ISSN No:-2456-2165

An Experimental Study for the Removal of Hardness of Water by Using Biosorbents

Padarthi Divya Sri[1], M. Purna Prasanna Kumar[2], M. Sai Charan[3], P. Madhana Gopal[4], M. Chakri Gopala Rohith[5]
[1,2,3,4,5]Bachelor of Engineering Student, Seshadri Rao Gudlavalleru Engineering College, Gudlavalleru, India

Dr. Subhashish Dey[6]
[6]Assistant Professor, Civil Department, Seshadri Rao Gudlavalleru Engineering College, Gudlavalleru, India

Abstract:- The presence of pollutants in aqueous solution particularly from hazardous heavy metals and metalloids is an important environmental and social problem. The hardness is one of the serious groundwater contaminants in rural areas. Hardness in both its gaseous and liquid form can be irritating to the eyes, respiratory tract and skin due to its alkaline nature. The biological effects of hardness in humans after acute exposures are dose-related depend on their concentration; the amount is taken by the body and duration of exposure. Biosorption is a physiochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure. It is metabolically passive process not require energy and number of contaminants in sorbent can remove is dependent on kinetic equilibrium and composition of the sorbents cellular surface. Every biosorbent had different physical, chemical and biological properties for heavy metals removal by biosorption from the water. The biosorption process can be made economical by regenerating and reusing of bio sorbent after removing the heavy metals. Various bioreactors can be used in biosorption for the removal of metal ions from large volume of water.

Keywords:- *Hardness, Biosorption, Kinetic equilibrium, Isotherm Data and Regeneration.*

I. INTRODUCTION

General Water hardness is defined as the measured content of divalent metal cations. Dissolved calcium (Ca++) and magnesium (Mg++) are the only two divalent cations found at appreciable levels in most waters. In natural water, both calcium and magnesium primarily exist bound to bicarbonate, sulphate or chloride. When hard water evaporates or is heated above 61°C/141°F, bicarbonate converts to carbonate and precipitates out with Ca++ to form calcium carbonate (CaCO3) scale. Levels of water hardness are, therefore, typically reported in mg/l as CaCO3 equivalent, although CaCO3 is not itself present in water. Several classification schemes exist for denoting degree of hardness but in general soft water contains less than 60 mg/l and hard water contains greater than 120 mg/l CaCO3 equivalent. The majority of the United States geography has hard water, while soft water is predominately located in coastal regions. Most tap water originates from local sources, but some municipalities may draw water from multiple – sometimes even remote – locations when necessary. As a result, variations in water hardness or softness can occur within a single municipality depending upon the specific source location and the time of year. Additionally, hard-water minerals, such as calcium carbonate, act to buffer pH shifts, while soft water, being lightly buffered, is prone to acidification by acid-forming compounds. The effects of water hardness on plumbing materials will vary with mineral concentration, temperature and pH.

➢ *Literature Review*

Different bio-sorbents used for removal of different impurities The further research has been represented that inactive/dead microbial biomass can passively bind metal ions via various physicochemical mechanisms. Therefore, research on biosorption have become an active field for the removal of metal ions or organic compounds. Mechanisms responsible for biosorption, although understood to a limited extent, may be one or combination of ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and micro-precipitation. In this review, an extensive list of biosorbent literature including our research results has been compiled to provide a summary of available information on a wide range of biosorbents for metal removal. As for the biosorbents, it can be easily available biomass or modified raw biomass to improve its biosorption application properties. The research reports on bio-adsorbents for the removal of Hardness are Beetroot peel, Banana peel, Orange peel, Pomegranate peel, Lemon peel, Marigold flower, Firecracker flower, Hibiscus flower, Chrysanthemum flower, Rose flower.

- Bio- waste was studied in removal of Hg by chemically modified cotton (Roberts and Rowland, 1973), removal of lead ions using soymida febrifugal bark (Banker and Dara 1985). Cr removal by rice husk carbon was studied by **Srinivasan** et al. (1988), Manju and Aniradhan (1990) used coconut fiber based pseudo activated carbon for Cr (VI) removal. Removal of Ni from aqueous solutions was studied using agricultural waste peanut hulls (Periasamy and Namasivayam, 1995). The use of Bio waste-based adsorbents became common in late 1990s and lot of materials have been studied so far, for example, sunflower plant dry powder for removal of heavy metals (Bhalke et al., 1999), eucalyptus globulus bark for removal of Ni and Cu (Dolultani et al., 1999).

- According to **Balaji** et al., Groundwater is mainly contaminated by anthropogenic activities like such as agricultural, domestic and industrial. The tests are conducted at West Mugapair, Chennai, where concentration of iron in the groundwater is relatively too high. In this study Coconut coir (COC) from agricultural waste have been selected as solid phase extractor for removal of total iron. These materials exhibit remarkable binding characteristics for removal of total iron. The highest percentage removal of total iron was observed at Coconut coir (96%).

➢ *Objectives of the Present Study*

- To collect the flower petals of marigold, hibiscus, rose, chrysanthemum, and fire cracker and fruit peels of banana, oranges, pomegranate, lemon, beetroot.
- To wash the peels and dry them under sunlight for nearly 2 weeks. To grind the dried or peels using mixer grinder into fine powder and sieve the powder with 2.36 mm sieve.
- To test the hardness in the distilled water and make it as sample water.
- To mix the bio-sorbent materials into the sample water separately, to find out which material gives the best performance.
- To optimize the sample under various parameters such as pH, temperature etc.
- To alter the pH of bio-sorbent mixed sample by adding ammonium buffer solution, indicator and murexide and take note on which value best removal efficiency was achieved, to keep the samples at certain temperatures and note the best suitable temperature for maximum efficiency.
- To rotate the samples at different speeds on heavy rotary shaker and note that the speed at which the best efficiency was achieved.
- To keep the samples aside for certain time periods to find out the best contact time.

II. WORK PROGRESS

➢ *Preparation of Bio-Adsorbents*

The process of preparation of bio-adsorbents is a simple procedure which involves collection of bio-degradable waste. The bio-degradable wastes which we are collected are Beetroot peel, Banana peel, Orange peel, Pomegranate peel, Lemon peel, Marigold flower, Firecracker flower, Hibiscus flower, Chrysanthemum flower, Rose flower. The waste material is thoroughly cleaned and sun dried. The dry material then grinded into powdered with the help of an electric grinder mixer and sieve the powder with 2.36 mm sieve. The powdered bio-adsorbents are stored in air tight plastic containers.

➢ *Procedure for Addition of Bio-Adsorbents in Water*

The powdered biosorbent materials are to be added to the contaminated water in order to perform the hardness test. For the hardness test, tap water is collected from the Water and Waste Water Engineering laboratory, Gudlavalleru Engineering college, Gudlavalleru which is located in Krishna district at Andhra Pradesh. The solution is divided into six equal parts of containing 200ml in each beaker and then the bio-adsorbent material is added in the form of 100mg, 200mg, 300mg, 400mg, 500mg and 600mg in six beakers respectively. Then the beakers are placed on heavy rotary shaker for a period of one hour and the solution is then filtered with the help of filter papers into a conical flask. A heavy rotary shaker is used for the purpose of uniform mixing, the unit is prepared with heavy mild steel sections it has adjustable speed limit. Filtration is a process of separating the suspended particles from the solution with the help of filter paper in order to obtain suspended free particle solution.

Fig 1 Procedure for Addition of Bio-Adsorbents in Water

➢ *Procedure for Hardness Removal*

- *Total Hardness*

✓ Hardness water with biosorbent material is placed on heavy rotary shaker for a period of one hour.
✓ After mixing, the solution is filtered with the help of filter paper.
✓ The filtered solution is then taken into a separate beaker.
✓ Take 20ml of sample in a conical flask.
✓ Add 2ml of ammonium buffer solution and 2 drops of chromium black T indicator.
✓ Fill the burette with the ethylene diamine tetra acetic acid (EDTA).
✓ Now titrate the sample until the wine-red colour changes to kerosene blue.
✓ Repeat the above process until two consecutive readings obtained. Amount of hardness present is obtained from the following formula Hardness (mg/L) = (volume of EDTA x 50 x Normality x 1000) / Volume of sample taken.

- *Calcium Hardness*

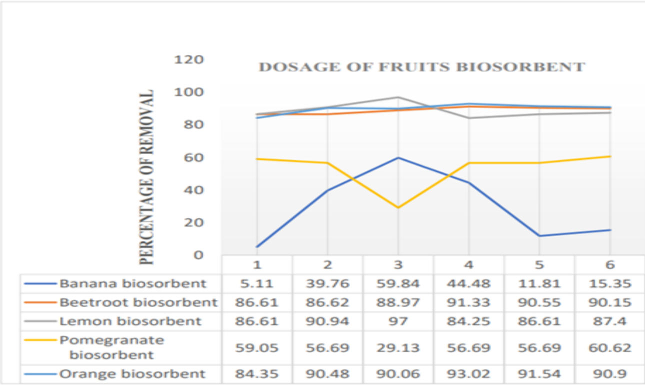
✓ Take 20ml of sample in a conical flask.
✓ Add 2ml of ammonium buffer solution and a pinch of murexide.
✓ Fill the burette with the ethylene diamine tetra acetic acid (EDTA).
✓ Now titrate the sample until the pale pink colour changes to purple.

ISSN No:-2456-2165

- ✓ Repeat the above process until two consecutive readings obtained. Amount of hardness present is obtained from the following formula Hardness (mg/L) = (volume of EDTA x 50 x Normality x 1000) / Volume of sample taken.

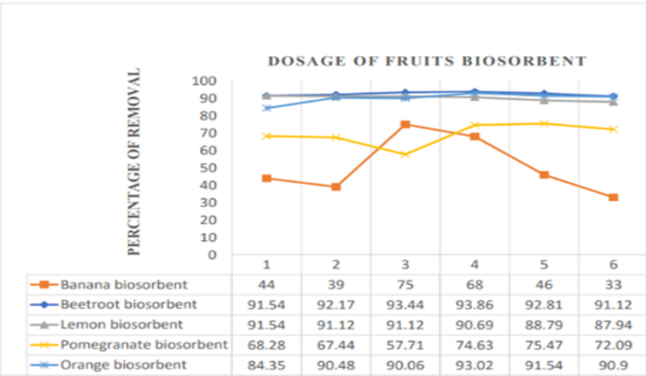
III. ANALYSIS COMPARISION OF SOLID AND FLOWER BIOSORBENTS FOR REMOVAL OF HARDNESS

Each biosorbent has its unique percentages in removal of hardness of contaminated water. Some biosorbents have high capacity in removal of hardness where as some have low capacity. The percentage removal of hardness of every biosorbent are compared.



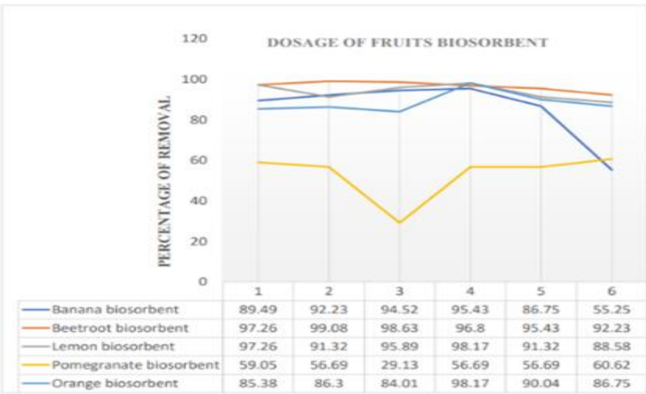
	1	2	3	4	5	6
Banana biosorbent	5.11	39.76	59.84	44.48	11.81	15.35
Beetroot biosorbent	86.61	86.62	88.97	91.33	90.55	90.15
Lemon biosorbent	86.61	90.94	97	84.25	86.61	87.4
Pomegranate biosorbent	59.05	56.69	29.13	56.69	56.69	60.62
Orange biosorbent	84.35	90.48	90.06	93.02	91.54	90.9

Fig 2 Comparison of total hardness removal for solid biosorbents



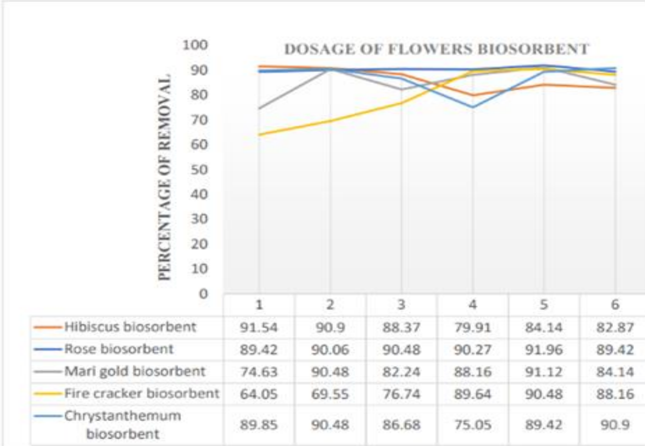
	1	2	3	4	5	6
Banana biosorbent	44	39	75	68	46	33
Beetroot biosorbent	91.54	92.17	93.44	93.86	92.81	91.12
Lemon biosorbent	91.54	91.12	91.12	90.69	88.79	87.94
Pomegranate biosorbent	68.28	67.44	57.71	74.63	75.47	72.09
Orange biosorbent	84.35	90.48	90.06	93.02	91.54	90.9

Fig 3 Comparison of calcium hardness removal for solid biosorbents



	1	2	3	4	5	6
Banana biosorbent	89.49	92.23	94.52	95.43	86.75	55.25
Beetroot biosorbent	97.26	99.08	98.63	96.8	95.43	92.23
Lemon biosorbent	97.26	91.32	95.89	98.17	91.32	88.58
Pomegranate biosorbent	59.05	56.69	29.13	56.69	56.69	60.62
Orange biosorbent	85.38	86.3	84.01	98.17	90.04	86.75

Fig 4 Comparison of magnesium hardness removal for solid biosorbents

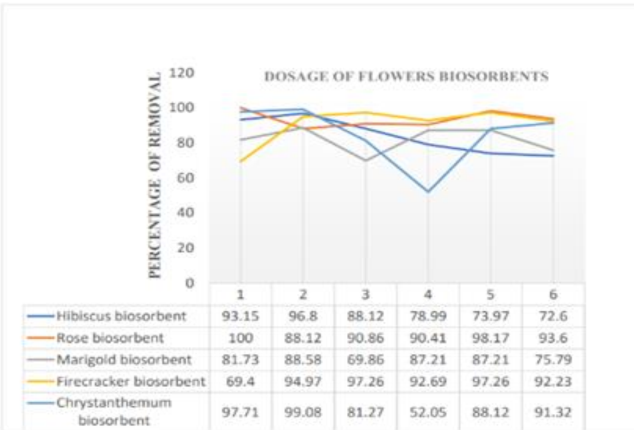


	1	2	3	4	5	6
Hibiscus biosorbent	91.54	90.9	88.37	79.91	84.14	82.87
Rose biosorbent	89.42	90.06	90.48	90.27	91.96	89.42
Mari gold biosorbent	74.63	90.48	82.24	88.16	91.12	84.14
Fire cracker biosorbent	64.05	69.55	76.74	89.64	90.48	88.16
Chrystanthemum biosorbent	89.85	90.48	86.68	75.05	89.42	90.9

Fig 5 Comparison of total hardness removal for flowers biosorbents

	1	2	3	4	5	6
Hibiscus biosorbent	90.15	85.82	88.58	80.7	92.51	91.73
Rose biosorbent	80.31	91.73	90.15	90.15	86.61	85.82
Marigold biosorbent	68.5	92.12	92.91	88.97	94.48	91.33
Fire cracker biosorbent	59.44	47.63	59.05	87	84.65	84.65
Chrysanthemum biosorbent	83.07	83.07	91.33	94.88	90.55	90.55

Fig 6 Comparison of calcium hardness removal for flowers biosorbents



	1	2	3	4	5	6
Hibiscus biosorbent	93.15	96.8	88.12	78.99	73.97	72.6
Rose biosorbent	100	88.12	90.86	90.41	98.17	93.6
Marigold biosorbent	81.73	88.58	69.86	87.21	87.21	75.79
Firecracker biosorbent	69.4	94.97	97.26	92.69	97.26	92.23
Chrystanthemum biosorbent	97.71	99.08	81.27	52.05	88.12	91.32

Fig 7 Comparison of magnesium hardness removal for flowers biosorbents

- ➢ *Optimization of Different Parameters in Hardness Removal from Water*

Beetroot and Rose shows the best result in removal of Hardness as compared with the other selected biosorbents. So, it is necessary to find out the optimum concentration of biosorbents, optimum pH, optimum temperature, optimum time, agitation speed and optimum dosage for removal of hardness from contaminated water.

- *Optimization in pH*

pH is a measure of the hydrogen ion (H+) concentration in the solution. It was used to determine the acidity or alkalinity of a substance. Keep the temperature in between 25-30ºC. Adjust the pH value 4 by using slope point and 7 by calibration process. From this study, it was observed that the optimum pH at which maximum biosorption occurred was in the range of 5.5- 7. This is not only helpful in easy monitoring of the further process, but cost economic as well because there is no need of additional pH regulation system.

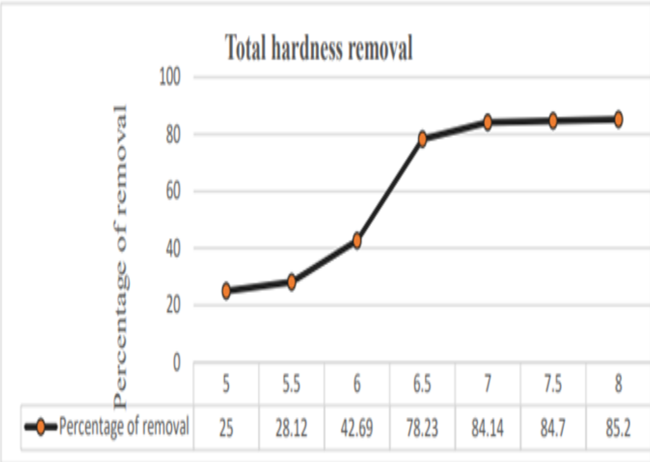


Fig 8 Optimization in pH for Hardness Removal of Beetroot Biosorbent

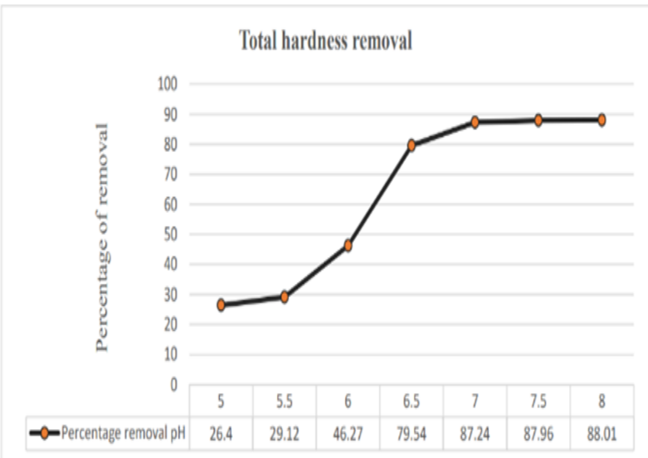


Fig 9 Optimization in pH for Hardness Removal of Rose Biosorbent

- *Optimization in Bio-Sorbent Dosage*

The dosage of biosorbents will produce certain effect with minimum of undesirable symptoms it can be calculated by mixing the bio-sorbent dosage in the surface water and ground water to remove the hardness content in the water. By adding the bio-sorbent powder to water at the rate of 100mg, 200mg, 300mg,400mg,500mg and 600mg and so on respectively up to the removal percentage of hardness to the sample of water. Where the hardness is removed was consider as removal dosage of sample. For hardness test the beetroot peel and rose best bio-sorbent consider removing in contamination at the rate of 220mg/150ml and 330/150ml.

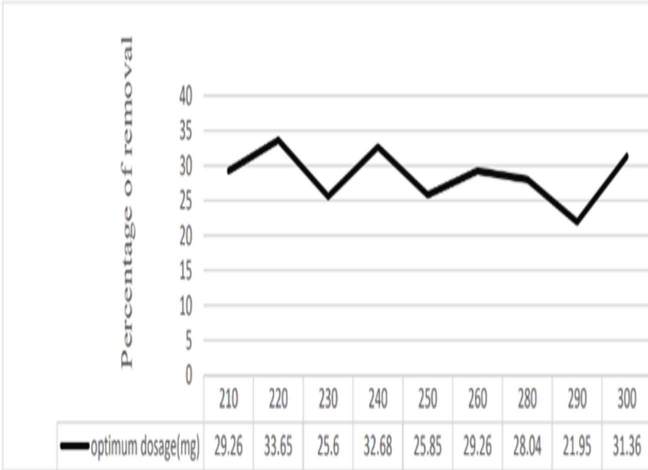


Fig 10 Optimization in Biosorbent dosage for Beetroot

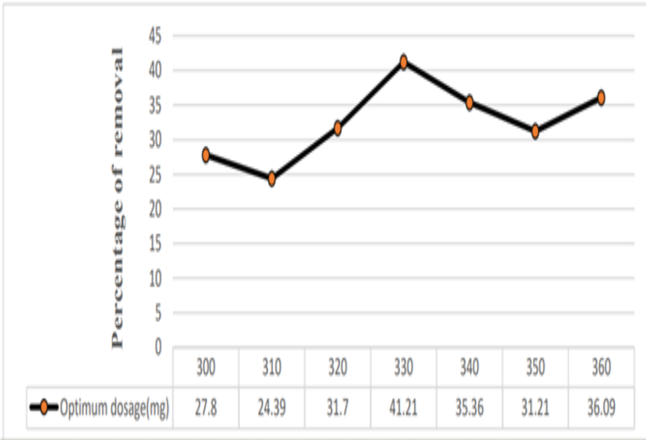


Fig 11 Optimization in bio-adsorbent dosage for Rose Graph

- *Optimization in Contact Time*

In the methodology adopted for the experiment, the contact time was kept at 0 to 150 minutes. However, as the rate of reaction is time dependent, an experiment was carried out in order to evaluate the reaction rate at variable contact periods. The other parameters were maintained constant, while varying the contact time. It is observed that there is incrimination with the increase in contact time up to 150 minutes. It is observed that Optimization in Contact Time for Beetroot is at 90min and for Rose it is 120min.

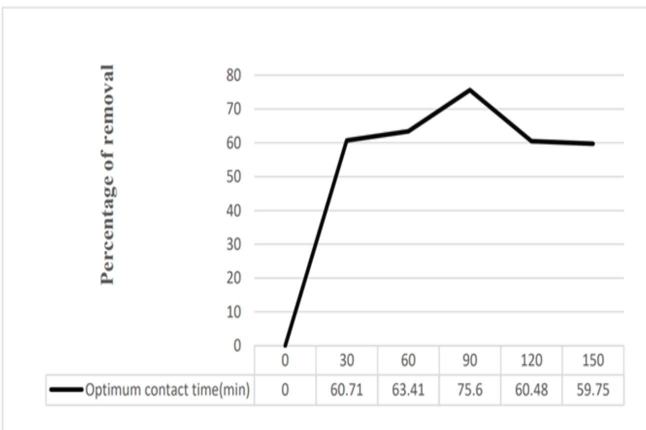


Fig 12 Optimization in contact time for Hardness removal for Beetroot Biosorbent

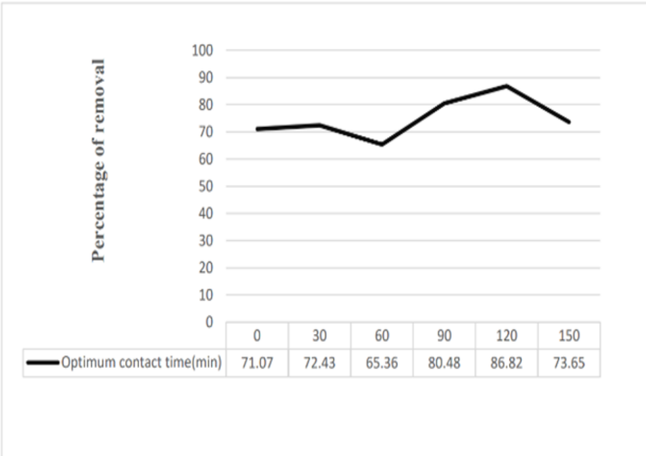


Fig 13 Optimization in contact time for Hardness removal for Rose Biosorbent

- *Optimization in Rotation Speed*

The rotation speed is also one of the very important factors affecting the hardness removal in the water. The rotation speed increases from 30rpm to120rpm and measured the hardness removal percentages. It is observed that Optimization in Rotation Speed for Beetroot is at 39.26 rpm and for Rose it is 37.31rpm.

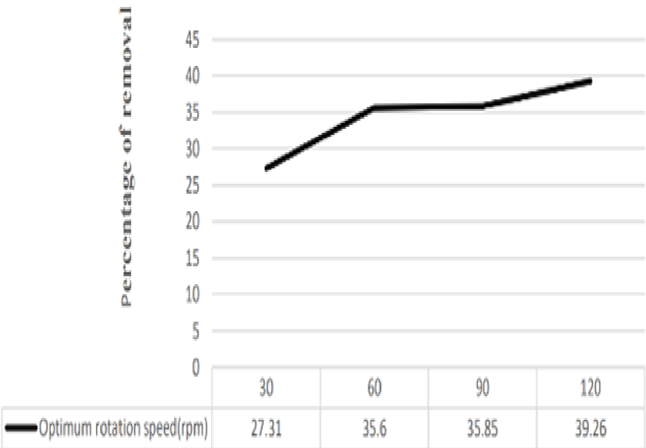


Fig 14 Rotation Speed for Beetroot Biosorbent

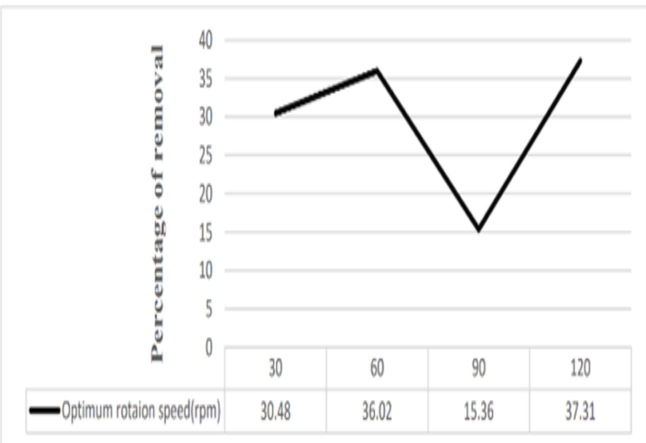


Fig 15 Rotation Speed for Rose Biosorbent

- *Optimization in Temperature*

The optimization of temperature is carried out between 30°-50°C using a thermostatically controlled incubator. The variations of adsorptions efficiency of Hardness on Beetroot biosorbent as function of solution temperatures. It was observed that the temperature does not have significant influence on the biosorption capacity in the studied range. It is observed that Optimization in Temperature for Beetroot is at 50°C and for Rose it is 35°C.

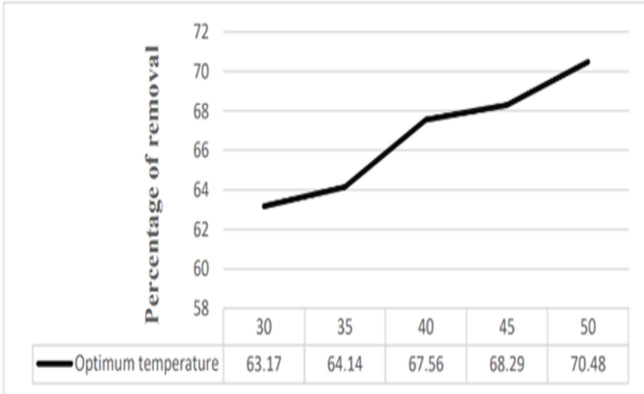


Fig 16 Optimization in Temperature for Hardness removal for Beetroot Biosorbent

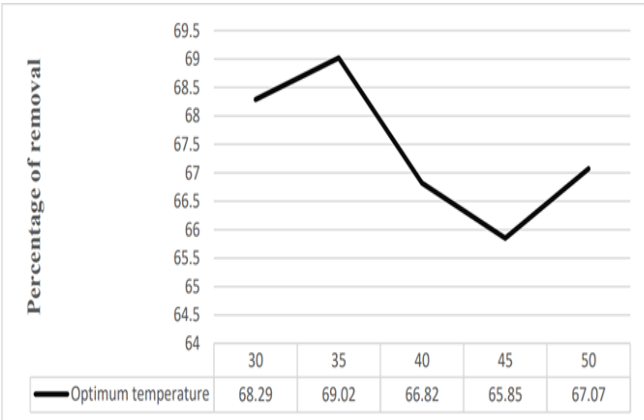


Fig 17 Optimization in Temperature for Hardness removal for Rose Biosorbent

- *Kinetic Study of Water*

Adsorptive materials have been widely investigated for removing heavy metal water pollutants and agricultural residues such as fruit peels seems to be a promising alternative due to its low cost and availability. This work attempts to study kinetics of Hardness adsorption onto different rose and beetroot peels-based biosorbents(OP,OPAC and OP-Chitosan).Batch experiments were carried to analyse adsorption process over time and fit the experimental data to kinetic models such as pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion. In this work, Beetroot & Rose biomass was used to prepare different biosorbents by physico-chemical modifications in order to use them for removing Hardness from aqueous solution. In addition, adsorption kinetics was studied to determine the kinetic model (pseudo first order, pseudo Second order).

➢ *Analyzing Different Locations of Water*

Now a days, due to over usage of Chemicals in different sectors Hardness and other Toxic matters are mixing with water which leads to massive water pollution. On consuming this polluted water various water borne diseases are wide spreading and effecting the health.One of the main pollutants in water is Hardness. For removing these hardness, we are using some Flora and some solid materials which we had collected from different locations. We had collected flowers Mari gold, Hibiscus, Chrysanthemum, Rose, Fire Cracker and solid materials like Beetroot, Pomegranate, Orange, Banana, Lemon. To test and remove the hardness we had collect the water, from below mentioned locations Mallovolu, Gudivada , Machilipatnam, Gudlavalleru.

Table 1 Removal of hardness (%) using Beetroot

Locations	Total hardness	Calcium hardness	Magnesium hardness
Mallavollu (surface water)	70%	71.66%	78.4%
Mallavollu (Ground water)	74.16%	75.55%	76.29%
Gudivada (surface water)	70.07%	71.24%	76.24%
Gudivada (Ground water)	82.14%	81.42%	84.36%
Gudlavalleru(surfa ce water)	74.39%	75.67%	76.25%
Gudivada(Ground water)	70.13%	71.16%	73.42%
Machilipatnam (surface water)	73.17%	72%	74.32%
Machilipatnam(Groundwater)	72.60%	62.5%	73.28%

Table 2 Removal of hardness (%) using Rose

Locations	Total hardness	Calcium hardness	Magnesium hardness
Mallavollu (surface water)	71.42%	73.33%	74.28%
Mallavollu (Ground water)	73.55%	76.7%	79.46%
Gudivada (surface water)	73.84%	65.71%	72.23%
Gudivada (Ground water)	83.03%	81.24%	85.55%
Gudlavalleru(surfa ce water)	81.18%	88.19%	88.27%
Gudivada(Ground water)	70.37%	71.29%	70.34%
Machilipatnam(surface water)	78.04%	77.29%	76.37%
Machilipatnam(Groundwater)	80%	79.28%	77.37%

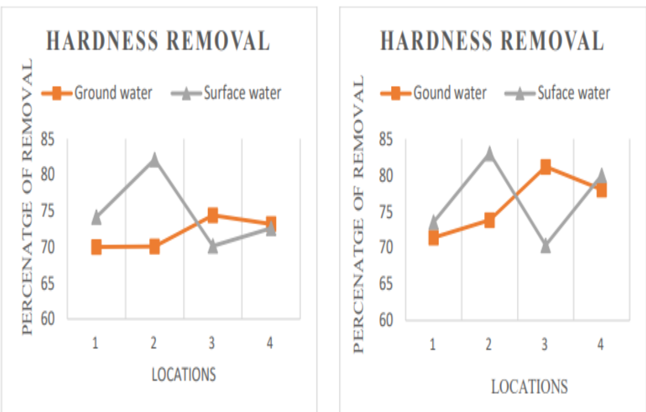


Fig 18 Hardness Removal by Adopted Biosorbents in Different Locations

IV. CONCLUSION

The Ten biosorbent materials are tested for hardness removal by adding them to hardness contaminated water. Beetroot and Rose bio-adsorbent shows the best result When comparing to Mari gold, Hibiscus, Chrysanthemum, Fire Cracker, Pomegranate, Orange, Banana, Lemon for removal of hardness and further it is tested in various optimum parameters.

➢ *Parameters of Beetroot:*

- *By using Beetroot, hardness is removed by 75.6%.*
- *The required temperature for this process is 45°C.*
- *The required pH for this process is 7-7.5.*
- *The required contact time for this process is 90 minutes.*
- *The required agitation speed for this process is 120 rpm.*

➢ *Parameters of Rose:*

- *By using Rose, hardness removal of 86.62% can be achieved.*
- *The required temperature for this process is 50°C.*
- *The required pH for this process is7-7.5.*
- *The required contact time for this process is 120 minutes.*
- *The required agitation speed for this process is 120rpm.*

Table 3 Removal of Hardness (mg/l) before and after addition of Biosorbents

Location	Initial Reading			Final Reading					
				Rose			Beetroot		
	TH (Mg/l)	CH (Mg/l)	MH (Mg/l)	TH (Mg/l)	CH (Mg/l)	MH (Mg/l)	TH (Mg/l)	CH (Mg/l)	MH (Mg/l)
Mallavollu (surface water)	350	300	50	260	103	157	290	183	87
Mallavollu (Ground water)	710	450	260	570	165	405	600	150	450
Gudivada (surface water)	325	175	150	275	55	210	275	100	175
Gudivada (Ground water)	560	210	350	400	150	250	525	205	320
Gudlavalleru (surface water)	335	275	60	225	25	200	310	115	195
Gudlavalleru (Ground water)	675	245	430	510	180	330	650	200	450
Machilipatnam (surface water)	410	125	285	340	100	240	350	110	240
Machilipatnam (Groundwater)	360	130	230	305	105	200	330	100	320

REFERENCES

[1]. Azam, F. and Ifzal, M. (2006): Microbial populations immobilizing NH4 + - N and NO3 - -N differ in the sensitivity to sodium chloride salinity in soil, Soil Biology and Biochemistry, 38(8):2491 – 2494.
[2]. Cleserl S. L., Greenberg E. A., Eaton D.A. (1999): Standard Methods for Examination of Water and Wastewater, American Public Health Association, 20th Edn.
[3]. Muller, M. (2000): Effects of Chloride transport inhibition and chloride substitution on neuron function and on hypoxic spreading – depression – like depolarization in rate hippocampal slices. Neuroscience; 97(1):33 – 45

ISSN No:-2456-2165

[4]. Wesson, L.G. (1969): Physiology of the human kidney, Grune and Stratton, pp 591.

[5]. WHO Regional Office for Europe, Sodium, Chlorides, and Conductivity in drinking water: a report on the WHO working group, Copenhagen (EURO Reports and Studies 2).

[6]. Zoeteman, BCJ. (1980): Sensory Assessment of Water quality, New York, NY, Pergamon Press

[7]. Department of National Health and Welfare (Canada) Guidelines for Canadian drinking water quality, supporting documentation, (1978), Ottawa.

[8]. Elsener, B. and Angst, U. (2007): Mechanism of electrochemical chloride removal, Corrosion Science, 49(12):4504 – 4522.

[9]. Fadeeva, V. K. (1971): Effect of drinking water with different chloride contents on experimental animals, Gigiena i sanitarija (in Russian), 36(6):1115 (Dialogue abstract No. 051634).

[10]. Gryndler, M., Rohlenova, J., Kopecky, J., Matucha, M., Chloride concentration affects soil microbial community.

[11]. Hajrasuliha, S. (1979): Accumulation and toxicity of chloride in bean plants, Plant and Soil, 55(1). Universal Journal of Environmental Research and Technology 422 Apte et al.

[12]. lsener, B. and Angst, U. (2007): Mechanism of electrochemical chloride removal, Corrosion Science, 49(12):4504 – 4522.

[13]. Patil, Y.B., and Paknikar, K.M. (1999): Removal and recovery of metal cyanide using a combination of biosorption and biodegradation processes. Biotechnology Letters, 31: 913 – 919.

[14]. Abdus- Salam N. and Adekola F.A.,2005, The influence of pH and adsorbent concentration on adsorption of lead and zinc on a natural Goethite, African J. of Sci. and Tech., 6 (2), 55-66.

[15]. Babel S and Kurniawan T. A., 2003, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, Journal of Hazardous Materials, 97 (1-3), 219-243.