Biosorption of Malathion pesticide using *Spirogyra* sp.

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Abstract— *The biosorption of Malathion from aqueous solution by green algal biomass was investigated. The green algae used were of the species Spirogyra and was collected from Neugal river near Sujanpur, Himachal Pradesh. Batch biosorption experiments were performed to examine the effect of contact time, pH, biomass concentration and initial Malathion concentration. The concentration of residual Malathion concentration after biosorption was determined using UV-Vis Spectrophotometer at a wavelength of 309 nm. The maximum adsorption was found to be at pH 7 after a contact time of 5 hours with initial Malathion concentration of 100 mg/L and biomass of weight 75 mg. The equilibrium biosorption data were analyzed using Langmuir and Freundlich isotherm. Freundlich isotherm was found to be more favorable than Langmuir isotherm.*

Keywords— ***algae, biosorption, isotherm, Malathion, pesticide.***

I. INTRODUCTION

The use of pesticide is essential for the modern agricultural practice. Pesticides not only kill unwanted pests and insects, they also increase the productivity of agriculture. In India, agricultural production increased by 100% while the cropping land increased by only 20% [1]. Pesticide residues that get released into the environment tend to stay in the environment for a very long time, and get accumulated throughout the food chain, making it hazardous to the environment. The U.S. Geological Survey conducted a study from which they reported that more than 90% of the water and fish samples that they collected from major rivers or water streams were contaminated with pesticides. The rivers and streams which were contaminated by pesticides were influenced by agriculture and urban land use [2]. Currently, India ranks 10th in the world pesticide consumption list [3] and the Indian agrochemical market is expected to reach U.S $ 6.3 billion by 2020 [4].

Pesticides are classified into many classes, out of which, organophosphates and organochlorines are deemed the most important ones. Malathion is an organophosphorus pesticide which is most commonly used in agriculture all over the world. It is used for killing insects on agricultural crops and stored products. It is also widely used for killing mosquitos in urban and residential areas. It is also used for the control of flies, household insects and head and body lice. In 2006, it was reported that approximately 15 million pounds of Malathion were used worldwide annually [5]. The Environmental Protection Agency has identified Malathion as a toxicity class III pesticide and a general use pesticide (GUP). Malathion interferes with the normal function of the nervous system and thus indirectly affects the function of other organs. The effect of exposure to Malathion on human health may include, but not limited to, difficulty in breathing, vomiting, diarrhoea, headaches, dizziness and loss of consciousness and death [6].

Several methods have been proposed for the removal/treatment of Malathion from raw water and wastewater such as electrocoagulation, advanced oxidation and coagulation/flocculation [7, 8, 9]. The limitations to these methods are that they are quiet expensive and the chemicals used for these methods require constant observation and it is preferable that they be handled by a skilled person. Adsorption with activated carbon is an easy and cost effective method for the removal of pesticides and has been extensively studied for the removal of Malathion [10- 11]. In recent years, studies about the removal of Malathion by biological materials have increased due to their easy availability, low cost and efficiency. Biosorption by activated sludge, isolated bacillus sp., *Rhizopus oryzae*, nanocellulose, algal biomass of *Chlorella vulgaris*, chesnut shells and the fungal biomass of *Phanerochaete chrysosporium* has been studied with positive results [12, 13, 14, 15, 16, 17, 18].

Either live or dead biomass can be used in biosorption process. Live biomass has been used for the removal of heavy metals in the past [19- 20]. The use of dead biomass is more desirable than the live ones as dead biomass do not require nutrients to sustain them and can be stored to be used later. While using live biomass, sorption as well as biodegradation may also occur and it is very difficult to distinguish which one of them has more contribution.

The present study investigates Malathion removal from aqueous solution by biosorption using green algal biomass of species Spirogyra, which is abundant in fresh water lakes and rivers. Laboratory batch experiments were carried out using a shaker-incubator at a constant temperature to determine the optimum contact time, pH, weight of biomass and initial Malathion concentration for maximum removal. Langmuir and Freundlich isotherms were used for determining the sorption capacity of *Spirogyra* sp.

II. MATERIALS AND METHOD

2.1 Malathion solution

Commercially available Malathion 50% E.C, Osothion, was used in this study.

2.2 Biomass

The green algae, Spirogyra sp., used in this study was collected from Neugal River near Sujanpur, located at 31.83ºN 76.50ºE, Himachal Pradesh. The algae was washed with distilled water to remove dirt and other impurities after which it was sundried for 6 hours and then it was kept in an oven for 48 hours at 130º C to make sure it was completely dead. The dead biomass was grounded using a pestle and mortar to get fine powder. The powdered biomass was kept in a crucible and stored in a desiccator until used.

2.3 Measurement of residual Malathion concentration

Pure solution of Malathion was scanned in an UV-Vis Spectrophotometer from Aligent Technology, Cary Series to determine the wavelength with maximum absorbance. Maximum absorbance was found at wavelength 309 nm. Using this wavelength, a standard curve of Malathion solution of known concentration (50 – 250 mg/L) was prepared. This data was used to determine the unknown concentration of residual Malathion concentration.

2.4 Batch Kinetic Study

Batch kinetic study was performed by taking 100 mL of Malathion solution in 250 mL Erlenmeyer flasks. Optimum removal of Malathion from the solution was determined based on contact time, pH, amount of biomass kept in contact with the pesticide solution and initial Malathion concentration. The flasks were kept in a shaker-incubator for a specific amount of time at 130rpm and the temperature of the incubator was kept at 27 ± 2º C. The pH of the solution was adjusted using 0.1M NaOH and 5% HCl. The final residual concentration of Malathion in the solution was determined using UV-Vis Spectrophotometer as mentioned before.

The amount of Malathion adsorbed by the algal biomass was calculated using the formula

$$Q_e = (C_0 - C_e)\, V/m \tag{1}$$

Where,

Q_e (mg/g) is the amount of Malathion adsorbed per unit weight of the algal biomass.

C_0 (mg/L) is the initial Malathion concentration.

C_e (mg/L) is the Malathion concentration at equilibrium

V (L) is the amount of Malathion solution.

m (g) is the amount of biomass used.

All tests were performed in triplets and their average was taken for the actual calculation.

2.5 Biosorption isotherm

To evaluate the biosorption performance, a graph between the sorbate in the solution and the amount of sorbate sorbed on the biosorbent is plotted. There are various isotherm models which have been proposed and used throughout the years. In this study, Langmuir and Freundlich isotherm are studied to evaluate the data.

The equation for Langmuir isotherm is

$$Q_e = Q_m b C_e / (1+b.C_e) \quad (2)$$

Where,

Q_e is the amount of Malathion adsorbed (mg/g)

Q_m is the maximum Malathion adsorbed per unit biomass (mg/g)

C_e is the equilibrium concentration of Malathion (mg/L)

b is the Langmuir equilibrium constant (L/mg) and it explains the affinity between the sorbent and sorbate..

The Langmuir isotherm equation can be arranged into linear form

$$C_e/Q_e = 1/b.Q_m + C_e/Q_m \quad (3)$$

Which can be further rearranged into?

$$1/Q_e = 1/b.Q_m\ C_e + 1/Q_m \quad (4)$$

A plot between $1/Q_e$ and $1/C_e$ will give intercept $1/Q_m$ and slope $1/b.Q_m$.

The Freundlich isotherm is described by the following equation

$$Q_e = k.C_e 1/n \quad (5)$$

Where,

k and n represents Freundlich constants. k indicates the adsorption/binding capacity (L/g) and n indicates the intensity of the adsorption i.e. the affinity between the sorbent and sorbate.

The linearized form of equation (4) can be written by taking logarithm on both sides

$$\ln Q_e = 1/n \ln C_e + \ln k \quad (6)$$

III. RESULTS AND DISCUSSION

3.1 Effect of contact time

After performing batch biosorption study, it was observed that with the increase in time, the percentage removal of Malathion increases. Highest Malathion removal was observed at 5 hours after which, the removal percentage remained constant. This can be explained by the fact that after 5 hours, all the active biosorption sites have been occupied by Malathion. The result of the contact time test is shown in Fig. 1.

3.2 Effect of pH

After performing biosorption test with different pH, it was found that highest amount of Malathion removal was achieved at pH 7, after which the removal percentage starts to decrease again, suggesting that at lower and higher pH, all the functional groups responsible for biosorption have bounded, thus resulting in lower biosorption. While, at neutral pH, the functional groups are free for biosorption. The result of Malathion removal with respect to pH is shown in Fig. 2.

3.3 Effect of biomass weight

Batch biosorption studies were done to determine the effect of weight of biomass made in contact with the Malathion solution for the removal of Malathion with varying weight of biomass. It was found that the removal of Malathion increased with increase in biomass concentration till 75 mg after which the removal decreased again, making 75 mg the optimum dose of biomass. This can be explained by the fact that with less amount of biomass, the amount of Malathion was much more such that there were not enough biomass surfaces where Malathion could bind on to. While at higher biomass concentration, all available sorption sites were not utilized causing agglomeration of the biomass which in turn decreases the amount of adsorption sites available. The result is shown in Fig. 3.

3.4 Effect of initial Malathion concentration

The biosorption process was found to be highly effected by the initial Malathion concentration. The result shown in Fig. 4 shows that Malathion removal decreases with increase in initial Malathion concentration. This is because with increase in Malathion concentration, there is not enough binding sites available for Malathion. And the Malathion molecules compete with each other for the available binding sites, thus reducing the biosorption efficiency.

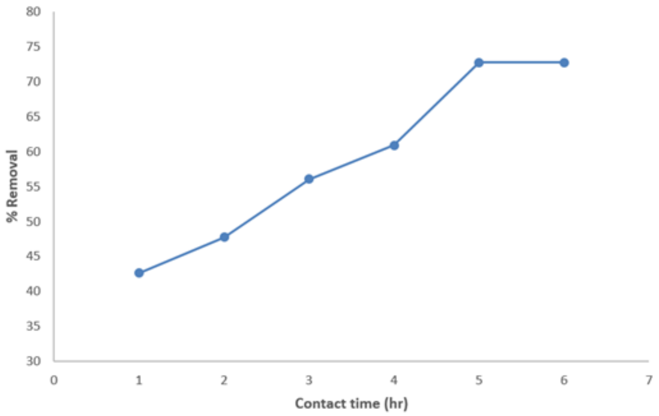

FIG. 1 EFFECT OF CONTACT TIME FOR THE REMOVAL OF MALATHION ON *SPIROGYRA* SP. BIOMASS

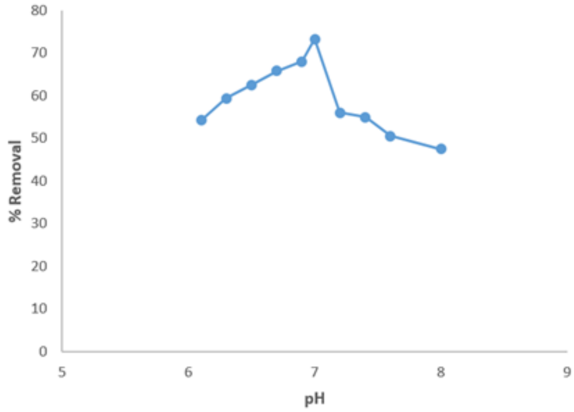

FIG. 2 EFFECT OF PH FOR THE REMOVAL OF MALATHION USING *SPIROGYRA* SP. BIOMASS

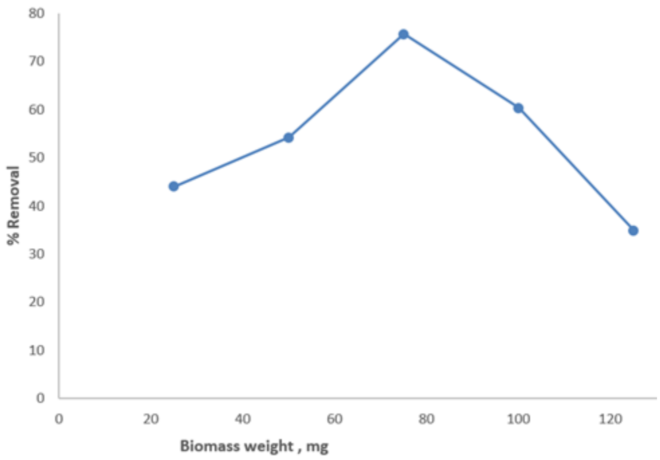

FIG. 3 EFFECT OF AMOUNT OF BIOMASS FOR THE REMOVAL OF MALATHION USING *SPIROGYRA* SP. BIOMASS

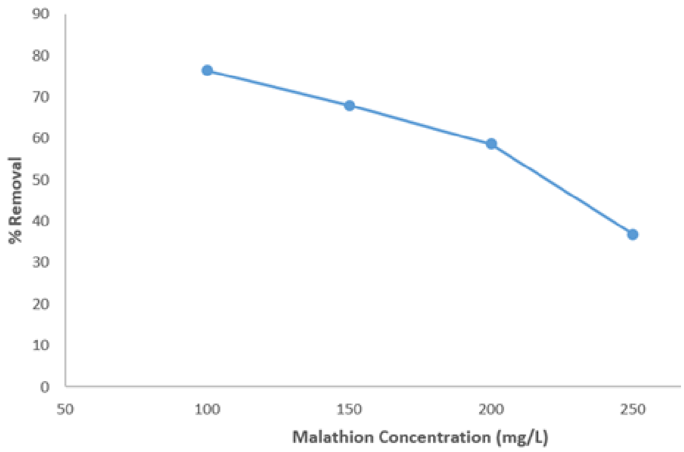

FIG. 4 EFFECT OF INITIAL MALATHION CONCENTRATION FOR THE REMOVAL OF MALATHION USING *SPIROGYRA* SP. BIOMASS

3.5 Biosorption isotherm analysis

For the isotherm study, 100ml of Malathion solution was taken in 250ml Erlenmeyer flasks with different initial Malathion concentration ranging from 50mg/L to 250mg/L. After preliminary kinetics study, it was found that equilibrium was reached at 5 hours. The solution was made in contact with constant amount of biomass (75mg) and the pH was fixed at 7. From the results, a graph between $1/C_e$ and $1/Q_e$ was plotted for Langmuir isotherm model (Fig. 5) and between ln C_e and ln Q_e for Freundlich isotherm (Fig. 6). The coefficient of correlation for Freundlich was found to be higher than that of Langmuir isotherm indicating that the biosorption follows Freundlich isotherm model. The sorption following Freundlich isotherm can mean that sorption occurred at heterogeneous surface or that the binding sites on the Spirogyra sp. have different affinities for the Malathion molecules.

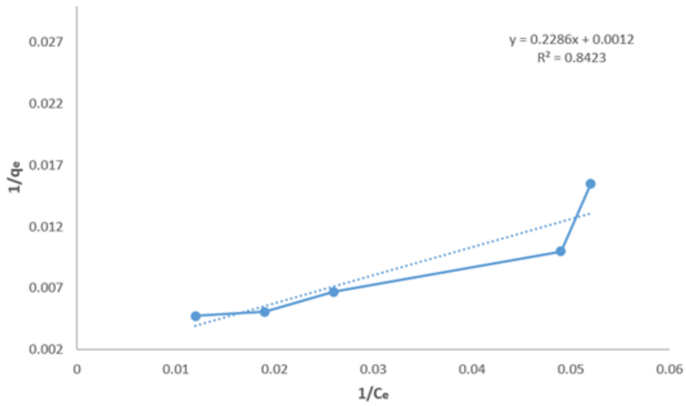

FIG.5 LANGMUIR ISOTHERM MODEL FOR THE REMOVAL OF MALATHION USING *SPIROGYRA* SP. BIOMASS

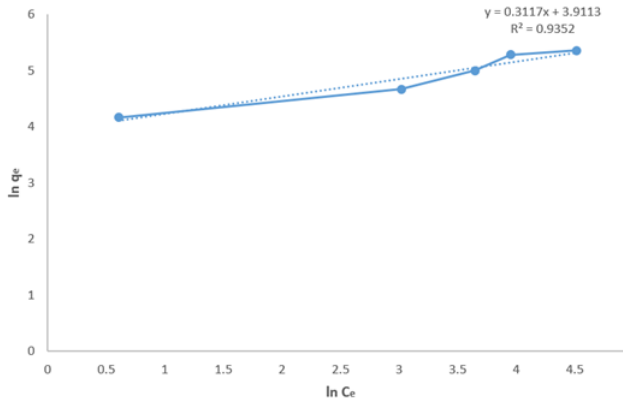

FIG. 6 FREUNDLICH ISOTHERM MODEL FOR THE REMOVAL OF MALATHION USING *SPIROGYRA* SP. BIOMASS

The values of Langmuir and Freundlich constants and their coefficient of correlation are shown in TABLE 1.

TABLE 1
R^2 AND CONSTANTS FOR LANGMUIR AND FREUNDLICH ISOTHERM

Langmuir			Freundlich		
Q_m	b	R^2	1/n	k	R^2
833.3 mg/g	0.00525 L/mg	0.8423	0.3117	49.96 $(mg/g)(L/mg)^{1/n}$	0.9352

IV. CONCLUSION

Malathion removal from aqueous solution by biosorption using Spirogyra sp. was studied. The residual Malathion concentration was determined using UV-Vis spectrophotometer. It was found that 76.34% of Malathion was removed from initial Malathion concentration of 100mg/L when the initial pH was kept at 7, using biomass concentration of 75mg and a contact time of 5 hours. Biosorption isotherm study showed that Freundlich isotherm was found to fit the experimental data more than Langmuir isotherm with R^2 value at 0.9352 indicating that sorption occurred on heterogeneous surface. Further studies can be done by pre-treating the biomass to see if Malathion removal increases with it.

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