Full Length Research Paper

Phosphate pollution control in waste waters using new bio-sorbents

M. Divya Jyothi, K. Rohini Kiran and K. Ravindhranath*

Department of Engineering, Chemistry and Post Graduate Chemistry, Bapatla Engineering College, (Autonomous), BAPATLA-522101, Guntur Dt., A.P., India.

Accepted 23 January, 2012

Thermally activated barks/stems and their ashes of *Ficus religiosa, Cassia auriculata, Punica granatum* and *Calotropis gigantean* are found to have remarkable affinity towards phosphate ions. The sorption characteristics of these bio-products towards phosphate from synthetically prepared waste waters have been studied with respect to various physicochemical parameters such as pH, sorption concentrations and equilibration times. Phosphate removal is found to be pH sensitive and also depends upon equilibration time and sorption concentration. Conditions have been optimized for the maximum extraction of phosphate; not less than 87% removal is noted in these sorbents. The sorption concentration so foreign anions like chlorides, sulphates, nitrates, fluorides and carbonates are marginal. Cations namely Ca²⁺, Mg²⁺, Cu²⁺, Zn²⁺, Fe²⁺ and Ni^{2+,} are synergizing the extraction of phosphate and hence % removal of phosphate is enhanced in their presence. The variations of D.O., BOD, COD, color and turbidity of the water samples after extractions with the successful sorbents developed in this work, are found to be within the permissible limits of water quality standards.

Key words: Phosphate pollution control, bio-sorbents, *Ficus religiosa, Cassia auriculata, Punica granatum* and *Calotropis gigantean.*

INDTRODUCTION

Phosphate pollution in natural waters bodies is attributed to agricultural run offs, domestic and industrial sewages (Gerard, 1998; Tchobanoglous et al., 2003). Excess concentrations of phosphate, cause eutrophication in lakes. This process leads to the depletion of dissolved oxygen levels in water, resulting in the loss aquatic life (Ames et al., 1970; Batchelor et al., 1987; Zhao and Sengupta, 1998; Kofinas and Kioussis, 2003).

Phosphate pollution is recognized as a major pollution problem throughout the world and some countries introduced phosphate control acts and in fact, the Switzerland banned the use of phosphate in detergents. Hence, increasing research interest is being envisaged in developing new methodologies in controlling phosphate pollution (Gerard, 1998; Tchobanoglous et al., 2003).

Traditionally phosphate is removed by chemical precipitation (Ames et al., 1970; Brattebo et al., 1986; Batchelor et al., 1987; Huang, 2000; Yee, 1966; Sona et al., 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 patents exist in this regard (Kioussis et al., 1999; Unnithan et al., 2002; Gerad, 1998; Baker et al., 1998; Huang and Chiswell, 2000; Tchobanoglous et al., 2003; USA Patents: 7285215, 2007; 4183808,1980 and 6881346, 2005.

The use of biomasses or bio-wastes of flora or fauna origin in controlling the pollution either in their native state or chemically modified, by evoking their surface sorption phenomenon, is another new trend in this aspect of research (Amir et al., 2005; Chubar et al., 2003; Dakiky et al., 2002; Iqbal et al., 2002; Shrihari and Raghavendra,

^{*}Corresponding author. E-mail: ravindhranath.sita@yahoo.co.in.

2003; Majeti and Kumar, 2000; Oklieimen and Onyenkpa, 1989; Orhan et al., 1993; Thomas et al., 2005; Urano et al.,1991; Srinivasan et al., 1988; Singh et al., 2000; Shrihari et al., 2003; Shukla et al., 2002; Sandhya, 2003; LuzE and Yohr, 2004; Cesar and Marco 2004; Imran, 2006). Imran (2010) discussed the increasing quest for active carbon adsorbents for controlling the toxic pollutants in wastewaters. Inglezakis et al. (2003) have explored the surface properties of clinoptlolite in removing simultaneously metal ions: Cu²⁺, Fe³⁺ and Cr³⁺ with anions: SO_4^{2-} and HPO_4^{2-} . Dinesh et al. (2006) have studied the phosphate removal by refined aspen wood fiber treated with carboxymethyl cellulose and ferrous chloride. Wood processing residues like sawdust, bark etc and some other agricultural residues like corncobs have been explored as bio-sorbents for controlling phosphate pollution (Shukla et al., 2002; Tshabalaka et al., 2004; Vaughan et al., 2001; Boujelben et. Al., 2008; Khan and Moheman. 2006: Han et al., 2003: Thomas et al., 2006). LuzE and Yoav (2004) discussed in their review article on the recent advances in removing phosphorous from waste water. Activated red mud has been used to remove phosphates from aqueous solutions (Shiao and Akashi, 1997; Yanzhong et al., 2006; Xin et al., 2011).

Bioremediation methods have been explored by various authors for the control of phosphate in polluted waters (Biswas et al., 2007; Heng et al., 2009; Akpor and Muchie, 2010; Lu and Huang, 2010; Ning et al., 2011; Zhang et al., 2011; Wilaiwan et al., 2010).

In the present work, barks or stems and their ashes of different plants for the removal of phosphates from polluted waters have been studied with respect to various physico chemical parameters and we tried to develop simple methodologies in controlling the phosphate pollution by evoking the sorption abilities of these biomaterials.

MATERIALS AND METHODS

Chemicals

All chemicals used were of analytical grade.

1) Stock solution of phosphate of 100 ppm concentration was prepared by dissolving requisite amount of A.R. grade potassium dihydrogen phosphate in a definite volume of double distilled water and it was suitably diluted as per the need.

2) Sodium molybdate solution: 12.5 g of sodium molybdate was dissolved in 500 ml of 10N. H_2SO_4 .

3) Hydrazine Sulphate solution: 1.5 g of Hydrazine Sulphate solution was dissolved in 1L of double distilled water.

Adsorbents

Diverse adsorbents of flora origin were used in this work. The stems/barks or their ashes of *F. religiosa, C. auriculata, P. granatum* and *C. gigantean* have been found sensitive to

phosphate ions (Figure 1). The methodology described hereunder pertains only to these sorbets.

F. religiosa plant is considered sacred by the followers of Hinduism, Jainism and Buddhism and it belongs to Moraceae family and is used in traditional medicine for about 50 types of disorders. *C. auriculata* is evergreen Indian shrub with vivid yellow flowers, belongs to *C. piniaceae* family and it grows in dry stony hills and is widely spread in central part of India and it possesses many medicinal properties. *C. gigantea* is a is a large shrub having traditional medicinal values, growing to 4 m tall and it belongs to Apocynaceae family and is widely grown in all types of soils. *P. granatum* is a fruit bearing deciduous shrub or small tree growing between five and eight meters tall and it belongs to Lythraceae family.

Barks or stems of *F. religiosa, C. anuriculata, P. granatum* and *C. gigantea* were cut, washed with tap water and then with distilled water. Thus obtained plant extracts were air dried and powdered to a fine mesh of size: less than 75 microns and the powders were activated thermally at 120°C for four hours in an over and were employed in this work. 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 (Gerard, 1998; Tchobanoglous et al., 2003; Trivedy, 1995). Weighted quantities of adsorbents were taken into previously washed 1 L/500 ml stopper bottles containing 500/250 ml of potassium dihydrogen 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 50 ml 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 830 nm against a reagent blank using U.V and visible spectrophotometer (Systornics make). Thus obtained optical density value was referred to standard graph (drawn between optical density 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 lons

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 10 fold excess (500 ppm) than the conc. of Phosphates (50 ppm). 500 ml of these solutions were taken in stopper bottles and then correctly weighted optimum quantities of the promising adsorbents (as decided by the Graphs A1 to 8; B1 and 2; C1 and 2) were added. Optimum pH was adjusted with dil. HCl or dil. NaOH using pH meter. The samples were shaken in



Ficus religiosa



Cassia auriculata



Calotropis gigantean

Punica Granatum

Figure 1. Plants explored for their affinity towards sorption of phosphates.

shaking machines for desired optimum periods and then small portions of the samples were taken out, filtered and analyzed for Phosphate. Percentage of extraction was calculated from the data obtained.

Effect of extractions on the other parameters

The synthetic water samples after extraction of phosphate with the successful sorbents developed in this work, at the optimum conditions of pH, time of equilibration and sorbents concentration, were filtered. Thus filtered water samples were analyzed for DO, BOD, COD, color and turbidity using standard procedures described else ware (APHA: 1998). The results are presented in the 4 to 7 columns of Table 1.

RESULTS AND DISCUSSION

The percentage removal of phosphate is studied under various parameters viz., time of equilibration, pH and

interfering ions with the promising adsorbents: thermally activated barks/stem powders or *ashes of F. religiosa, C. auriculata, P. granatum* and *C. gigantean.* The results obtained are presented in the Graphs A1 to 8; B1 and 2; C1 and 2 and Table 1.

The following observations are significant:

Effect of equilibration time: Percentage of extraction of phosphate increases with time for a fixed adsorbent at a fixed pH and after certain duration, the extractability remains constant, that is, an equilibrium state has been reached. In other words, there will not be any further adsorption after certain time of equilibration (Graphs A1 to 8).

Effect of pH: The extractions are found to be pH sensitive. As pH increases, the maximum extractability of

Table 1. Effect of interfering lons on the extractability of	phosphate.
--------------------------------------------------------------	------------

S/No	Adsorbent	Max. extraction	D.O/ BOD/ COD (ppm)	BOD÷COD Ratio	Color in Hazen Units	Turbidity	Extractability of phosphate in presence ten fold excesses (500 ppm) of interfering ions at optimum conditions phosphate concentration :50 ppm										
5/NO.		at optimum conditions					SO42-	NO3 -	Cl	F	CO ₃ ²⁻	Ca ²⁺	Mg ²⁺	Cu ²⁺	Zn ²⁺	Fe ²⁺	Ni ²⁺
1	Bark powder	87.0%	4.5,				83.2%	84.9%	84.0%	85.9%	86.2%	90.3%	91.6%	95.9%	94.0%	96.5%	97.4%
	of F. religiosa	pH:10,	20.1 and	0.70	18	5.2 NTU	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10	pH:10,
		5.0 h	28.6				3.5 h	2.5 h	1.5 h	1.5 h	2.5 h	2.0h	3.0 h	3 h	2.0 h	2.5 h	4.5 h
2	Bark powder	97.0%	5.1,				93.4%	93.5%	94.6%	95.0%	95.0%	98.5%	98.8%	99.2%	989%	99.0%	98.9%
	of C auriculata	pH:10,	18.2 and	0.73	20	6.2 NTU	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10	pH:10,	pH:10,	pH:10;	pH:10,
		5 .0 h	25.1				4.5 h	1.5 h	2.5 h	2.5 h	3.5 h	2.5 h	2.0 h	3.5 h	2.5 h	2.5 h	4.0 h
3	Bark powder	89.0%	5.6,				85.0%	85.6%	86.0%	87.5%	87.2%	90.8%	91.9%	94.8%	93.4%	97.5%	94.%
	of P granthusm	pH:10,	16.1 and	0.68	17	3.8 NTU	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10;	pH:10,
	orr . grantnashr	5 .0 h	23.6				3.0 h	2.5 h	2 h	2.5 h	2.0h	3.0 h	2.0 h	2.0 h	2.5 h	2.0 h	2.0 h
4	Ctom noudor	90.0%	3.9,				84.6%	85.7%	86.7%	87.3%	86.4%	91.2%	92.2%	93.7%	94.8%	95.6%	94.2%
	of C zvantia	pH:10,	15.4 and	0.59	23	6.1 NTU	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10	pH:10,
	or c. zyganila	5 .0 h	26.2				2.0 h	2.0 h	3.0 h	3.5 h	3.0 h	2.5 h	4 .0 h	1.5 h	3.5 h	2.0 h	2 .5 h
5	Bark ash of	93.0%	49,				89.6%	90.5%	91.0%	92.1%	92.6%	93.8%	94.2 %	95.2%	95.8%	96.4%	95.7%
	E religiosa	pH:10,	7.1 and	0.77	12	3.2 NTU	pH:10,	pH: 10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10;	pH:10,
	r. Tellylosa	5 .0 h	9.2				3.0 h	2.5 h	2.0 h	3.0 h	2.0 h	3.5 h	3.0 h	2.0 h	3.5 h	2.0 h	2.5 h
6	Bark ash of	100.0%	6.1,				95.3%	96.0%	96.5%	975%	97.5%	100.0%	100.0%	100.0%	100.0%	100%	100%
		pH:10,	5.2 and	0.86	13	2.1 NTU	pH:10,	H:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10;	pH:10,
	o. aunoulata	4.0 h	6.6				1.5 h	3.5 h	3.0 h	3.5 h	2.5 h	1.5 h	2.0 h	3.5 h	1.5 h	1.5 h	3.0h
7	Dark ask of D	93.0%	6.4,				89.7%	91.0%	92.0%	92.6%	92.7%	94.8%	95.5%	96.7%	97.2%	98.3%	98.2%
	Bark ash of P.	pH:10,	4.9 and	0.88	10	4.6 NTU	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10	pH:10,
	grannusm	5 .0 h	5.6				2.0 h	1.5 h	2.0 h	3.5 h	3.0 h	3.5 h	2.0 h	2.0 h	3.0 h	1.5 h	1.5 h
9	Stom ash of	94.0%	5.1,				91.2%	92.5%	92.3%	93.2%	93.4%	96.2%	96.8%	97.2%	98.8%	96.4%	97.5%
	C gigontoon	pH:10,	4.6 and	0.90	15	53 NTU	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10,	pH:10;	pH:10,
	o. yiyantean	5.0 h	5.1				3.5 h	2.0 h	1.5 h	2.0h	3.5 h	3.5 h	3.5 h	3.0 h	2.5 h	1.5 h	3 .5 h

phosphate at optimum equilibration times, is increasing for a fixed adsorbent concentration (Graphs A1 to 8; B1 and 2).

a) In the case of bark powders of *F. religiosa*, the extraction is found to be 21.9% at pH 2; 31.6% at pH 4; 50.7% at pH 6; 55.6% at pH 8 and 87.0% at

pH 10 after 5 h of equilibration. The brark powder of *C. auriculata* is found to extract 23.5% at pH 2; 39.8% at pH 4; 51.2% at pH 6; 58.4% at pH 8 and



Graph A1. Time Vs percentage of removal of phosphate.



Graph A2. Time vs. percentage of removal of phosphate.

97.0% at pH 10 after 5 h. The stem powders of *C. gigantean* is found to extract 24.9% at pH 2; 36.2% at pH 4; 46.8% at pH 6; 57.5% at pH 8 and 90.0% at pH 10

after 5h. Bark powder of *P. granatum* is found to extract 23.7% at pH 2; 32.3% at pH 4; 44.9% at pH 6; 60.9% at pH 8 and 89.0% at pH 10 after 5 h.



Bark powder of *P. granatum* Phosphate concentration 50 ppm Sorbent concentration 2 g/L

Graph A3. Time vs. percentage of removal of phosphate.



Graph A4. Time vs. percentage of removal of phosphate.

b) With ash of barks of *F. religiosa*, percentage of phosphate extractability is found to be 23.4% at pH 2; 33.7% at pH 4; 51.9% at pH 6; 58.7% at pH 8 and 93.0% at pH 10 after 5 h of equilibration time. Ash of barks of *C. auriculata* is found to extract 26.7% at pH: 2; 41.9% at pH 4; 54.3% at pH 6; 59.8% at pH 8 and 100.0% at pH 10

after 4 h. Ash of barks of Punica granatum is found to extract 25.5% at pH 2; 34.4% at pH 4; 46.7% at pH 6; 62.4% at pH 8 and 93.0% at pH 10 after 5 h. Calotropis gigantean ash is found to extract 26.3% at pH 2; 38.3% at pH 4; 48.9% at pH 6; 58.7% at pH 8 and 94.0% at pH: 10 after 5 h of equilibration.



Graph A5. Time vs. percentage of removal of phosphate.



Graph A6. Time vs. percentage of removal of phosphate.



Bark ash of P. granatum Phosphate concentration 50 ppm

Graph A7. Time vs. percentage of removal of phosphate.

Stem ash of C. gigantean Phosphate concentration 50 ppm Sorbent concentration 2 g/L 100 -Ж 90 Percentage removal of phosphate 80 - pH=2 70 pH=4 60 – pH=6 50 – pH=8 - pH=10 40 30 20 10 0 0 5 10 15 Time (h)

Graph A8. Time vs. percentage of removal of phosphate.



Graph B1. pH vs. percentage removal of phosphate.

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 (Graphs C1 and 2). The optimum dosage is found to be 1.0 g/L for barks/stems powders of *F. religiosa*; 1.5 gm/L for *C. gigantean*; 2.0 g/L for *P. granatum* and C. *auriculata* (Graph C1).

With bark/stem ashes, the optimum sorbent dosage needed for maximum removal of phosphate, is found to be markedly less than with powders of barks or stems. The optimum sorbent concentration is found to be 0.75 g/L in the case of ashes of *F. religiosa*; 1.0 g/L for the ashes of *C. auriculata*; 1.25 g/L for the ashes of *C. gigantean*; and 1.5 g/L for ashes of *P. granatum* (Graph C2)

Effect of interfering ions

The extractability of phosphate ions in presence of ten fold excess (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 sorbents at optimum conditions of maximum extraction. The results are presented in the Table 1.

The following observations are significant:

1) Chlorides, sulphates, nitrates, fluorides and carbonates have marginal effect on the percentage of extraction of phosphates.

2) Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} , Fe^{2+} and Ni^{2+} have markedly enhanced the percentage of extraction of phosphates. As for example: the percentage of extraction is 87.0% at pH:10 after 5 h of equilibration time with bark powder of *F. religiosa* while in the presence of Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} , Fe^{2+} and Ni^{2+} ions, the percentage of extraction phosphate is enhanced to 90.3, 91.6, 95.9, 94.0, 96.5 and 97.4% respectively (Table 1: item 1). The same trend was observed in the case of remaining adsorbents; further, it is interesting to note that the extraction time is



Graph B2. Ph vs. percentage removal of phosphate.



Graph C1. Sorbent dosage vs. percentage removal of phosphate.



Graph C2. Sorbent dosage vs. percentage removal of phosphate.

also decreasing considerably (Table 1).

Effect of extractions on the other physicochemical parameters of waters

The variations of DO; BOD, COD and their ratio; color; and turbidity at the optimum conditions of extraction with the successful sorbents, have been studied and the obtained results are presented in the 4 to 7 columns of Table 1. The observations are:

1) With the activated stem/bark powders of *F. religiosa*, *C. auriculata*, *P. granatum* and *C.gigantean*, D.O is found to be respectively 4.5, 5.1, 5.6 and 3.9 and with their ashes, 4.9, 6.1, 6.4 and 5.1 ppm, at the optimum conditions of extraction (4th column of Table 1).

2) BOD/COD ratios are found to be less for sorbents derived from bark powders than for their respective ashes. As for example, the BOD/COD value with bark powders of *P. granatum* is found to be 0.68 ppm while with their ashes 0.88 ppm (5th column of Table 1).

3) BOD and COD values are within the permissible limits of water quality standards.

4) The turbidity values are found to be within permissible limits of 10 NTU. The maximum turbidity is found to be 6.2 NTU in all the sorbents of study. The low values of turbidity are due to the fact that the solutions after the optimum period of equilibration are filtered.

5) The color of the treated sample of water is relatively more with bark powder based sorbents than with their respective ashes as sorbents. The maximum color is found to be 23 units in the case of bark powders of *C. gigantean* and 10 units in the case of ashes of *P. granatum* (vide column number 6 in Table 1). However all these values are within the permissible limits of 25 units. Even these trace colors can be removed by just treating water with chlorine solution or chloramines.

DISCUSSION

The available data is inadequate to propose sound theoretical explanations for each observation made as it needs surface studies of "adsorbent and adsorbate interactions" using more sophisticated instruments and methodologies and it is beyond the aims of this work.

 H_3PO_4 is a tribasic acid having pK1 = 2.15; pK2 = 7.20;

pK3 = H₃PO₄ is a tribasic acid having pK1 = 2.15; pK2 = 7.20; pK3 = 12.3 yielding three series of salts, NaH₂PO₄, Na₂HPO₄ and Na₃PO₄. The acid vs. base titration curve shows three steps with inflexions at pH: 4.5; 9.5; 12.35; the first inflexion, correspond to the formation of NaH₂PO₄ and second corresponding to Na₂HPO₄. The optimum pH found in our experiments is: 10 and at this pH, the phosphate exists as HPO₄².

The barks or stems of the bio-sorbents may be having some natural compounds which have affinity towards phosphate at high pH values that is when the phosphate exists as HPO_4^2 form. Further, these natural materials may have of metal ions like Ca, Mg, Cu, Zn, Fe, Al and these di/trivalent metal ions form sparingly soluble salts with of HPO_4^2 which are gelatinous in nature and are being trapped in the matrixes of the bio-adsorbents and thus resulting in the increase of percentage removal of phosphate. This is more so in the case of ashes as adsorbents, 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 confirming as per the expected nature of extraction. Percentage of extractability is less affected in the presence anions chosen for study viz., chlorides, sulphates, nitrates, fluorides and carbonates while with the divalent cations, the percentage extraction of phosphate is increased. This kind of synergic effect may be due to the formation of sparingly soluble gelatinous precipitates of metal phosphates which are trapped or occulted in the matrix of the sorbents.

CONCLUSIONS

1) The sorption abilities of thermally activated bark powders of *F. religiosa*, *C. auriculata*, *P. granatum* and stem powders of *C. gigantean* and their ashes, have been studied with respect to pH, sorption dosage and equilibrium time.

2) It is found that phosphates have remarkable affinity towards these sorbents.

3) The extractability is pH sensitive and the maximum extraction is found at pH: 10 in all the sorbents; further, it depends on time of equilibration and sorption concentration.

4) The minimum dosage needed for the maximum removal of phosphate is found considerably less for bark/stem ashes than for bark/stem powders

5) We claim that the removal of phosphate with bark powders of *F.religiosa*, *C. auriculata*, *P. granatum* and stem powders of *C. gigantean* is 87.0, 97, 89 and 90.0% respectively at pH 10, 5 h of equilibration and with optimum dosages of sorbents.

6) With the ashes of barks/stems, percentage of removal of phosphate is enhanced: 93% for *F. religiosa*, 100% for *C. auriculata*, 93% for *P. granatum* and 94% for *C. gigantean*, at pH 10 after an equilibration period of 5 h with optimum sorbent dosages.

7) Inteference: Tenfold excess of anions like chlorides, sulphates, nitrates, fluorides and carbonates have less affected the percentage of extraction of phosphate at the optimum conditions cited in Table 1. while ten fold excesses of cations viz., $Ca^{2+},Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}$ and Ni^{2+} ions are synergizing the extraction of phosphate and thereby percentage removal of phosphate is increased. Further, it is noted that the time of equilibration needed for maximum extraction of phosphate is less in presence of ten fold excess of cations than without the said cations.

8) D.O., BOD, COD, color and turbidity of the water samples after extraction, with the successful sorbents of this work at optimum conditions of pH, equilibration time and sorbent concentration, are found to be within the permissible limits of water quality standards.

REFERENCES

- Akpor OB, Muchie M (2010). "Bioremediation of polluted wastewater influent: Phosphorus and nitrogen removal". Sci. Res. Essays. 5(21): 3222-3230.
- Ames LL, Robert B (1970). "Phosphorous Removal from Effluents in Alumina Columns" J. Water Pollut. Control Federation. 42(5): R161-R172.
- Amir HM, Dariush N, Forugh V, Shahrokh N (2005). "Tea waste as an adsorbent for heavy metal removal from industrial waste waters". Am. J. Appl. Sci., 2(1): 372-375.
- APHA (1998). Standard methods for the examination of water and waste water. American Public Health Association, Washington D.C., 20th Edition.
- Baker MJ, Blowes DW, Ptacek CJ (1998). "Laboratory development of permeable reactive mixtures for the removal of phosphorus from onsite waste water disposal systems" Environ. Sci. Technol., 32: 2308-2316.
- Batchelor B, Dennis R (1987). "A Surface Complex Model for Adsorption of Trace Components from Wastewater" J. Water Pollut. Control Federation. 59(12): 1059-1068.
- Biswas BK, Inoue K, Ghimire KN, Ohta S, Harada H, Ohto K, Kawakita H (2007). "The adsorption of phosphate from an aquatic environment using metal-loaded orange waste" J. Colloid Interface Sci., 312: 214-223.
- Boujelben N, Bouzid J, Elouear Z, Feki M, Jamoussi F, Montiel A (2008). "Phosphorus removal from aqueous solutions using iron coated natural and engineering sorbents" J. Hazard. Mater., 151(1): 103-110.
- Brattebo H, Odegaard H (1986). "Phosphorus Removal by Granular Activated Alumina" Water Res., 20(8): 977-986.
- Cesar RTT, Marco AZA (2004). "Biosorption of heavy metals using rice milling by-products: Characterization and application for removal of metals from aqueous solutions" Chemosphere. 54(7): 987-995.
- Chubar N, Carvalho JR, Neiva CMJ (2003). "Cork Biomass as Biosorbent for Cu(II), Zn(II) and Ni(II)", Colloids and Surfaces A:Physicochemical and engineering aspects. 230(1-3): 57-65. cost adsorbents fro remediation of tri and hexavalent chromium from water" J. Hazard. Mater., 137(2): 762-781.

Dakiky M, Khamis M, Manassra A, Mereb M (2002). "Selective adsorption of Chromium (VI) in Industrial Waste Water using Lowcost Abundantly Available Adsorbents", Advances in Environmental Research. 6(4): 533-540.

Dinesh M, Charles U, Pittman J (2006). "Activated carbons and low

- Gerard K (1998). Environmental Engineering, McGraw-hall International Editions.
- Han JS, Hur N, Choi B, Min SH (2003). "Removal of phosphorous using chemically modified lignocelluloses materials" In: 6th Inter-regional Conference on Environmnent-Water. Land and Water use Planning and Management, Albacete, Spain. 1-1.
- Heng L, Jingyu R, Wen Y, Xiaohai L, Jiaqiang W, Wudi Z (2009). "Removal of phosphate from polluted water by lanthanum doped vesuvianite" J. Hazard. Mater., 168(1): 326-330.
- Huang SH, Chiswell B (2000). "Phosphate removal from wastewater using spent alum sludge" Water Sci. Technol., 42 (2-3): 295-300.
- Imran A (2010). "The Quest for Active Carbon Adsorbent Substitutes: Inexpensive Adsorbents for Toxic Metal Ions Removal from Wastewater" Sepn. Purfn. Rev., 39: 95-171.
- Imran A. Gupta VK (2006). Advances in Water Treatment by Adsorption Technology", Nature London. 1: 2661-2667.
- Inglezakis VJ, Zorpas A, Loizidou MD, Grigoropoulou HP (2003)."Simultaneous removal of Metals Cu^{2+} , Fe^{3+} , and Cr^{3+} with anions SO_4^{2-} and HPO_4^{2-} using clinoptilolite, Microprous and Mesoporous materials. 61: 167-171.
- Iqbal M, Saeed A, Akhtar N (2002). "Petiolar felt-sheath of palm: a new biosorbent for the removal of heavy metals from contaminated water", Bio Res. Technol., 81(2): 153-155.
- John N (1983). "Use of water hyacinth in the treatment of effluents from rubber and oil palm industries" Int. Conf. Water Hyacinth., 7-11.
- Khan SV, Moheman A (2006). Poll. Res. 25(1): 99.
- Kioussis DR, Wheatonk FW Ofinas P (1999). "Phosphate binding polymeric hydro gels for aquaculture wastewater remediation", Aquacultural Eng., 19:163-178.
- Kofinas P, Kioussis DR (2003). "Reactive Phosphorous removal from aquaculture and poultry production systems using polymeric hydro gels" Environ. Sci. Technol., 37(2): 423.
- Lu XM, Huang MS (2010). "Nitrogen and phosphorus removal and physiological response in aquatic plants under aeration conditions" Int. J. Environ. Sci. Technol., 7(4): 665-674.
- Luze De-Bastan, Yoav B (2004). "Recent advances in removing phsophorous from waste water and its future use as fertilizer" Water Res., 38: 4222-4246.
- Majeti NV, Kumar R (2000). "A review of chitin and chitosan applications" React. Funct. Polym. 46: 1-27.
- Ning P, Bart HJ, Li B, Lu X, Zhang Y (2011). "Phosphate removal from wastewater by model La (III) zeolite adsorbents" J. Environ. Sci., 20(6): 670-674.
- Oklieimen FE, Onyenkpa VU (1989). Bio Wastes. 29:11.
- Orhan Y, Buyukgungor H (1993). "Removal of heavy metals by using Agricultural wastes" Water Sci. Technol., 28: 247-255.
- Sandhya B, Tonni AK (2003). "Low Cost adsorbents fro heavy metals uptake from contaminated water: a review. J. hazard. Mater., 97: 219-243.
- Shiao SJ, Akashi K (1997). "Phosphate Removal from Aqueous Solution from Activated Red Mud" J. Water Pollut. Control Federation. 49 (2): 280-285.
- Shrihari S, Raghavendra SK (2003). Pol. Res., 22(4): 507.
- Shukla A, Zhang YH, Dubdey P, Margrave JL, Sukla SS (2002). "The role of sawdust in the removal of unwanted materials from water. J. Hazard. Mater., 95: 137-152.
- Singh DK, Srivastava B (2000). Ind. J. Pollut. Control. 16(1): 19-24.
- Sona S, Souza SFD (2004). International workshop on "Marine Pollution and Ecotoxicology" National Institute of Oceanography, Goa. 94-99.
- Srinivasan K, Balasubramanian N, Ramakrishnan TV (1988). "Studies on Chromium removal by rice husk carbon" Ind. J. Environ. Health. 30: 376.
- Tchobanoglous G, Burton FL, Stensel HD (2003). Wastewater Engineering: Treatment and Reuse, 4th Edition, Metcalf and Eddy, New York.

- Thomas LE, Soo-Hong MJ, Han S (2006). "Phosphate removal by refined aspen wood fiber treated with carboxymethyl cellulose and ferrous chloride" Bio Res. Technol., 97: 2371-2376.
- Trivedy RK (1995). "Pollution Management in Industries", Environmental Publications, Ed: 2, Karad, India.
- Tshabalaka MA, Karthikeyan KG, Wang D (2004). "Cationized milled pine bark as an absorbent for oththophate anions" J. Appl. Polym. Sci. 93: 1577-1583.
- United States patent 7285215 (2007); 4183808 (1980); 6881346 (2005).
- Unnithan MR, Vinod VP, Anirudhan TS (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.
- Urano K, Tachikawa H (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.
- Vaughan T, Seo CW, Marshal WE (2001). "Removal of selected metal ions from awqueous solution using modified corncobs" Bio Res. Technol., 78: 133-139.
- Vogel AI (1961). "A Text Book of Quantitative Inorganic Analysis including Elementary Instrument Analysis", Edition-III, ELBS.
- Wilaiwan C, Rober JW, Kanda P, Thanapon S, Rafal MG, Glen EF, Wassana Y (2010). "Phosphate removal by anion binding on functionized Nanoproous sorbents" Environ. Sci. Technol., 44(8): 3073-3078.
- Xin FZ, Hong YL, Peng HS, Jun FW, Yi FG (2011). "Removal of Phosphate from aqueous solutions by using Red Mud", Advanced Materials Research Vols., 291: 1804.
- Yanzhong L, Liu C, Luan Z, Peng X, Zhu C, Chen Z, Zhang Z, Fan J,Jia Z (2006). "Phosphate removal from aqueous solutions using raw and activated red mud and fly ash" J. Hazard. Mater., 137(1): 374.
- Yee (1966). "Selective removal of Mixed Phosphates by Activated Alumina" J. Am. Water Works Assoc., 58: 239-247.
- Zhang L, Wan L, Chang N, Liu J, Duan C, Zhou Q, Li X, Wang X (2011). "Removal of phosphate from water by activated carbon fiber loaded with lanthanum oxide" J. Hazard. Mater., 190(1-3): 849-855.
- Zhao D, Sengupta AK (1998). "Ultimate removal of phosphate from waste water from using a new class of polymeric ion exchanges" Water Res. 32(5): 1613-1625.