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Removal of mercury by biosorption onto sphaeroplea algae

To curtail mercury pollution problem, adsorbent based on Sphaeroplea algal biomass were tried for the removal of mercury ion from aqueous solution. Dried and powdered biomass were activated with acid (1N HNO$_3$), alkali (1N NaOH) and washed thoroughly and dried in oven. The effect of initial concentration, pH and contact time was studied in batch experiments. The percentage removal of mercury decreased with increase in initial concentration, due to the limited number of available active sites on the surface of natural and acid treated algae to accommodate higher concentration of mercury ions. The effect of the pH indicated that the percentage removal increases with decrease in pH. At pH 7 the maximum removal of 60% of mercury is achieved in natural and 85% in acid treated algae. The percentage removal of mercury increases with increase in contact time and availability of active sites. The maximum removal of mercury at pH 7 shows that 240 mts is sufficient to remove above 85% of mercury

***Keywords**: Removal of mercury, Sphaeroplea algae, biosorption, water pollution, heavy metals*

1. INTRODUCTION

Quality of drinking water has become the main international subject. Presence of trace metals in drinking water has been related to certain type of cancers, cardiovascular diseases and other severe health problems in animals and human beings [1]. In the majority of cases, the problem of heavy metals is not related to a single metal but to a combination of metals originating from one or several sources. In spite of several research works, there is still a lack of effective means for the treatment of water and wastewater containing heavy metals.

The presence of mercury, in quantities is excess of limits is a serious matter of concern from a public health point of view. Mercury is considered as cumulative poison that usually affects the gastrointestinal track, nervous system and sometimes both. Mercury poisoning causes damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormal in pregnant women. Several methods are employed to remove mercury form the industrial effluent. Some of them are chemical precipitation, electrochemical methods, reverse osmosis, ion exchange and adsorption.

Several adsorbents have been used to remove mercury. Among them the most often used one is activated carbon [2-5] Dates nut [3], activated carbon derived from Eichhorina crassipes [6] and modified tamarind nut carbon [7] have also been used to remove mercury.

Chung et al [8] have used non – living protonated biomass of Ulva Lactuca to remove mercury. Ahmad et al [9] have used a naturally available Lateritic soil for the removal of mercury from industrial effluents. Usually the researchers study the influence of initial concentration, pH, contact time, adsorbent dose, adsorbent particle size on the efficiency of removal of metals. The type of adsorption isotherm (freundlich / Langmuir) has also been investigated in detail.

The present work is undertaken

(i) to remove mercury by using an inexpensive biomass obtained from prawn pond algae, namely, Sphaeroplea algae.

(ii) To investigate the influence of initial concentration, pH and contact time on the efficiency of removal of mercury.

2. EXPERIMENTAL

2.1. Materials

2.1.1. Apparatus

1. Systronics digital Spectrophotometer with 1.0 cm quartz cells was used for color measurements

2. Elico digital pH meter with combined glass electrode was used for pH measurements

3. Rotary mechanical shaker was used for equilibrations studies

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2.1.2. Reagents

Unless otherwise specified all reagents used were of analytical grade and distilled water was used for dilution purpose.

2.1.3. Regents of batch studies

The stock solution was prepared by dissolving 1.354 g of Mercury [II] chloride in water and diluting to 1000 ml. Appropriate volumes of stock solution were suitably diluted with water to obtain and concentration of 10 mg/L for batch experiments.

2.2. Reagents for Mercury [II] determination

2.2.1. Standard Mercury [II] Solution

Appropriate volumes of stock solution (1000 mg/L) were diluted with water to provide a solution containing 10 mg/L of mercury [II].

2.3. Buffered potassium iodide solution (2.0%)

5 g of Potassium iodide and 5 g of potassium hydrogen phthalate were dissolved in water. A few crystals of sodium thiosulphate were added and the solution was diluted to 250 ml.

2.4. Rhodamine 6G solution (0.005%):

0.05 g of the dyestuff was dissolved in water and diluted to one litre.

2.5. Gelatin solution(1%):

1 g of gelatin was dissolved in boiling water cooled and diluted to 100 ml. This solution was prepared on the day of use.

2.6. EDTA Solution (0.05m):

9.3 g of the disodium salt was dissolved in water and diluted to 500 ml.

2.7. Methods

2.7.1. Batch experiments

Batch experiments were conducted in ploythene bottles of 300 ml capacity provided with screw caps. The polythene bottles were washed well with chromic acid before and after use.

150 ml of the solution containing 25 mg/L of ions under investigation was taken in the bottle. After the addition of algal biomass, the bottles were equilibrated for specific periods of time in a rotary mechanical shaker. At the end of the equilibration period, the solutions were filtered using a G-3 crucible if necessary and the concentration of respective ions were established by spectrophotometer. The experiments were carried out under different experimental conditions.

2.7.2. Experimental conditions

i) Effect of initial mercury (II) concentration:

These studies were performed by keeping pH 7, particles size (300μ), contact time (4 hrs), adsorbent dose (1gm/L), as constant except varying the initial concentration of mercury (II) from 5-50 ppm.

ii) Effect of pH:

pH effect was studied by taking a specific concentration (25ppm), adsorbent dose(150mg), contact time (240mts), particle size (300 μ) and varying the pH values form 1-10 using dilute NaOH (or) HCl solutions.

iii)Effect of contact time

The studies were conducted by 150 ml of 25 ppm solution with 150mg of 300 μ size particles of the adsorbent at a pH 7 for a different time period of 30-360 mts.

2.7.3. Analytical procedure for the determination of mercury(II):

A suitable aliquot (up to 10 ml) containing not more than 10mg of mercury was transferred into a 25ml volumetric flask 5ml each of 0.05M EDTA, buffered potassium iodide and Rhodamine 6G solutions (1ml) were added and made up to the mark with water and the absorbance in 1cm cells was measured at 575nm with reference to a reagent blank. A calibration graph 5-50mg of mercury was prepared by following the above procedure and the concentration in the sample aliquot was established by reference to the calibration graph.

2.7.4. Procurement of adsorbent

Sphaeroplea (prawn pond algae) were locally collected, washed, dried and powdered. The algae were activated by acid digestion using 1N HCl for 2 hours at 80ºC and washed with distilled water dried in an air-oven at 120ºC for 4 hours. The powder was sieved to get various particle sizes such as 150, 300, 450, 600, 900, 1200, 1800 microns respectively.

3. RESULTS AND DISCUSSION

Water is one of the major elements essential for sustenance of all forms of life and is available in abundance in nature covering approximately three fourths of the surface of the earth. The chemical nature of water is one of the most important criteria that determines its usefulness for a specific need and as such not all the waters are fit for drinking; hence the problems of scarcity of drinking water.

The presence of mercury, in quantities in excess of limits is a serious matter of concern from a public health point of view. Mercury is considered as cumulative poison that usually affects the gastrointestinal track, nervous system and sometimes both. Mercury poisoning causes damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormal in pregnant women. Several methods are employed to remove Hg from the industrial effluent. Some of them are chemical precipitation, electro chemical methods, reverse osmosis, ion exchange and adsorption etc.

However, the above techniques are relatively expensive involving either elaborate and costly equipment or high cost of operation with ultimate disposal problems. Hence to curtail mercury pollution problem, the biomass obtained from prawn pond algae Sphaeroplea is used for the removal of mercury from the synthetic solution.

The influence of initial concentration, pH and contact time on the extent of bio-sorption has been evaluated. Batch technique was used to obtain the equilibrium data.

Calibration curve of mercury ion is shown in Figure 1 (Table 1)

Table 1 - Calibration curve of mercury ion is shown in

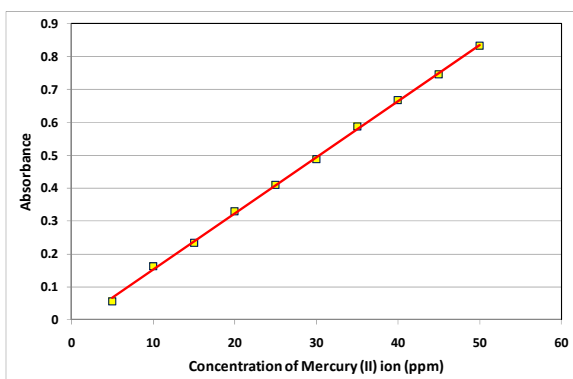| Initial concentration of Hg^{2+} ion (ppm)	Absorbance
5	0.056
10	0.163
15	0.234
20	0.329
25	0.409
30	0.488
35	0.587
40	0.667
45	0.746
50	0.833

Figure 1 - Calibration curve for mercury ion

3.1. Effect of initial adsorbate concentration

The adsorption capacity of natural and acid treated bio-mass algae was systematically studied by varying the initial concentration of mercury ions between 5 and 50 mg/L. The results are tabulated in Table 2 and 3 and Figure 2.

Table 2 - Effect of initial concentration of removal of mercury ion by natural algae: Volume of $[Hg^{2+}]$ ion = 150ml, pH = 7, Contact time = 240 mts, Particle size = 300μ, Adsorbent dose = 150 $C_e = [Hg^{2+}]_{eq}$, $q_{ad} = [Hg^{2+}]_{ad}$

Intial Concentration (ppm)	C_e	q_{ad}	% Removal
5	1.91	3.09	61.79
10	3.97	6.03	60.28
15	6.05	8.95	59.67
20	8.76	11.24	56.19
25	11.57	13.43	53.72
30	14.75	15.25	50.84
35	18.33	16.67	47.63
40	22.58	17.42	43.56
45	26.73	18.27	40.61
50	30.91	19.09	38.19

Table 3 - Effect of initial concentration on the extent of removal of mercury ion by acid treated alga: Volume of $[Hg^{2+}]$ ion = 150ml, pH = 7, Contact time = 240 mts, Particle size = 300μ, Adsorbent dose = 150mg $C_e = [Hg^{2+}]_{eq}$, $q_{ad} = [Hg^{2+}]_{ad}$

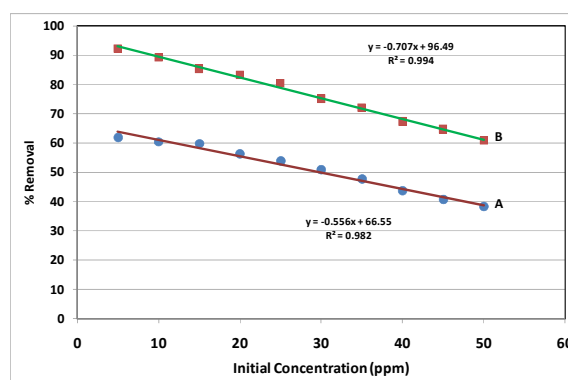| Intial Concentration (ppm)	C_e	q_{ad}	% Removal
5	0.39	4.61	92.21
10	1.08	8.92	89.25
15	2.21	12.79	85.32
20	3.35	16.65	83.26
25	4.89	20.11	80.41
30	7.46	22.54	75.13
35	9.81	25.19	71.98
40	13.07	26.93	67.32
45	15.89	29.11	64.68
50	19.58	30.42	60.83

Figure 2 - Effect of initial concentration on the removal of mercury ion by sphaeroplea alga: A: Natural alga, B: Acid treated alga

The percentage removal of mercury ion is a function of initial concentration and it varies directly with the concentration of the adsorbate. The bio-sorbents were active in removing Hg^{2+} ions from 92% to 60% (in acid treated alga) and 62% to 38% (in natural alga) when the initial concentration of mercury ion was increased form 5 to 50 mg/L with a contact time of 4hr with a adsorbent dose of 1gm/L at a pH of 7 with a particle size of 300 microns.

The decrease in the extent of percent removal of Hg^{2+}ions with increase in initial concentration may be due to reduction in immediate adsorption as a result of lack of available active sites for the high initial concentration of mercury ions.

Similar observations have been reported by Kannan et al [3] when they studied the removal of mercury by adsorption onto indigenously prepared dates nut and commercial activated carbons.

3.2. Effect of pH

The pH of the aqueous solution is an important controlling factor in the adsorption process and thus the role of hydrogen ion concentration was examined from solutions at pH values from 1 to 10 with 150ml of standard solution of 25 mg/L of mercury ion for a contact time of 240 minutes with a dose of 1gm/L having a particle size of 300 micron. The influence of pH on the sorption rate is shown in Figure 3 and Tables 4 and 5.
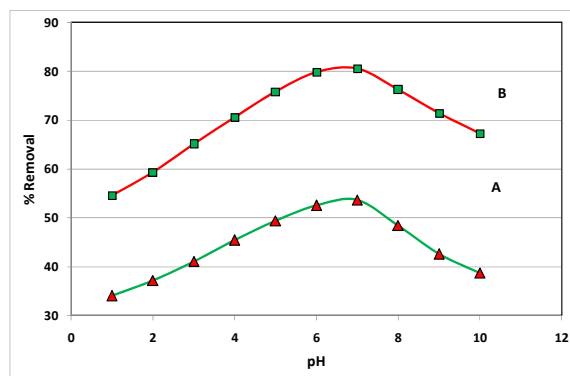

Figure 3 - Effect of pH on the removal of mercury ion by sphaeroplea algae: A: Natural alga, B: Acid treated alga

An increase in the extent of removal of mercury ions with decrease in the pH of the solution was observed. 54% and 80% removal was observed at pH 7 in the case of natural and acid treated Sphaerophlea algal biomass. Hence further studies were conducted at this pH. The percentage of adsorption increased almost linearly between 1 and 7 attaining a maximum removal at pH 7 in both the cases and then decreases (39% and 67%).

With increasing pH of the aqueous solution, the negative charge density of the adsorbent increase. Thus the uptake of the Hg^{2+} ions with increasing pH which

might be ascribed to an increasing negative charge density on the adsorbent surface and this also accounts for a downfall in the sorption of Hg^{2+} at low hydrogen ion concentration. Hence for the further studies a optimum pH of 7 is chosen.

Table 4 - Effect of pH on the extent of removal of mercury ion by natural alga: Volume of $[Hg^{2+}]$ ion = 150ml, $[Hg^{2+}]$ ion = 25 ppm, Contact time = 240 mts, Particle size = 300μ, Adsorbent dose = 150mg, $C_e = [Hg^{2+}]_{eq}$, $q_{ad} = [Hg^{2+}]_{ad}$

pH	C_e	q_{ad}	% Removal
1	16.48	8.52	34.06
2	15.69	9.31	37.21
3	14.72	10.28	41.11
4	13.65	11.35	45.41
5	12.64	12.36	49.42
6	11.87	13.13	52.53
7	11.58	13.42	53.68
8	12.88	12.12	48.46
9	14.35	10.65	42.59
10	15.31	9.69	38.76

Table 5 - Effect of pH on the extent of removal of mercury ion by acid treatedalga: Volume of $[Hg^{2+}]$ ion = 150ml $[Hg^{2+}]$ ion = 25 ppm, Contact time = 240 mts, Particle size = 300μ, Adsorbent dose = 150mg, $C_e = [Hg^{2+}]_{eq}$, $q_{ad} = [Hg^{2+}]_{ad}$

pH	Ce	qad	% Removal
1	11.35	13.65	54.61
2	10.16	14.84	59.36
3	8.73	16.27	65.09
4	7.35	17.65	70.58
5	6.05	18.95	75.81
6	5.04	19.96	79.83
7	4.86	20.14	80.58
8	5.94	19.06	76.25
9	7.13	17.87	71.47
10	8.17	16.83	67.31

An increase in the percent removal of mercury with increase in pH has been reported by Kadirvelu et al when they studied the removal of mercury form aqueous solutions onto an activated carbon derived from Eichhorina Crassipes [6].

3.3 Effect of contact time

The studies of effect of contact time were conducted by agitating 150ml of 25 ppm Hg^{2+} ion solution for a period of 60 to 480 mts with a adsorbent dose of 1gm/L and a particle size of 300 microns at a pH 7. The results were shown in Tables 6 and 7 and Figure 4.

Table 6 - Effect of contact time on the extent of removal of mercury ion by natural alga : Volume of $[Hg^{2+}]$ ion = 150ml, $[Hg^{2+}]$ ion = 25 ppm, pH = 7, Particle size = 300µ, Adsorbent dose = 150mg, $C_e = [Hg^{2+}]_{eq}$, $q_{ad} = [Hg^{2+}]_{ad}$

Contact time (mts)	C_e	q_{ad}	% Removal
60	14.22	10.78	43.12
120	13.63	11.37	45.49
180	12.69	12.31	49.22
240	11.71	13.29	53.17
300	11.42	13.58	54.32
360	10.77	14.23	56.92
420	10.28	14.72	58.87
480	9.61	15.39	61.58

Table 7 - Effect of contact time on the extent of removal of mercury ion by acid treated alga: Volume of $[Hg^{2+}]$ ion = 150ml, $[Hg^{2+}]$ ion = 25 ppm, pH = 7, Particle size = 300µ, Adsorbent dose = 150mg, $C_e = [Hg^{2+}]_{eq}$, $q_{ad} = [Hg^{2+}]_{ad}$

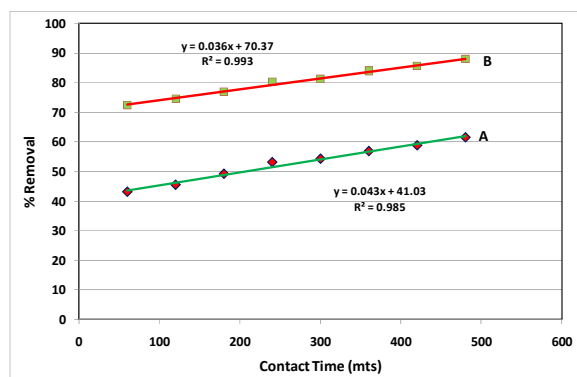| Contact time (mts)	C_e	q_{ad}	% Removal
60	6.89	18.11	72.41
120	6.37	18.63	74.52
180	5.78	19.22	76.89
240	4.94	20.06	80.23
300	4.71	20.29	81.19
360	4.03	20.97	83.88
420	3.61	21.39	85.56
480	3.02	21.98	87.92

Figure 4 - Effect of contact time on the removal of mercury ion by sphaeroplea algae: A: Natural alga, B : Acid treated alga

It is found that the removal of mercury ion increases with increases in the contact time to some extent. Further increase in contact time does not increase the update due to deposition of mercury ions on the available adsorption sites on adsorbent material. Nearly 53% and 84% of the ultimate adsorption capacity occurs within 240 mts of the contact time for the natural and acid treated alga.

The initial rapid adsorption subsequently gives way to a very slow approach to equilibrium and saturation is reached in 240 mts. For further optimization of other parameter the contact time 240 mts was considered as the equilibrium time corresponding to the adsorbate and adsorbent.

Kannan et al [3] have reported that the percentage removal of mercury increased with increase in the contact time.

4. CONCLUSION

To curtail mercury pollution problem, adsorbent based on Sphaeroplea algal biomass were tried for the removal of mercury ion form aqueous solution.

Dried and powdered biomass were activated with acid (1N HNO_3), alkali (1N NaOH) and washed thoroughly and dried in oven. The effect of initial concentration, pH and contact time was studied in batch experiments.

The percentage removal of mercury decreased with increase in the initial concentration due to the limited number of available active sites on the surface of natural and acid treated alga to accommodate higher concentration of mercury ions.

The effect of the pH indicated that the percentage removal increases with decrease in pH. At pH 7 the maximum removal of 60% of mercury is achieved in natural and 85% in acid treated alga.

The percentage removal of mercury increases with increase in contact time and availability of active sites. The maximum removal of mercury at pH 7 shows that 240mts is sufficient to remove above 85% of mercury.

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