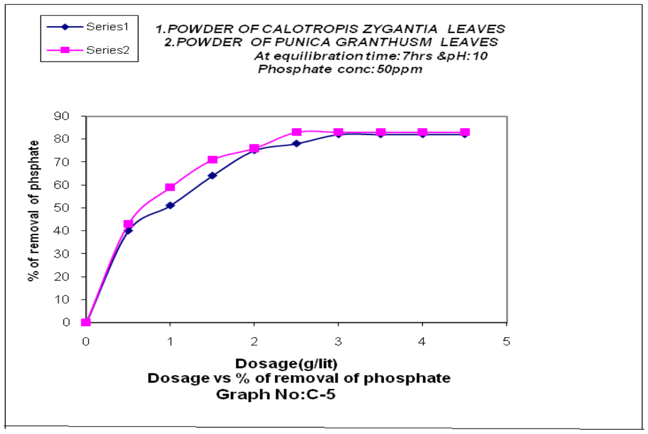
Dosage vs % of removal of phosphate
Graph No:C-2



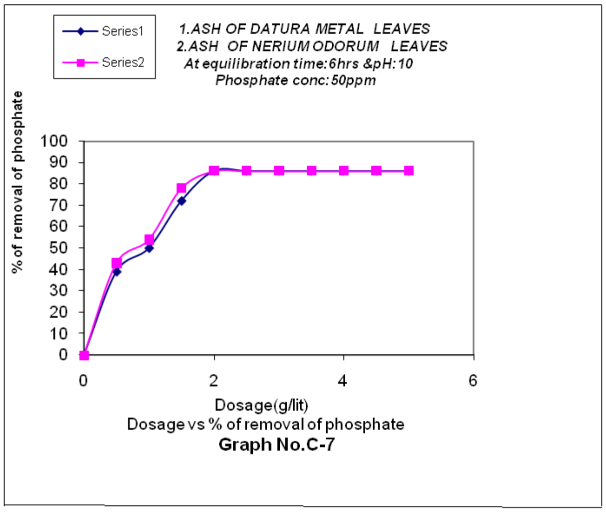
Dosage vs % of removal of phosphate
Graph No:C-3



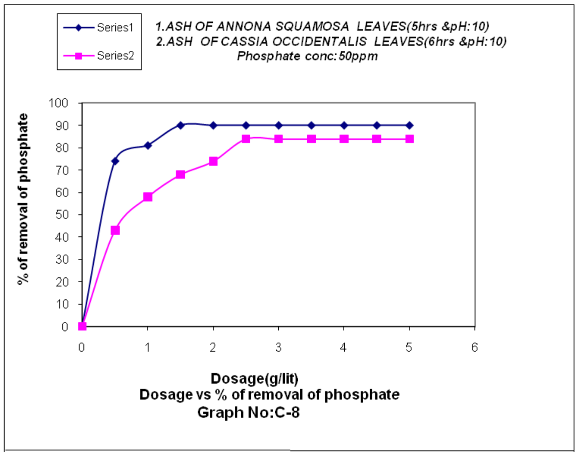
Dosage vs % of removal of phosphate
Graph No:C-4



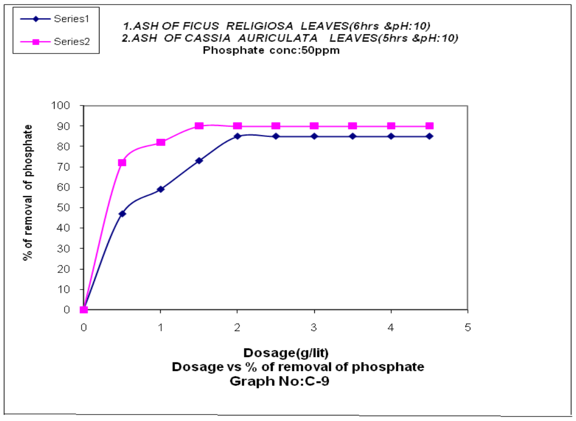
Dosage vs % of removal of phosphate
Graph No:C-5



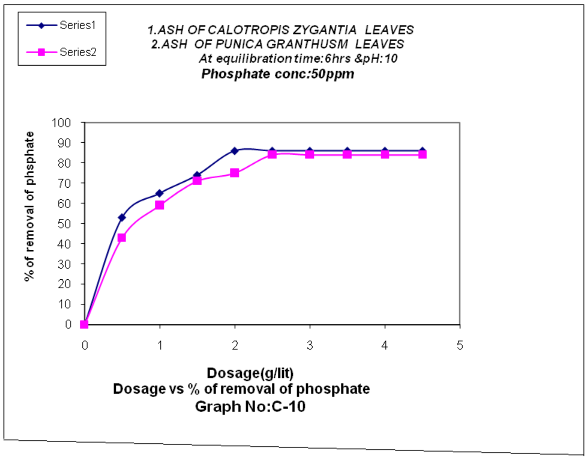
Dosage vs % of removal of phosphate
Graph No.C-7



Dosage vs % of removal of phosphate
Graph No:C-8



Dosage vs % of removal of phosphate
Graph No:C-9



Dosage vs % of removal of phosphate
Graph No:C-10

C: 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 the successful adsorbents at optimum conditions of extractability. The results are presented in the Table:1:A and B. 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. They are not interfering with the extraction of phosphate at the optimum pH conditions and at the time of equilibration time. (Vide Table Nos: :1: A & B).

2 It is interesting to note that the extractability is markedly enhanced in presence of Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+} and Ni^{2+} ions. As for example: the % of extraction is 80.0% at pH:10 with Powder of Datura metal leaves 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 85.3%, 89.3% 87.2%, 88.9%, 87.8% and 88.1% respectively (vide Table No.: 1:A: item No.3). The same trend was observed in the case of remaining adsorbents of interest. (Vide Table No.:1: A).

3 The % of extraction is 82.0%at pH:10, with leaves ash of Cassia Occidentalis while in the presence of Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+} and Ni^{2+}, the % of extraction is enhanced to 84.7%, 85.9%, 87.3% , 88.3%, 89.3%, 88.0% respectively (vide Table No:1:B:item No.6). The same trend was observed in the case of remaining adsorbents of interest. (vide Table No.: 2:1:B).

DISCUSSION

To propose sound theoretical grounds for the each observation made is rather complicated 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 endeavors of this work. However, the behaviors may generally be understood as follows:

1. H_3PO_4 is a tribasic acid and has dissociation constants each is decreasing successively by factors of nearly 10^3 : pK_1=2.15;pK2:7.20;pK3: 12.3. Accordingly the acid gives three series of salts, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 and 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 cannot be detected directly by means of a colored indicator(Vogel,1961).
2. The functional groups present in the lingo celluloses' materials(barks, leaves etc.) are OH-/-COOH groups and are having affinity towards the phosphates with increase of pH. This is reflected in the increase in % of extractability with increase in pH.
3. 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.
4. Ashes are the oxides of some heavy metals containing large amounts of silica and oxides of metals So, these ashes, contains '-OH' groups and "-O-" and the observed behaviors of increase in extractability with the increase in pH, may be attributed to the affinity of phosphates at high pH value of solutions towards these groups and also to the formation of sparingly soluble salts with the metallic ions in the ashes.

   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.

5. 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., SO42- , NO32- , Cl- and Carbonate. In the case of 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 A thorough investigation is made in exploring the surface sorption abilities of some waste materials of plant origin in controlling Phosphates from polluted waters.

2 The leaves and their ashes of the plants presented in this work have been found to have affinity towards Phosphates at high pH values and at optimum conditions of equilibrium time and sorbent dosage.

3 The ashes show more sorption abilities towards Phosphate than powders of raw materials..

4 We claim the maximum removal of 88.0% at pH: 10 with the powders of leaves of Annona squamosa and Cassia Auriculata at 6 hrs equilibration time and at the adsorbent dosage of 2gm/lt.. With ashes leaves of Annona squamosa and Cassia Auriculata , the maximum of 90%and 89% removal of Phosphate has been found respectively at pH 10 for 5hrs equilibration time and at the adsorbent dosage of 1.5gm /lt.

5 The minimum dosage needed for the maximum removal of phosphate is found less for leave ashes than for powders of leaves.

6 Interferences: Anions, namely Chlorides, Sulphates, Nitrates, Fluorides and Carbonates are found to marginally effected the %of extraction at the optimum conditions cited in the Table::1: A and B. It is found that cations viz., Ca2+,Ni2+, Cu2+,Co2+ Zn2+, Fe2+ and Mg2+ ions are synergizing the extraction and thereby % of removal of phosphate is increased even in the presence of 500 ppm of the said ions. This is an interesting point and need further investigation.

ACKNOWLEDGEMENTS

Authors thank UGC for granting the financial aid for conducting this research work

REFERENCES

1 A. Shukla, Y.H. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, (2002) "The role of sawdust in the removal of unwanted materials from water", J. Hazard Mater, 95, 137-152 .

2 Ames et al., "Phosphorous Removal from Effluents in Alumina Columns," (1970)J. Water Pollution Control Federation,. 42, No. 5, Part 2,. R161-R172

3 M.J. Baker, D.W. Blowes, C.J. Ptacek,(1998) "Laboratory development of permeable reactive mixtures for the removal of phosphorus from onsite waste water disposal systems", Environ. Sci. Technol.,32,2308-2316

4 B, Batchelor, and R. Dennis, (1987). "A Surface Complex Model for Adsorption of Trace Components from Wastewater", J. Water Pollution Control Federation, 59(12):1059-1068.

5 H. Brattebø, and H. Ødegaard,(1986) , "Phosphorus Removal by Granular Activated Alumina," Water Res., 20, No. 8, 977-986

6 N. Boujelben et. Al., (2008) "Phosphorus removal from aqueous solutions using iron coated natural and engineering sorbents", J. of Hazardous Materials, 151(1), 103

7 D.R. Kioussis , F.W. WheatonK. Ofinas, P., (1999)"Phosphate binding polymeric hydro gels for aquaculture wastewater remediation", Aquacultural Eng. 19,163-178

8 Gerard Kiely, "Environmental Engineering", (1998)MacGraw-Hill International Edn.

9 Huang "Removal of Phosphate by Powdered Aluminum Oxide Adsorption,(1997) J. Water Pollution Control Federation, 7, 1811-1817

10 J.S.Han, N. Hur, B. Choi, S.H.Min,(2003) "Removal of Phosphorous using chemically modified lingocelluloses materias" In: 6th Inter- regional Conference on Environmnent-Water,"Land and Water Use Planning and Management", Albacete, Spain, pp. 1-11

11 LuzE. De-Bastan and Yoav Bashan,(2004) "Recent advances in removing phsophorous from waste water and it s future use as fertilizer (1997-2003)", Water Research, 38, pp 4222-4246 (2004) - a review article and other reference in it.

12 M.A.Tshabalaka, K.G. Karthikeyan, D. Wang, (2004)"Cationized milled pine bark as an absorbent for oththophate anions", J. Appl.Polym. Sci. 93,1577-1583)

13 M.J.Baker, D.W. Blowes, C.J. Ptacek,(1998) "Laboratory development of permeable reactive mixtures for the removal of phosphorus from onsite waste water disposal systems", Environ. Sci. Technol. , 32, 2308-2316

14 M.R.Unnithan V.P.Vinod, T.S.Anirudhan,(2002) "Ability of Iron(III)loaded carboxylated polyacrylamide-grafted saw dust to remove phosphate ions from aqueous solution and fertilizer industry waste water: adsorption kinetics and isotherm studies., J. Appl. Polym. Sci. , 84, 2541-2553

15 Metcalf and Eddy, (2003) "Waste Water Engineering" Edition-IV

16 A.N. Onar , N. Balkaya and T. Akyurz, (1996)Environmental Technology, 17(2), 207-213

17 S.J. Shiao, K. Akashi,(1997) "Phosphate Removal from Aqueous Solution from Activated Red Mud," J. Water Pollution Control Federation, 49 (2), 280-285

18 S.H. Huang,. and B. Chiswell, (2000) "Phosphate removal from wastewater using spent alum sludge", Water Science and Technology, 42 (2-3), 295-3000

19 Sona Saxena and S.F.D. Souza, (2004)International workshop on "Marine Pollution and Ecotoxicology" National Institute of Oceanography, Goa, p 94-99 and the references in it.

20 T.Vaughan, C.W. Seo, W.E. Marshal, (2001)"Removal of selected metal ions from aqueous solution using modified corncobs, Bioresour. Technol. 78, 133-139

21 Thomas L. Eberhardt, Soo-Hong Min James, S. Han, (2006)"Phosphate removal by refined aspen wood fiber treated with carboxymethyl cellulose and ferrous chloride" Bioresource Technology, 97, 2371-2376

22 R.K.Trivedy,.(1983)1 "Water Hyacinth for pollution control , bio gas paper, pulp, animal feed and manure" Environ. Ecol. 1:139-143.

23 R.K. Trivedy, R.K. and B. V. Khommane(1985) "Absorption of nutrients, from industrial waste water by water hyacinth, Com. Physion, Ecol, 10; 123-128

24 R.K. Trivedy, " Pollution Management in Industries", Environmental Publications, Ed:2, Karad, India, 1995

25 United States patents 7285215

26 United States patents 4183808

27 United States patents 6881346

28 K. Urono . H. Tachikawa (1991) "Process Development for Removal and Recovery of Phosphorous from Wastewater by a New Adsorbent. 1: Preparation Method and Adsorption Capability of a New Adsorbent", Ind. Eng. Chem. Res., 30(8) 1893-1896

29 V.J.Inglezakis, A. Zorpas, M.D. Loizidou, H.P.Grigoropoulou, (2003) "Simultaneous removal of Metals Cu2+, Fe3+, and Cr3+ with anions SO42- and HPO42- using clinoptilolite", Microporous and Mesoporous materials , 61, 167-171

30 Arthur I. Vogel,(1961) " A Text Book of Quantitivtive Inoorganic Analysis including Elementary Instgrument Analysis", Edition-III , ELBS

31 Xin Feng Zhu et. Al (2011) "Removal of Phosphate from aqueous solutions by using Red Mud", Advanced Materials Research Vols., 291, 1804 and various references in it.

32 Yee, "Selective removal of Mixed Phosphates by Activated Alumina"(1966) J Amer. Water Works Assoc., 58, pp 239-247 (1966)

33 Yanzhong Li et. Al.,(2006) "Phosphate removal from aqueous solutions using raw and activated red mud and fly ash", J. of Hazardous Materials, 137(1), 374