IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

PHYSICOCHEMICAL, HEAVY METAL ANALYSIS AT THUVAKUDI VILLAGE POND WATER, TRCHY AND EFFECTIVE REMOVAL OF Fe (III) ION BY NEWLY CONSTRUCTED CGS-POP COMPOSITE

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ABSTRACT

The present research study on various physicochemical parameters and trace metals in the vicinity of Thuvakudi Village Pond and nearby ground water in Trichy, Tamil Nadu, is a main source of water for irrigation system, other bore wells, industrial use and underground water intake for drinking purpose in near vicinity of the pond by residents envisage an alarming condition of water quality. In this research study the suitability of underground water for drinking and the contamination levels in the pond by human and industrial activities has been investigated in two seasonal variations during pre-monsoon and post monsoon period. The results are compared with various national and international water quality standards and justifying the same with some remedial measures by creating awareness among the living community. An attempt was made to remove heavy metal such as Fe (III) ion by using (CGS-POP) composite made up of Crumb rubber, Graphite and Saw dust mounted on Plaster of Paris. The mechanism is simple adsorption and ion exchange between the trace metal and the adsorbent layer.

KEY WORDS: Irrigation, Bore well, CGS-POP composite, Plaster of Paris, Ion exchange., etc

I.INTRODUCTION

Lakes and ponds (also known as lentic systems) are a diverse set of inland freshwater habitats that exist across the globe and provide essential resources and habitats for both terrestrial and aquatic organisms. Although widely distributed and vital for many species, including humans, these habitats account for just over 3% of the Earth's surface (Downing *et al*. 2006)[3].A pond is a body of standing water either natural or artificial, that is usually smaller than a lake [2]. The study area pond is natural one and is an isolated depression like vernal pools and prairie potholes and they contain shallow water with marsh and aquatic plants and animals. The biodiversity of freshwater habitats is increasingly threatened by human activities. Habitat loss, eutrophication, acidification, chemical contamination, global warming, and exotic species are just some of the factors that have directly or indirectly impacted lentic systems (Brönmark & Hansson 2002) [4]. Ponds are increasingly recognized for their high contribution to regional biodiversity and the provisioning of vital ecosystem services [5]. However, increased human impact, such as nutrient loading, overstocking with fish and reduced water level fluctuation, have resulted in a worldwide deterioration of pond habitats and the local and regional loss of species. Restoration and conservation measures are therefore increasingly applied in efforts to restore pond habitats [6]. Threat posed by the heavy metals has been increasing globally rendering many water bodies unfit for human consumption. This could be due to the increase in concentrations of these metals above natural background. Risk assessment revealed that high chronic daily intake and metal index were beyond acceptable limit indicating high risk and exposure to toxic metals.[7]

II.GEOGRAPHICAL INFORMATION

The topology of Thuvakudi is almost flat with a few isolated hillocks rising above the surface. The city spread over an area of 14.371 square kilometres (5.549 Sq. Miles) is situated between Tiruchirappalli and Tanjore Districts. In 2011, the town had a population of 38,887. The town is a part of the fertile Cauvery delta region, but manufacturing industries and stone quarrying are the major occupations.[7][18]

III.STUDY AREA

Thuvakudi is located at 10.756389°N, 78.801111°E. The average elevation is 88 metres (289 ft).Thuvakudi Municipality village pond is situated in Tiruchirappalli district in the Indian state of Tamil Nadu. It is an industrial town housing more than 250 industries and is located in the National Highway NH 65 between Tiruchirappalli and Thanjavur. The town has a dry weather, making it suitable for dry crops like cotton, chillies, and millets.[18]

IV. MATERIALS AND METHOD

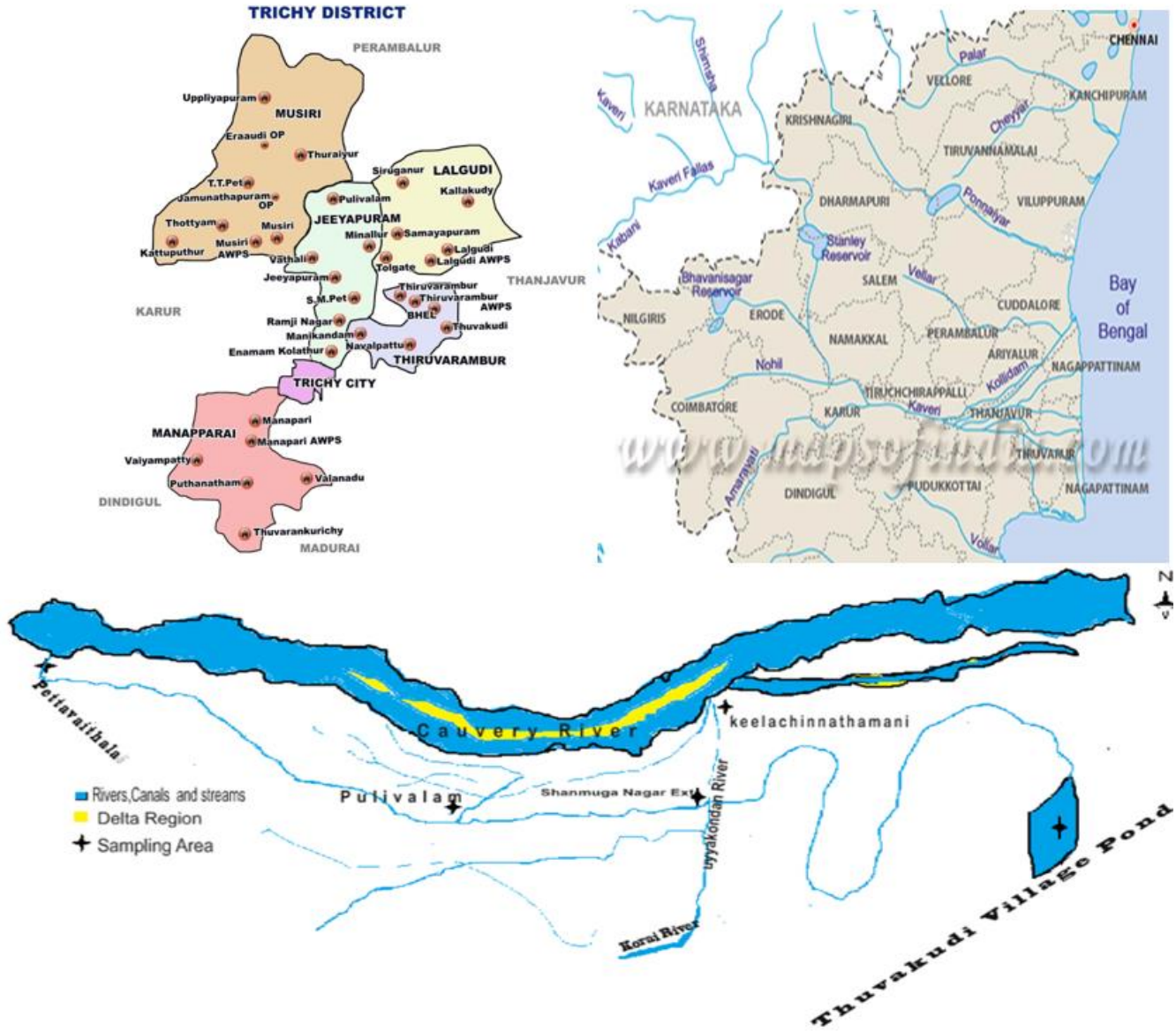

Fig 1: Map Showing The Study Area And River Canals

4.1 Sample collection

The study area covers the following sampling site namely Barakath Nagar, Eechankadu, RECT Nagar, Kungumapuram and Thuvakudi village pond. The ground water samples from bore well are collected at each sampling point except pond water. The samples outsourced to testing lab to evaluate the physicochemical and heavy metals analysis. Analysis was carried out for various water quality parameters such as Temperature, pH, electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO), total hardness (TH), calcium (Ca) magnesium (Mg), sodium (Na), potassium (K), nitrate (NO_3), sulphate (SO_4) and phosphate (PO_4) using standard method. All The reagents used for the analysis were AR grade and double distilled water was used for preparation of solutions. The heavy metal analysis such as Fe, Co, Cd, Ni, Cr, Cu, Zn were carried out in AAS spectroscopic method by using ICE AAS-3300 model from Thermo Fischer make instrument.

4.2 Construction of (CGS-POP) Composite

The Plaster of Paris obtained from commercial shop was activated around 100 ◦C in a hot air oven for 5 hrs it was taken out, ground well to fine powder and stored in a vacuum desiccator. Commercially available fine grade graphite is activated in hot air oven at 50◦ C for 2 hours period. A finely crushed crumb rubber from tyre was treated with dilute HCl acid leaching and alkaline by Sodium carbonate leaching to remove dust and unwanted materials. Finally, the crumb rubber is washed with distilled water and filtered. The raw crumb rubber is dried in an oven around 40◦C to 50◦C and preserved in a dedicator for 4 hours. The commercially available saw dust is washed with distilled water and dried in a hot air oven at 30◦C for 1-hour period.

4.2.1 Mixing Proportion and preparation of Stock Solution

A 50 g of activated Plaster of Paris dry powder is mixed with 10g of graphite, 10 g of crumb rubber and 10 g of saw dust. It is taken in a 500 ml glass beaker in the ration of 5:1:1:1 .A stock solution of the adsorbate containing 1000 mg/L (1000PPM) of Fe (III) was prepared by dissolving the calculated quantity of Ammonium Iron (III) Sulphate Dehydrate in de-ionized water.

4.2.2 Experimental Method

A 50 ml (50ppm) of the stock solution containing Fe (III) ions is poured in the beaker containing CGS-PP mixer and make up to 200 ml deionised water. The set up was mounted in a hot plate and the temperature is set for 50◦C. The setup is stirred manually or mechanically. 10 ml HCl acid is poured in the sample to maintain the pH at 5. The setup can stand for 3 hours period. The sample is filtered off by watt man filter paper (40NO-pour size) and sent for AAS study for efficiency of recovery by the (CGS-POP) composite layer. The initial and final concentration is noted. In the same way another sample at pH 9 was estimated by adding 25% of 10 ml of aqueous ammonia solution. The initial and final concentration of Fe (III) ions is estimated by AAS studies. The sample water is tested with different contact time interval such as 3 hours, 6 hours and 9 hours periods in both the pH condition and at same temperature 50◦C

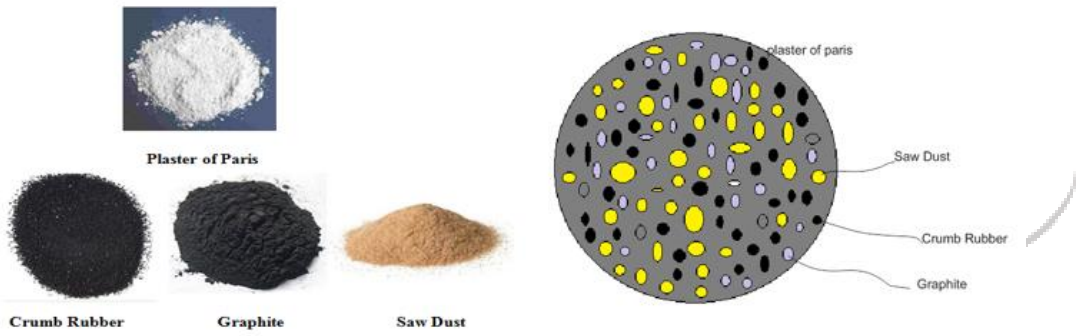

Fig:2. Showing pre-treatment process and final CGS-POP composite mixing proportions

V.RESULT:

Table: 1 Correlation matrixes for different heavy metal elements present in Thuvakudi village pond compared with other sampling sites

	Cd	Cu	Fe	Pb	Zn
Cd	1				
Cu	0.95753	1			
Fe	-0.1333	-0.2597	1		
Pb	0.95306	0.94784	0.05153	1	
Zn	0.8292	0.81135	0.22216	0.9152	1

S. No	Sampling stations	Season	Trace metal parameters (mg/l or ppm = water)						
			Cd	Cr	Cu	Fe	Ni	Pb	Zn
1.	Thuvakudi Village Pond water	Pre-Monsoon	0.16	BDL	0.22	2.16	BDL	0.12	0.67
		Post Monsoon	0.18	BDL	0.26	2.10	BDL	0.14	0.66
2.	Kungumapuram	Pre-Monsoon	0.12	BDL	0.18	1.94	BDL	0.10	0.42
		Post Monsoon	0.13	BDL	0.19	2.02	BDL	0.11	0.58
3.	RECT Nagar	Pre-Monsoon	0.10	BDL	0.12	3.44	BDL	0.10	0.59
		Post Monsoon	0.11	BDL	0.14	3.68	BDL	0.11	0.61
4.	Barakath Nagar	Pre-Monsoon	0.08	BDL	0.08	2.98	BDL	0.08	0.44
		Post Monsoon	0.12	BDL	0.10	3.12	BDL	0.09	0.46
5.	Eechangadu	Pre-Monsoon	0.05	BDL	0.04	1.99	BDL	0.05	0.33
		Post Monsoon	0.06	BDL	0.05	2.20	BDL	0.06	0.36

BDL – Below detectable limit; Cd – Cadmium; Cr – Chromium; Cu – Copper; Fe – Iron; Ni – Nickel; Pb – Lead; Zn - Zinc

Table:3 Heavy metal concentrations in different sampling points compared with pond water of Thuvakudi, Trichy district, Tamil Nadu – 2016.

S. No	Heavy Metal	ppm Level	WHO Health Limit
1.	Cadmium	(0.05-0.18)	0.003
2.	Copper	(0.04 -0.26)	2
3.	Iron	(1.94-3.68)	No Guidelines
4.	Lead	(0.05-0.14)	0.01
5.	Zinc	(0.33-0.67)	3
6.	Nickel	BDL	0.02
7.	Chromium	BDL	0.05

Table: 4 Comparison of Heavy Metal with WHO Guidelines [8] [18]

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Table: 5 The below table shows the recovery of Iron (III) at various conditions on CGS-POP Composite.

		Contact Time		
Sample 1 at pH 5 and 50°C	Concentration (Mg/L)	Initial	**3 Hrs**	**6 Hrs**	**9 Hrs**
		50	50	50
		Final	23.5	29..3	37.5
Sample 2 at pH 9 and 50°C		Initial	50	50	50
		Final	19.5	20.3	22.6

	pH	TDS	EC	DO	BOD	TA	TH	Ca	Mg	Na	K	HCO3	CO3	Cl	SO4	NO2	PO4
pH	1																
TDS	0.76527	1															
EC	0.73716	0.966151	1														
DO	-.41225	-0.00929	0.10591	1													
BOD	0.82285	0.789469	0.846892	-0.0325	1												
TA	0.70285	0.951546	0.964386	0.06682	0.87523	1											
TH	0.41156	0.846272	0.899071	0.42359	0.71521	0.90741	1										
Ca	0.25081	0.525432	0.698008	0.66039	0.59105	0.63907	0.78932	1									
Mg	0.56847	0.736611	0.874277	0.33028	0.77558	0.79421	0.81833	0.8663	1								
Na	0.69873	0.711831	0.815663	-0.1145	0.88046	0.8353	0.67193	0.6262	0.81195	1							
K	0.69138	0.841628	0.867606	0.01217	0.87876	0.9401	0.81422	0.6268	0.71905	0.8717	1						
HCO3	0.88868	0.876898	0.907265	-0.143	0.91171	0.88804	0.69557	0.5637	0.80233	0.8994	0.894	1					
CO3	0.61172	0.787825	0.906389	0.20471	0.81157	0.85372	0.81685	0.837	0.92301	0.9007	0.8309	0.8787	1				
Cl	0.77499	0.931438	0.901878	-0.2516	0.74128	0.88145	0.70782	0.3729	0.64337	0.7398	0.7494	0.8303	0.7416	1			
SO4	0.8681	0.862787	0.870366	-0.2816	0.89419	0.88877	0.64293	0.4283	0.67981	0.8764	0.8398	0.9135	0.7903	0.9243	1		
NO2	0.52797	0.792375	0.88449	0.25893	0.82615	0.90132	0.87786	0.8137	0.81602	0.8635	0.8929	0.8156	0.9441	0.7354	0.7938	1	
PO4	0.79625	0.907	0.949685	-0.1043	0.86139	0.92131	0.76414	0.5988	0.83617	0.916	0.8603	0.9553	0.9235	0.917	0.94	0.8712	1

Table: 2.

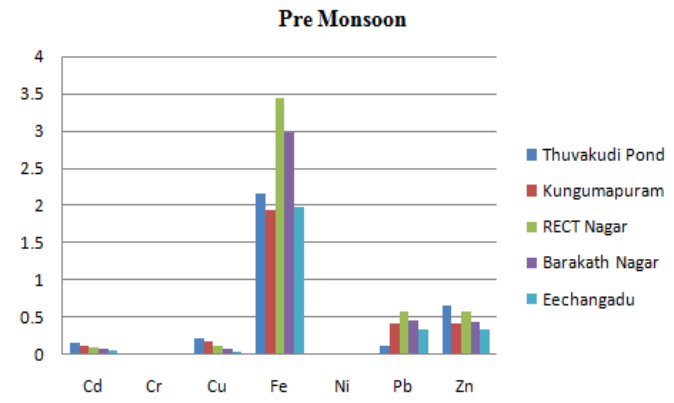
Physicochemical parameters in five different sampling points compared with pond water of Thuvakudi , Trichy district, Tamil Nadu –2016

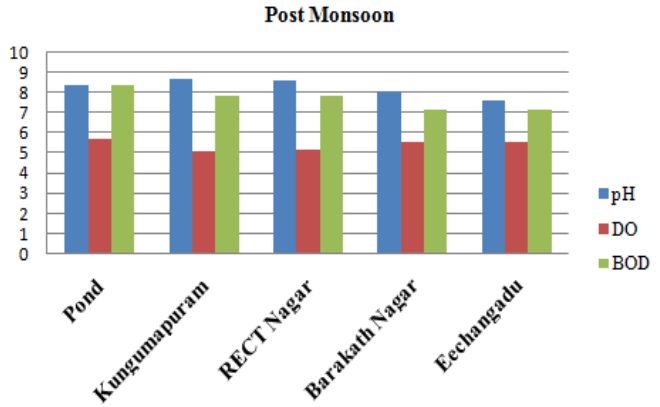
S.No	Sampling stations	Season	pH	TDS mg/l	EC µS/cm	DO mg/l	BOD mg/l	TA mg/l	TH mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l	Na^{+} mg/l	K^{+} mg/l	HCO_3^- mg/l	CO_3^- mg/l	Cl^- mg/l	SO_4^{2-} mg/l	$N\text{-}NO_2^-$ mg/l	$O\text{-}PO_4$ mg/l
1.	Thuvakudi Village Pond water	Pre Monsoon	8.38	726.0	1240.63	5.4	8.2	95.4	181.6	81.4	86.5	78.4	54.6	84.3	12.0	216.4	74.2	13.4	16.2
		Post Monsoon	8.40	735.0	1300.86	5.7	8.4	97.8	188.8	92.6	86.0	80.1	60.6	86.8	14.0	220.6	79.8	19.8	16.8
2.	Kungumapuram	Pre Monsoon	8.51	716.0	1100.78	4.9	7.6	86.6	159.6	63.9	60.7	58.8	47.5	77.8	9.0	220.8	70.4	8.8	13.6
		Post Monsoon	8.72	722.0	1199.62	5.1	7.9	89.9	168.4	76.6	76.6	66.4	49.8	80.2	10.3	224.6	75.6	9.6	14.4
3.	RECT Nagar	Pre Monsoon	8.55	650.0	1010.48	4.9	8.1	79.8	149.8	71.2	69.8	72.6	46.8	78.8	9.9	188.8	65.8	8.8	12.8
		Post Monsoon	8.62	677.0	1062.63	5.2	7.9	83.4	151.6	76.4	72.6	68.8	48.8	81.2	10.4	190.6	70.2	9.8	13.6
4.	Barakath Nagar	Pre Monsoon	7.88	640.0	978.96	5.3	6.9	72.8	148.8	73.8	69.6	56.6	32.6	66.5	9.6	188.5	46.4	6.8	11.6
		Post Monsoon	8.12	658.0	998.20	5.6	7.2	74.8	156.6	76.2	70.6	48.2	38.8	70.8	8.8	164.4	30.6	5.2	9.8
5.	Eechangadu	Pre Monsoon	7.58	614.0	850.60	5.2	6.6	71.8	146.4	68.8	56.6	52.6	40.6	62.2	7.5	158.4	28.8	4.8	8.4
		Post Monsoon	7.66	624.0	886.30	5.6	7.2	74.4	154.2	71.6	59.4	45.9	36.6	58.8	6.9	160.8	35.6	5.6	7.6

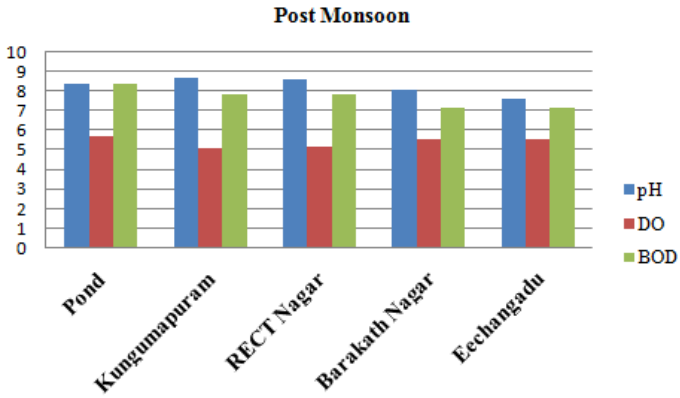
TDS – Total dissolved solids; EC – Electrical conductivity; Sali – Salinity; DO – Dissolved oxygen; BOD – Biological dissolved oxygen; TA – Total alkalinity; TH – Total hardness; Ca – Calcium; Mg – Magnesium; Na – Sodium; K – Potassium; HCO_3 – Bicarbonate; CO_3 – Carbonate; Cl – Chloride; SO_4 – Sulphate; N-NO2 – Nitrite; O-PO_4 – Ortho-phosphate.

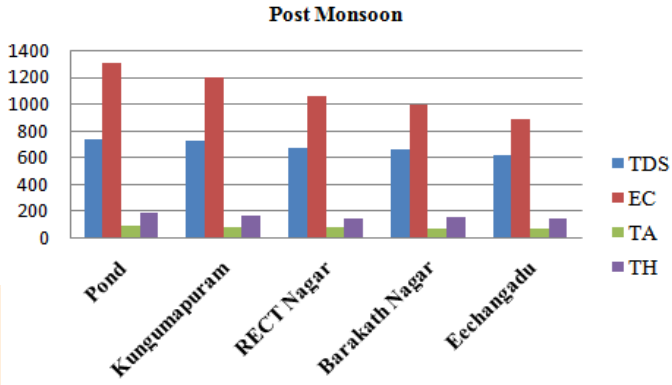
Table:6 Correlation matrix for different physiochemical quality parameters of Thuvakudi village pond compared with other sampling sites.

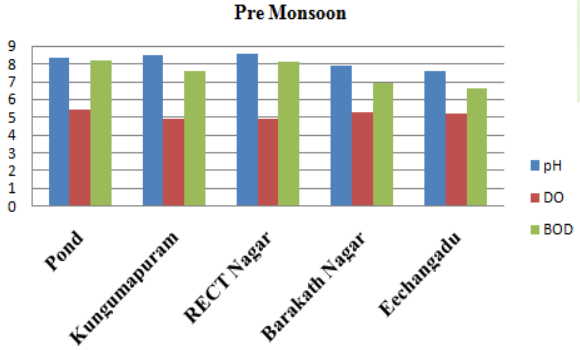
Fig:3 Graphical Representation of Physicochemical Data and Heavy Metals At Pre And Post Monsoon

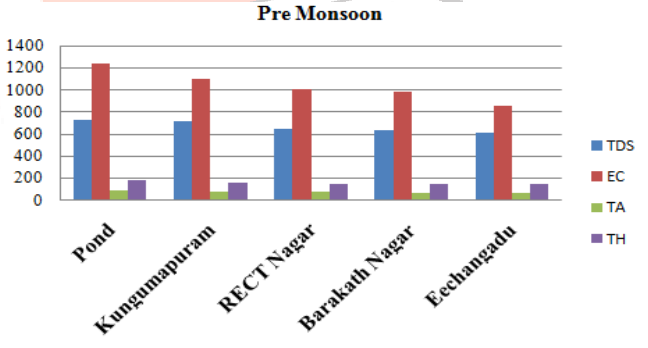


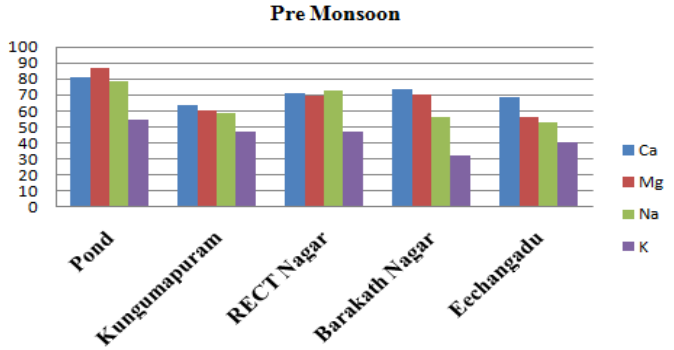


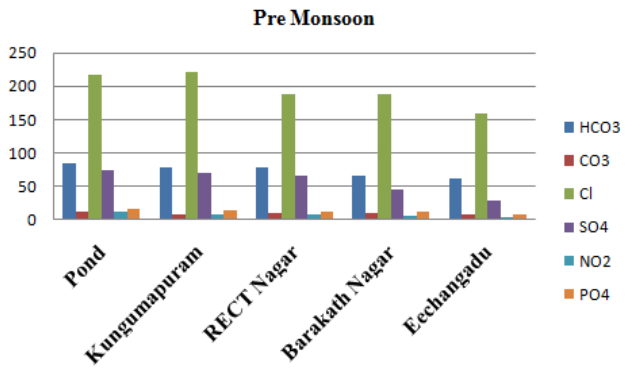


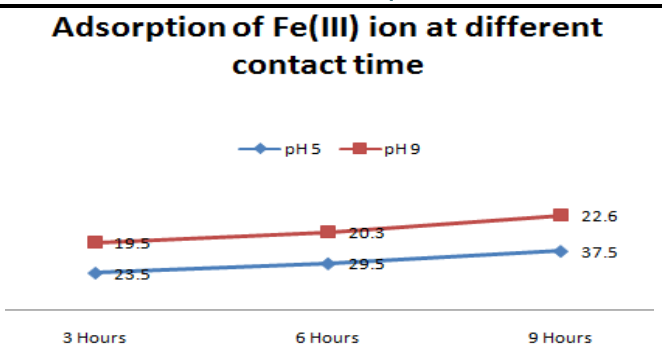




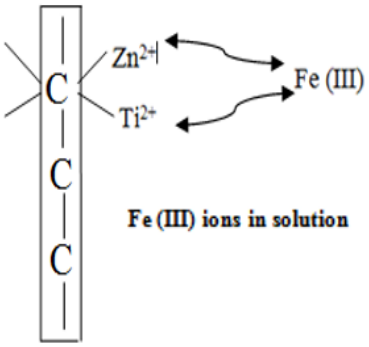






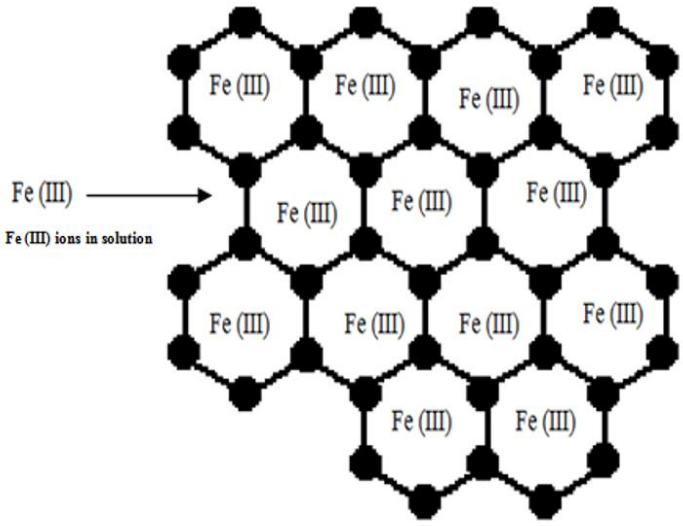


Crumb Rubber as Sorbent Material-Mechanism



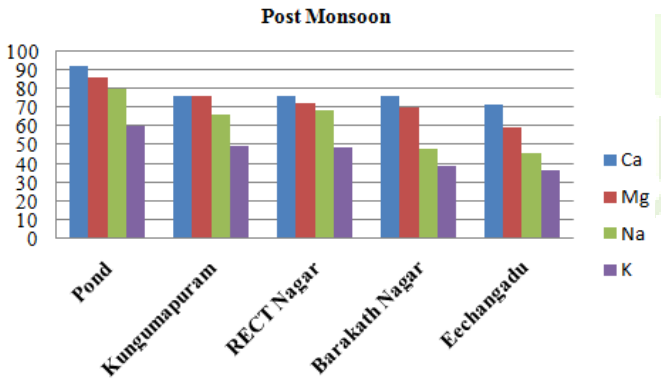
Iron exchange between Zn^{2+} and Ti^{2+} ion with Fe (III) ion in solution

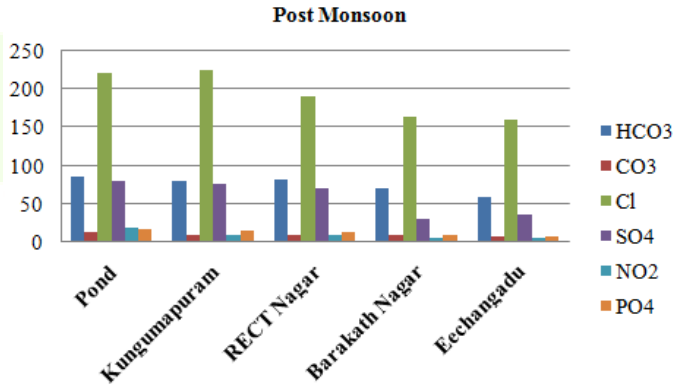
Graphite as Sorption Medium



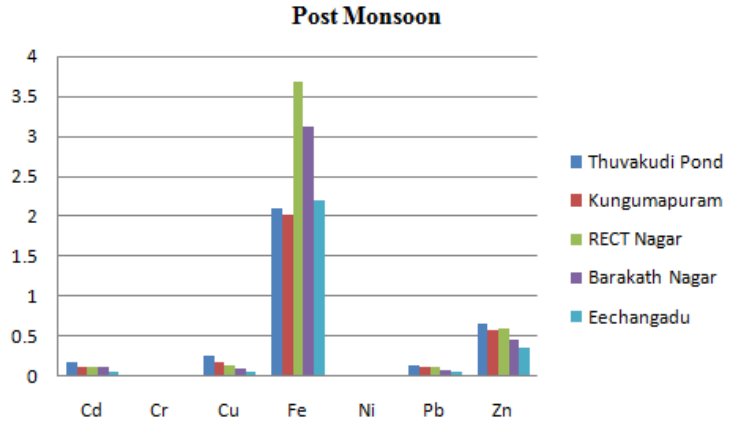
Sorption of Fe (III) ion occur at the intra space of graphite molecule

Maximum adsorption at pH 5 and at 9 hours period
Fig:4. Graph showing Adsorption of Fe (III) ion





ADSORPTION AND ABSORPTION MECHANISM OF (CGS-POP) LAYER



VI.DISCUSSION

From the above correlation matrix, it is found that all the parameters show the positive correlation except DO. EC shows all values positive correlation. DO shows positive correlation except with BOD, Sodium, bicarbonate, chloride, sulphate, and phosphate. All parameters are complied with WHO standard and many national and international standards except BOD. Since Cadmium, Copper, Lead shows a high degree of heavy metal deposition in natural bore wells water as wells as in pond water at nearby vicinity of Thuvakudi. The deposition of iron heavy metal is acceptable level, and all other heavy metals are not up to WHO limits.

6.1 Adsorption and Absorption Mechanism Of (CGS-POP) Composite

6.1.1 Crumb Rubber as sorbent material-Mechanism [12][16]

Studies have found that the components of a crumb rubber that absorb many inorganic metals are mainly polymeric materials and partially other materials such as Carbon-Black. In addition to that it also contains additives such as (TiO_2 and ZnO_2) additionally it also contains trace amounts of metals such as copper and zinc are found in steel belted tyres. The possible mechanism is shown in Figure.

6.1.2 Graphite as Sorption Medium [13][14] [15]

The size of graphite powder is usually 0.1mm about the size of coarse sand is usually have larger internal surface area and smaller internal pores, which make the particle with a faster adsorption rate and high interaction rate with heavy metals. The possible mechanism is shown in Figure.

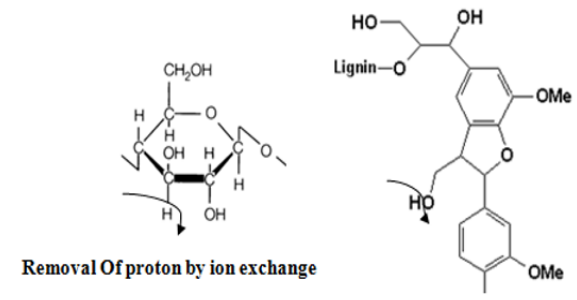
6.1.3 Sawdust as Adsorbent Material [11][13]

Sawdust, having a great potential as an adsorbent, has attracted the most attention of the scientific dealing with different aspects of wastewater purification by biosorption. Not much attention has been paid so far to the mechanism of bonding of the metal ions on to sawdust. The researchers dealing with the sawdust adsorption supposed that an ion exchange mechanism between metal ions and some functional groups existing in the lingo cellulosic composition molecular structure was able to replace protons by some metal ion species from the aqueous phase.

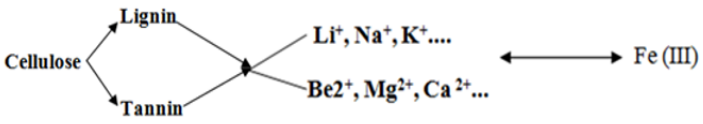
It is mainly composed of cellulose (45-50%) and lignin (23-30%). It is proved that an exchange of earth-alkali and alkali metals ions and hydroxyl, carboxylic and phenolic groups from organic molecules which can bond with heavy metal ions from aqueous phase. The possible mechanism is shown in Figure.

6.1.4 Plaster of Paris as Adsorption Medium [17]

Sawdust as Adsorbent Material

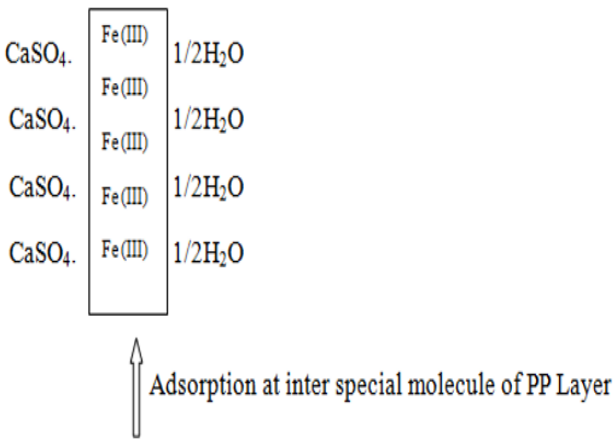


Removal Of proton by ion exchange



Removal of Alkali and Earth Alkali by ion exchange mechanism in saw dust

Plaster of Paris as Adsorption Medium



The plaster is made by calcinating gypsum, a process which involves exposing the gypsum to remarkably high temperature to create calcium sulphate and then grinding it into a fine white powder. The chemical structure of calcinated gypsum is $CaSO_4$. ½ H_2O.The adsorption property is due the adsorption at the intra molecular space between $CaSO_4$ and water molecule because the bond strength between them is weak, thus by accommodating higher rate of heavy metal adsorption with respect to pH and Temperature. The adsorption of Fe (III) ion is found be maximum at pH 5 and at 9 hours period. Hence the thermodynamics of adsorption rate is dependent on contact time and pH condition.

VII. CONCLUSION

Since Thuvakudi is an area in which more metal fabrication industry involving pig iron and cast-iron moulding, casting. Copper smelting, Nickel, lead, and zinc based small scale units are running, which leaves an untreated water to the passage of canals and streams and finally reaches the Thuvakudi village pond as its destination.[7][18] The intrusion of cadmium in human body shows biological amplification and accumulates inside kidneys, liver, pancreas, and spleen. Copper, zinc, nickel, titanium, etc. cause toxaemia and change in enzyme functioning.[4][5][6]

VIII. ACKNOWLEDGEMENT

The authors like to thank the Government of Tamil Nadu, Water Resource Organizations, Public Works Department (PWD), Trichy region for their valuable information of water resources in Trichy region and the Thuvakudi Municipality. I would also like to thank my colleagues and supporters for encouraging me to do this research work.

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