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Waste Water Bioremediation Using Natural Combination Of Leaves

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Abstract— Industrial as well as domestic waste water contains heavy metals which are hazardous above a certain limit. Heavy metal pollution results from industrial activities and many a times, they are directly discharged into the main streams and rivers. These heavy metals cause nature degradation, represent a major loss of non-renewable resources and pose a huge problem in health and ecology. Bioremediation through adsorption on biomass has attracted many researchers as it is cost effective and efficient. In the present study, removal of Copper and Zinc metal ions has been evaluated by adsorption on natural combination of leaves. The variation in metal ion concentrations after and before adsorption was analyzed by using Atomic Absorption Spectrophotometer. Experimental data showed maximum removal efficiency of Copper ions to be 86.28% by Tulsi and Methi leaves combination after 1 day of contact period. The maximum uptake of Zinc ions, 82.47%, showed by Custard Apple and Eucalyptus leaves combination. All the three combinations viz. Calotropis Procera-Tulsi, Custard Apple-Tulsi and Custard Apple-Eucalyptus showed good results for Zinc ions as the removal efficiencies ranges 71-82%. The results from this study indicate that using combination of leaves as an adsorbent may be an efficient and economic means for removing heavy metals ions from aqueous solutions.

Keywords— Adsorption, Atomic Absorption Spectrophotometer, Bioremediation, Calotropis Procera, Copper, Custard Apple, Eucalyptus, Heavy metals, Methi, Tulsi, Zinc

I. INTRODUCTION

Industrial wastewater contains high levels of heavy metals that may pollute the water once it is discharged to the nature. These metals include arsenic, chromium, copper, zinc, aluminum, cadmium, lead, iron, nickel, mercury, and silver. Heavy metals are elements that have more than five times the specific gravity than that of water. They are one of the most toxic types of water pollutants. At least 20 metals are considered to be toxic, and approximately half of these metals are emitted to the environment in quantities that are hazardous to the environment, in addition to the human health [1]. Some of the treatment processes that have been used to remove heavy metals from wastewater include precipitation with coagulation and flocculation, ion exchange, complexation of dry biomass and adsorption [2]. However, there are limitations: Precipitation produces large quantities of heavy metals rich waste sludge; ion exchange and biomass methods are costly and cannot be readily applied to large scale applications [2]. Adsorption as a process, employed due to its low cost and applicability on large scales. Adsorption is commonly being done using activated carbon, which adsorbs dissolved organic substances in the water treatment [3]. Although activated carbon has its advantages, such as its effectiveness in removing colors and its applicability on wide variety of organic compounds, it has limitations that prevent it from treating highly soluble organics, and high concentrations or organic and inorganic compounds. In addition to these, cost of operation is high [3]. Other adsorbents that have been used include synthetic polymers and silica-based substances [4, 5]. However, these materials are more costly

compared to activated carbon. Hence, there is a perceived necessity and growing interest in finding adsorbents that are more cost-effective and produce fewer limitations including high temperatures and pressures. Therefore, finding suitable materials and operating conditions are essential to address the concerns of heavy metal pollution. Biosorption is an effective and versatile method and can be easily adopted in low cost to remove heavy metals from large amount of industrial wastewaters. Recent studies have showed that heavy metals can be removed using plant materials such as palm pressed fibers and coconut husk [6], water fern *Azolla filiculoidis* [7], peat moss [8], duck weed *Wolffia globosa* [9], lignocellulosic substrate extracted from wheat bran [10], *Rhizopus migricans* [11], cork and yohimbe bark wastes [12, 13] and leaves of indigenous biomaterials, *Tridax procumbens* [14]. The present research work has been done to examine the removal ability of different combinations of leaves, viz. Lemon, Tulsi and Methi leaves for Copper; Calotropis Procera, Custard Apple, Tulsi and Eucalyptus for Zinc, and to find out an effective combination that adsorbed the heavy metals in optimum concentrations from their aqueous solutions. The effect of adsorption period and varying dose of adsorbents on metal adsorption was examined.

II. MATERIALS AND METHODOLOGY

2.1. Preparation of leaves

The leaves that were used as adsorbent material were collected from one crop, one tree and four types of plant respectively. Plant leaves of Custard Apple, Lemon, Calotropis Procera and Tulsi while crop leaves of Methi and tree leaves of Eucalyptus were collected. All plant leaves were collected from nearby plants grown in Shreenathpuram area and Rajasthan Technical University Kota, Rajasthan. Methi leaves were purchased while Eucalyptus tree leaves were obtained from locally grown tree. After the collection of leaves, they were washed in tap water and again with de-ionized water to take away dust, sand, clay and other impurities. The washed leaves were then left to dry for one or two days in shade at room temperature and then in an oven at 100ºC so that they can be crushed and grinded into a fine powder. The powder was sieved into 300 micron constant size.

2.2. Preparation of synthetic waste water

The initial concentrations used were 2ppm for Copper and 1ppm for Zinc. A stock solution of 1000 ppm of both Copper and Zinc was prepared in distilled water with Zinc (II) Sulfate and Copper (II) Sulfate. Both the working solutions were obtained by diluting the stock solution with distilled water.

2.3. Instrumentation

Atomic Absorption Spectrophotometer (Electronics Corporation Of India Limited) is used to determine the presence and quantity of metal in a solution. It can be used to determine about 70 different metals in a solution.

2.4. Adsorption Studies

Lemon, Tulsi, Methi, Calotropis Procera, Custard Apple and Eucalyptus leaf powder were categorized for both the heavy metals on the basis of their highest metal ion uptake as per the previous studies. For Copper, Lemon, Tulsi and Methi were selected. For Zinc, Calotropis Procera, Custard Apple, Tulsi and Eucalyptus were chosen. Combinations of leaves (two at a time) are made in ratios, viz. 90:10, 80:20, 70:30 and 60:40. Ratios were made in a way that leaves with more efficiency for certain metal has given greater part of the ratio. The batch experiment was conducted for three sets of adsorption duration. One was for the duration of 1 day or 24 hrs. The other one was for the duration of 5 days and the last one was for the duration of 10 days to evaluate the efficiency in different durations. 50 ml of an aqueous solution was taken in 100 ml small air tight plastic

container for the experiment and 0.50 g of dried combined powder was added to it. This is how all the samples were made. Experiments were done at room temperature and the samples were left for 1, 5 and 10 day duration. Then after the adsorption duration, the adsorbents were separated from the aqueous solution with the help of filter papers. The solutions then put for testing, done by AAS (Atomic Absorption Spectrophotometer).

The initial and final metal concentrations were analyzed for change in the concentration of heavy metals Copper and Zinc to find the ability of leaves to remove these metals.
The removal of metal ion by the biosorbent was calculated by equation 1:

$$\text{Removal } \% = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

C_o and C_e are initial and equilibrium liquid phase metal ion concentrations (mg/l) respectively. The amount of metal ion absorbed by the biosorbent was calculated by using equation 2:

$$q_e = \frac{C_o - C_e}{m} \times V \quad (2)$$

q_e (mg/g) is the amount of metal ion absorbed per unit mass of adsorbent, V is the volume of the metal ion solution, m is the mass of biosorbent and C_o and C_e are the initial and equilibrium liquid phase metal ion concentrations (mg/l) respectively.

III. RESULTS AND DISCUSSION

3.1. For Copper

3.1.1. Lemon Methi Combination

Table 1. CONCENTRATION OF COPPER ION USING DIFFERENT RATIOS OF LEMON-METHI LEAVES COMBINATION

Lemon-Methi leaves combination ratio	Day 1 collected sample numbers	Concentration of Copper ion in the solution (mg/l)	% Removal	Day 5 collected sample number	Concentration of Copper ion in the solution (mg/l)	% Removal	Day 10 collected sample numbers	Concentration of Copper ion in the solution (mg/l)	% Removal
----	Sample no.0	2.391		Sample no.0	2.391		Sample no.0	2.391	
90	Sample no.1	1.401	41.405 26976	Sample no.21	0.613	74.362 1916	Sample no.25	0.89	62.777 0807
80	Sample no.2	1.468	38.603 09494	Sample no.22	0.697	70.849 0171	Sample no.26	0.974	59.263 9063
70	Sample no.3	1.284	46.298 61982	Sample no.23	0.898	62.442 4927	Sample no.27	1.041	56.461 7315
60	Sample no.4	1.502	37.181 09578	Sample no.24	0.932	61.020 4935	Sample no.28	1.25	47.720 619

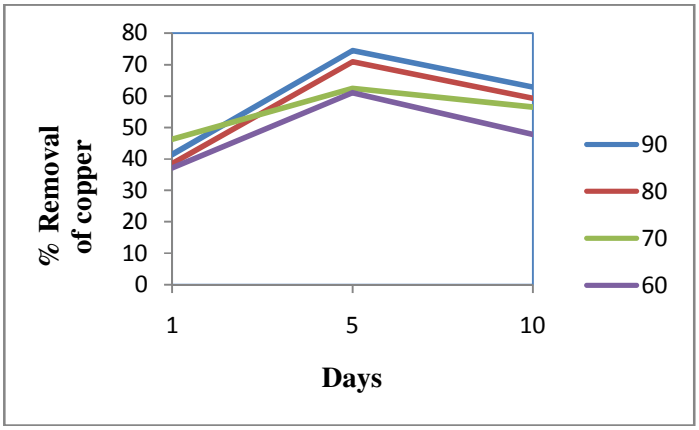

Fig. 1 Graph showing percentage removal of Copper with Lemon Methi combination

From table 1 and fig. 1, it can be observed that after 5 days, nearly all combinations of Lemon-Methi shows better removal in which 90:10 had shown highest removal i.e. 74.36% removal. So, it can be inferred that 5 days and 90:10 ratio is the most feasible condition.

3.1.2. Lemon Tulsi Combination

TABLE 2. CONCENTRATION OF COPPER ION USING DIFFERENT RATIOS OF LEMON-TULSI LEAVES COMBINATION

Lemon-Tulsi leaves combination ratio	Day 1 collected sample numbers	Concentration of Copper ion in the solution (mg/l)	%Removal	Day 5 collected sample numbers	Concentration of Copper ion in the solution (mg/l)	%Removal	Day 10 collected sample numbers	Concentration of Copper ion in the solution (mg/l)	%Removal
----	Sample no.0	2.391		Sample no.0	2.391		Sample no.0	2.391	
90	Sample no.5	1.209	49.435382 69	Sample no.13	0.789	67.00 12547	Sample no.29	0.999	58.21 83187
80	Sample no.6	1.066	55.41 6143 87	Sample no.14	1.066	55.41 61439	Sample no.30	0.882	63.11 16688
70	Sample no.7	0.965	59.64 0317 86	Sample no.15	0.722	69.80 34295	Sample no.31	0.63	73.65 1192
60	Sample no.8	0.697	70.84 9017 15	Sample no.16	1.066	55.41 61439	Sample no.32	0.706	70.47 26056

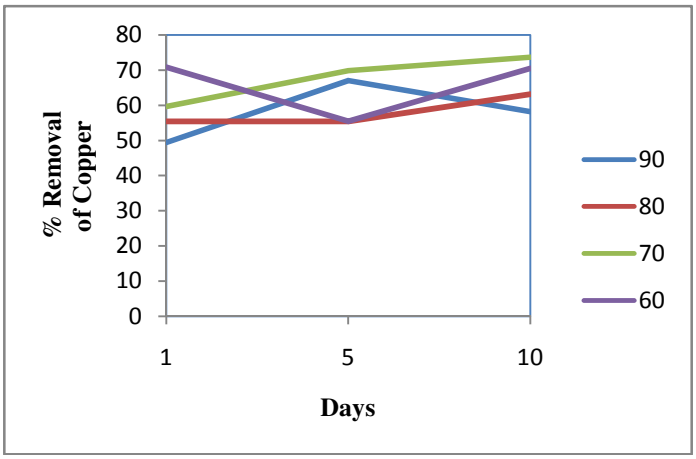

Fig. 2 Graph showing percentage removal of Copper with Lemon Tulsi combination

From here, in table 2 and fig. 2, it can be observed that Lemon-Tulsi combination showed better results after day1, day5 as well as day10. In this study, 73.65% is the highest percentage removal shown by 70:30 ratio and has shown better results consistently after all three sets of time periods. So, it can be inferred that 10 days and 70:30 ratio is the most optimum condition.

3.1.3. Tulsi Methi Combination

Table 3. CONCENTRATION OF COPPER ION USING DIFFERENT RATIOS OF TULSI-METHI LEAVES COMBINATION

Tulsi-Methi leaves combination ratio	Day 1 collected sample numbers	Concentration of Copper ion in the solution (mg/l)	%Removal	Day 5 collected sample numbers	Concentration of Copper ion in the solution (mg/l)	%Removal	Day 10 collected sample numbers	Concentration of Copper ion in the solution (mg/l)	%Removal
----	Sample no.0	2.391		Sample no.0	2.391		Sample no.0	2.391	
90	Sample no.9	0.328	86.2818 9042	Sample no.17	0.898	62.442 4927	Sample no.33	0.915	61.731 4931
80	Sample no.10	0.328	86.2818 9042	Sample no.18	0.898	62.442 4927	Sample no.34	0.488	79.590 1297
70	Sample	0.53	77.8335 4245	Sample	0.546	77.164 3664	Sample	0.848	64.533 6679

	no.11			no.19			no.35		
60	Sample no.12	0.588	75.40777917	Sample no.20	0.546	77.1643664	Sample no.36	0.823	65.5792555

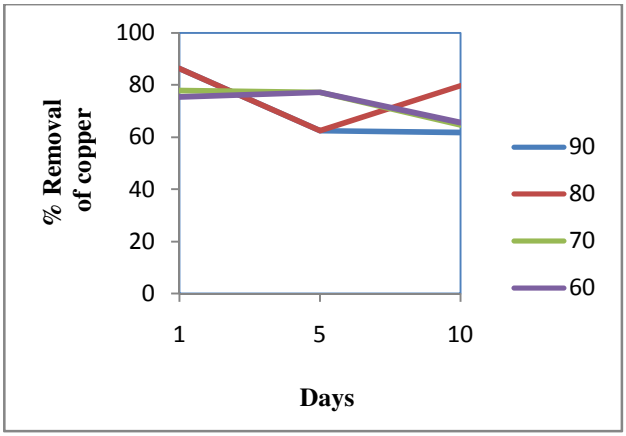

Fig. 3 Graph showing percentage removal of Copper with Tulsi Methi combination

It is observable through table 3 and fig.3, that Tulsi-Methi is not showing any continuous trend in removal of copper ions throughout the three sets of time periods. Although, 86.28% is the highest removal percentage shown by both 90:10 and 80:20 ratios after 1 day. In fact, this ratio has shown far better results just after 1 day of the experiment. So, it can be inferred that 90:10, 80:20 ratios and 1 day is the optimum condition.

3.2. For Zinc

3.2.1. Calotropis Procera Custard Apple Combination

Table 4. CONCENTRATION OF ZINC ION USING DIFFERENT RATIOS OF CALOTROPIS PROCERA-CUSTARD APPLE LEAVES COMBINATION

Calotropis Procera-Custard Apple leaves combination ratio	Day 1 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal	Day 5 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal	Day 10 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal
----	Sample no.0	0.873		Sample no.0	0.873		Sample no.0	0.873	
90	Sample no.37	0.543	37.80068729	Sample no.61	0.64	26.6895762	Sample no.89	0.421	51.7754868

80	Sample no.38	0.554	36.54066438	Sample no.62	0.605	30.69874	Sample no.90	0.404	53.722795
70	Sample no.39	0.417	52.23367698	Sample no.63	0.68	22.1076747	Sample no.91	0.386	55.7846506
60	Sample no.40	0.436	50.05727377	Sample no.64	0.662	24.1695304	Sample no.92	0.364	58.3046964

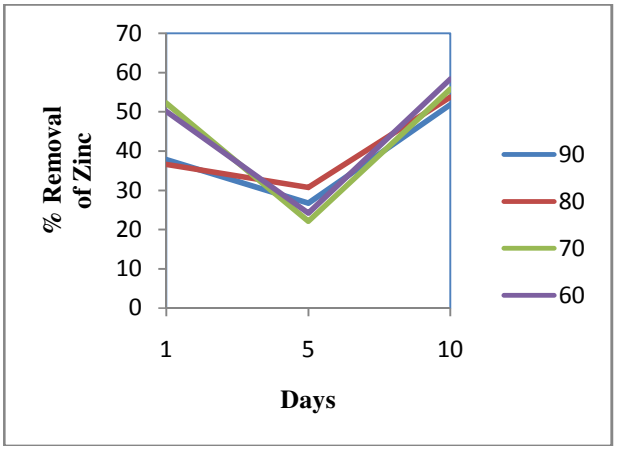

Fig. 4 Graph showing percentage removal of Zinc with Calotropis Procera Custard Apple combination

It can be seen here from table 4 and fig. 4, that this combination is not showing satisfactory results. Although, the best percentage removal among all, has been given by 60:40 ratio after 10 days i.e. 58.30%. A trend of decrease in percentage removal is being observed after 5 days as compared to the results after 1 day by all the ratios and then increment after 10 days whose results are better than all three sets of time periods.

3.2.2. Calotropis Procera Tulsi Combination

Table 5. CONCENTRATION OF ZINC ION USING DIFFERENT RATIOS OF CALOTROPIS PROCERA-TULSI LEAVES COMBINATION

Calotropis Procera -Tulsi leaves combination ratio	Day 1 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal	Day 5 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal	Day 10 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal
----	Sample no.0	0.873		Sample no.0	0.873		Sample no.0	0.873	
90	Sample no.41	0.495	43.29896907	Sample no.65	0.715	18.0985109	Sample no.85	0.478	45.2462772

80	Sample no.42	0.489	43.9862543	Sample no.66	0.711	18.556701	Sample no.86	0.401	54.0664376
70	Sample no.43	0.504	42.26804124	Sample no.67	0.631	27.720504	Sample no.87	0.43	50.744559
60	Sample no.44	0.517	40.77892325	Sample no.68	0.591	32.3024055	Sample no.88	0.254	70.9049255

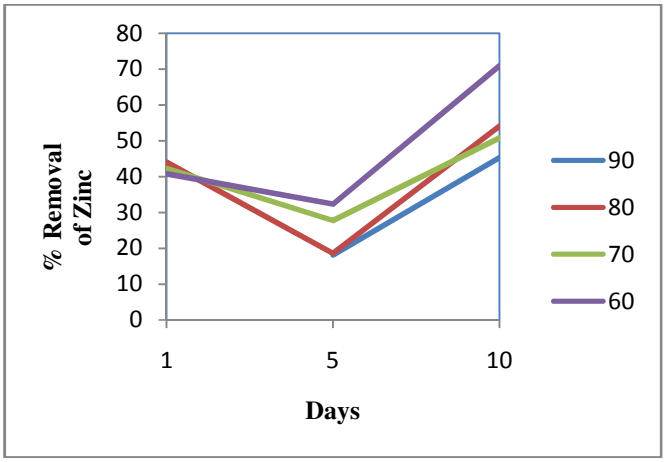

Fig. 5 Graph showing percentage removal of Zinc with Calotropis Procera Tulsi combination

As observed in table 5 and fig.5, the results shown by this combination are not satisfactory after 1 day and 5 days time period. Decrement after 5 days as compared to day 1 results and then sudden increase in percentage removal of zinc ion concentration after 10 days are observed. Results after 10 days are satisfactory and are better than all three sets of time periods in which 70.90% i.e. approximately 71% removal is observed by 60:40 ratio which is maximum. So, it can be inferred that 60:40 ratio and 10 days is the optimum condition.

3.2.3. Calotropis Procera Eucalyptus Combination

Table 6. CONCENTRATION OF ZINC ION USING DIFFERENT RATIOS OF CALOTROPIS PROCERA-EUCALYPTUS LEAVES COMBINATION

Calotropis Procera-Eucalyptus leaves combination	Day 1 collected sample	Concentration of Zinc ion in the solution (mg/l)	%Removal	Day 5 collected sample	Concentration of Zinc ion in the solution (mg/l)	%Removal	Day 10 collected sample	Concentration of Zinc ion in the solution (mg/l)	%Removal
----	Sample no.0	0.873		Sample no.0	0.873		Sample no.0	0.873	
90	Sample no.49	0.454	48	Sample no.73	0.65	25.544	Sample no.105	0.422	51.660

						1			9
80	Sample no.50	0.422	51.66	Sample no.74	0.633	27.4914	Sample no.106	0.511	41.4662
70	Sample no.51	0.459	47.42	Sample no.75	0.551	36.8843	Sample no. 107	0.404	53.7228
60	Sample no.52	0.395	54.75	Sample no.76	0.453	48.11	Sample no. 108	0.314	64.0321

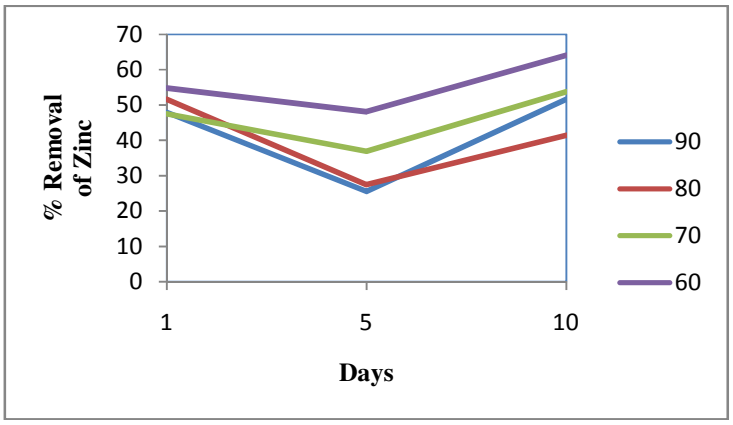

Fig. 6 Graph showing percentage removal of Zinc with Calotropis Procera Eucalyptus combination

Results after 10 days are satisfactory and are better than all three sets of time periods in which 64.03% removal is observed by 60:40 ratio which is maximum, as can be seen from table 6 and fig. 6. So, it can be inferred that 60:40 ratio and 10 days is the optimum condition.

3.2.4. Custard Apple Eucalyptus Combination

Table 7. CONCENTRATION OF ZINC ION USING DIFFERENT RATIOS OF CUSTARD APPLE- EUCALYPTUS LEAVES COMBINATION

Custard Apple-Eucalyptus leaves combination ratio	Day 1 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal	Day 5 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal	Day 10 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal
----	Sample no.0	0.873		Sample no.0	0.873		Sample no.0	0.873	
90	Sample no.45	0.307	64.83	Sample no.69	0.259	70.3322	Sample no.97	0.256	70.6758
80	Sampl	0.307	64.8	Sampl	0.289	66.8	Sample	0.282	67.69

	e no.46		3	e no.70		958	no.98		76
70	Sample no.47	0.153	82.47	Sample no.71	0.267	69.4158	Sample no.99	0.237	72.8522
60	Sample no.48	0.212	75.72	Sample no.72	0.25	71.3631	Sample no.100	0.267	69.4158

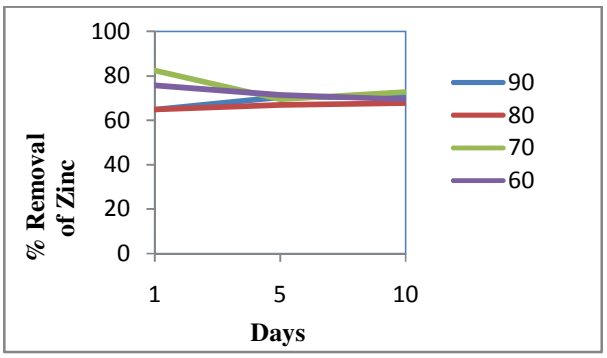

Fig. 7 Graph showing percentage removal of Zinc with Custard Apple Eucalyptus combination

It can be observed by table 7 and fig. 7, that this combination has given far better results in removing zinc ions from the solution. Above 64% removal percentage has been shown by all the three sets of time periods. 60:40 ratio is showing decreasing percentage in successive days and has given 75.72% removal in just one day, so, this ratio is optimum for 1 day only. 90:10 and 80:20 ratios are showing increasing percentage removal in successive days but the results are not much high. The best removal efficiency is shown by 70:30 ratio after 1 day i.e. 82.47% which is the optimum condition.

3.2.5. Custard Apple Tulsi Combination

Table 8. CONCENTRATION OF ZINC ION USING DIFFERENT RATIOS OF CUSTARD APPLE-TULSI LEAVES COMBINATION

Custard Apple-Tulsi leaves combination ratio	Day 1 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal	Day 5 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal	Day 10 collected sample numbers	Concentration of Zinc ion in the solution (mg/l)	%Removal
----	**Sample no.0**	**0.873**		**Sample no.0**	**0.873**		**Sample no.0**	**0.873**	
90	Sample no.53	0.364	58.3	Sample no.77	0.217	75.1432	Sample no.93	0.231	73.5395
80	Sample no.54	0.273	68.73	Sample no.78	0.178	79.6105	Sample no.94	0.22	74.7995
70	Sample no.55	0.311	64.38	Sample no.79	0.27	69.0722	Sample no.95	0.227	73.9977

60	Sample no.56	0.392	55.1	Sample no.80	0.227	73.9977	Sample no.96	0.22	74.7995

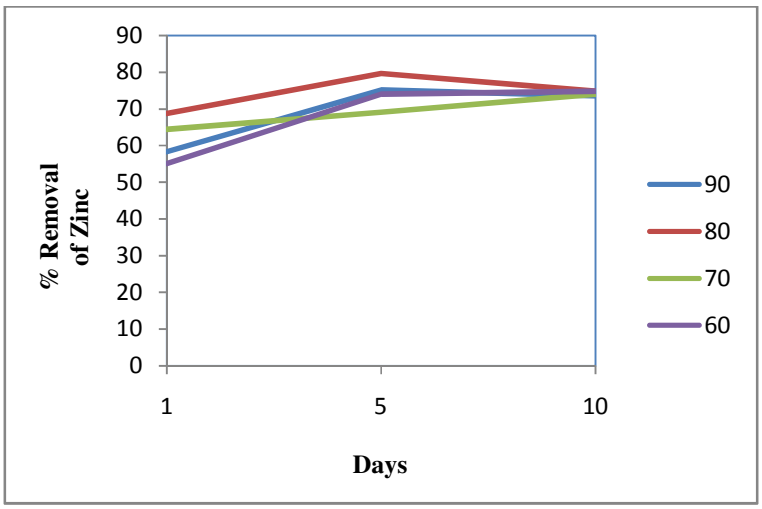

Fig. 8 Graph showing percentage removal of Zinc with Custard Apple Tulsi combination

From here, in table 8 and fig.8, we can conclude that results after 5 days and 10 days are satisfactory. In the present study 79.61% is the highest removal efficiency shown by 80:20 ratio after 5 days which is the optimum condition.

IV. CONCLUSION

The removal of copper and zinc metal ions in synthetic wastewater by using biosorption technology was studied in batch experimental systems. Based on the results, the following conclusions can be drawn. Combination of leaves is an efficient biomaterial for removal of copper and zinc ions from synthetic wastewater. Tulsi and Methi leaves combined in 90:10 and 80:20 ratios are able to show maximum of 86.28% removal of copper ions after 1 day period. Custard Apple and Eucalyptus leaves combined in 70:30 ratio has shown maximum of 82.47% removal of zinc ions after 1 day period. Also, Custard Apple and Tulsi leaves combined in 80:20 ratio has shown maximum of 79.61% removal of zinc ions after 5 day period. This process can be effectively used in the heavy metals removal in industrial wastewater.

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