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Removal of Arsenic from aqueous solutions using *Turbinaria vulgaris sp.* as biosorbent

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ABSTRACT

Biosorption of heavy metals is an effective and cheapest technology for the treatment of industrial wastewaters. The removal capacity of Arsenic from aqueous solutions through biosorption using turbinaria vulgaris sp. was studied in batch experiments. Parameters like contact time, metal ion concentration, biosorbent dosage, pH were studied at initial concentration 20,40,60,80,100mg/l. The experimental results were analysed by Langmuir, Freundlich models. Biosorption kinetic data were fitted with the pseudo-second-order kinetic model. The rate constant, the initial biosorption rate, and the equilibrium biosorption capacity were determined.

Keywords: Arsenic, Turbinaria vulgaris sp., Biosorption, Isotherm models, Kinetic models.

I. INTRODUCTION

Copper smelting generates large amount of wastewater containing considerable amounts of inorganic compounds such as heavy metals and arsenic species. These wastewaters origin from sulphuric acid plants, which treat the SO_2 containing gases from the smelter. In order to maintain a high quality of fresh water resources, these effluents have to be treated before the water can be returned to the ecosystems. Existing treatment methods such as sulphide or hydroxide precipitation create sludge that is difficult to handle. Furthermore, these methods consume considerable amounts of reagents in order to precipitate, coagulate and flocculate the contaminants. During the last decades, the use of biosorbents has become interesting due to high adsorption capacities, low costs and regenerability of the sorbent. Algae have been used for pharmaceutical reasons for detoxification of heavy metals in the human body due to a very efficient adsorption of the contaminants, and this effect could be used to remove heavy metals from industrial wastewaters. Different algae have been applied to wastewater treatment during the last decade. One of the interesting algae that could be used to remove heavy metals from these contaminated waters is the turbinaria vulgaris. The objective with this work is to test the sorption capacities and kinetics of arsenic(V) of air-dried and size reduced algae turbinaria vulgaris sp.. It will be analysed if the biosorption of arsenic follows the second-order Lagergren model, which often can be used to simplify the sorption kinetics. Finally, it will be evaluated if either the Freundlich or Langmuir isotherms can describe the arsenic biosorption capacity of turbinaria vulgarsi sp[1] .

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II. EXPERIMENTAL PROCEDURE

2.1 Preparation of biomass

The turbinaria vulgaris sp. used in the present survey were gathered from the suryalanka beach, Bapatla, Andhra Pradesh, INDIA. The collected algae were washed with deionized water several times to get rid of unwanted material. The washing procedure was kept till the wash water contains no dirt. The washed algae were then totally dried in sunlight for 10 days. The dried leaves were then cut into small pieces and powdered using domestic mixer. In the present study the powdered materials in the range of 75-212 μm average particle size were then immediately used as biosorbent without any pre-treatment.

2.2 Preparation of stock solution

Arsenate solution was prepared by dissolving solid $Na_2HAsO_4$7H2O in distilled water. Ionic strength of solutions was adjusted by adding (0.1N) HNO_3 and(0.1N) NaOH were used for pH adjustment. All chemicals used in this work were of analytical grade[2].

2.3 Biosorption Experiments

Arsenic removal capacity of turbinaris vulgaris was investigated by varying pH, initial arsenic ions concentration, biomass dosage and, temperature, while keeping the volume of reaction mixture as 30ml. Mixing was carried out in orbital shaker at 120 rpm. Samples were collected and filtered using What man filter paper. Residual arsenic in solution was measured using Atomic Absorption Spectroscopy. Triplicate experiments were conducted and the mean values have been recorded. Blank experiments were also run to ensure biosorption.

III. RESULTS AND DISCUSSION

3.1 Effect of pH:

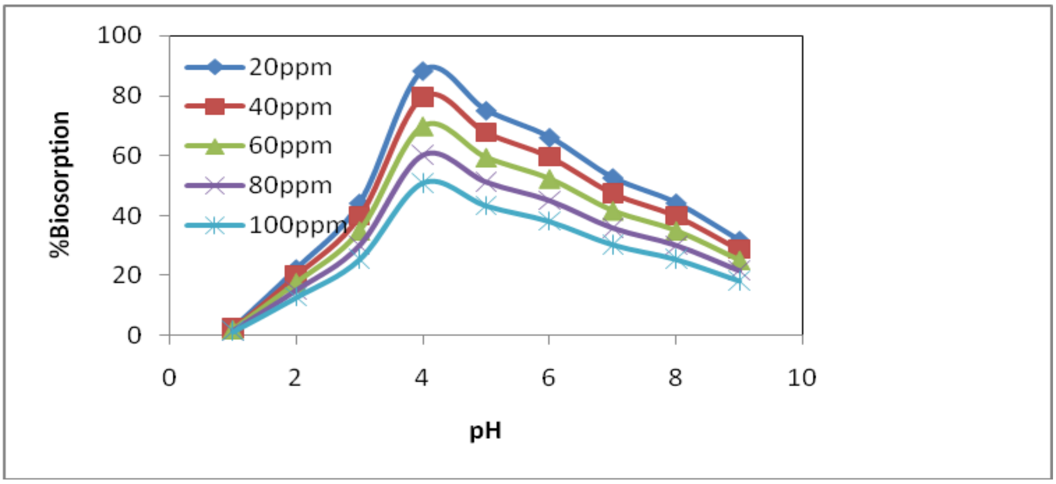

Fig1: Effect of pH on arsenic removal by *turbinaria vulgaris sp.* for 20, 40, 60, 80, 100mg/l. metal and 0.1g/30ml.of biosorbent concentration.

The variation of pH of metal solution is highly effected on the biosorption process for removal of metal ions from aqueous solutions using turbinaria vulgaris sp. as a biosorbent. This parameter is directly effects the surface charges of the biosorbent as well as the degree of ionization of different metal ions in the aqueous solution. The effect of pH on biosorption of arsenic at constant temperature (303 K) and time of agitation 60 min is shown in Fig. 1. The maximum removal of efficiency 88.31% is obtained at pH 4.0.

3.2 Effect of contact time

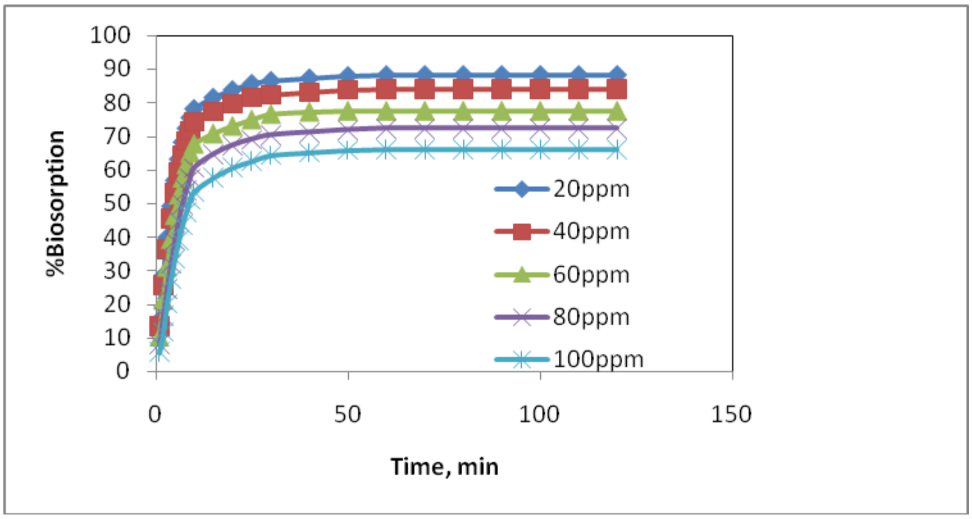

Fig. 2: Effect of contact time on arsenic removal by *turbinaria vulgaris sp.* for 40, 60, 80, 100mg/l metal and 0.1g/30ml.of biosorbent concentration.

The biosorption experiments were conducted for different lead concentrations from 20 mg/l- 100 mg/l with the function of agitation time and biosorption capacity of turbinaria vulgaris sp. are demonstrated in Fig.2. The adsorption effectiveness of arsenic ions increases gradually with increasing contact times and reaches equilibrium at around 60 min, at which point the maximum amount arsenic is removed from the solution.

3.3 Effect of initial metal ion concentration

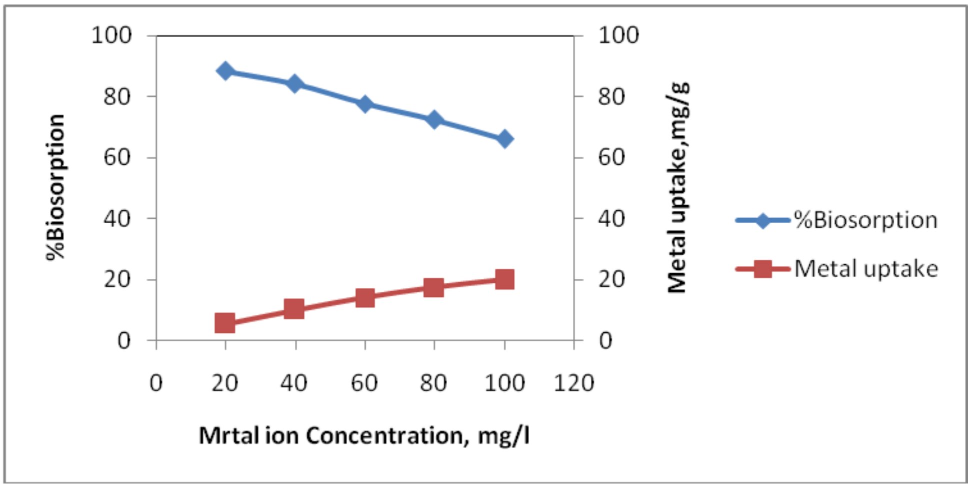

Fig. 3: Effect of metal ion concentration on biosorption capacity of arsenic by *turbinaria vulgaris sp.* of 0.1g/30ml of biosorbent concentration

The Fig.3. Demonstrates the biosorption behavior by using turbinaria vulgaris sp. biosorbent at the different solute concentration in stock solution from 20 mg/l -100mg/l, optimum pH 4.0, agitation time 60 min, the weight of turbinaria vulgaris sp. biosorbent is 0.1 grams and the temperature is 303K. The outcomes got from the data, investigated that the biosorption efficiency has declined from 88.31 % - 66.08% and the amount of arsenic deposited on the surface of the turbinaria vulgaris sp. biosorbent is increased from 5.29mg/g-19.82 mg/g with increases solute concentration.

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3.4 Effect of biosorbent dosage:

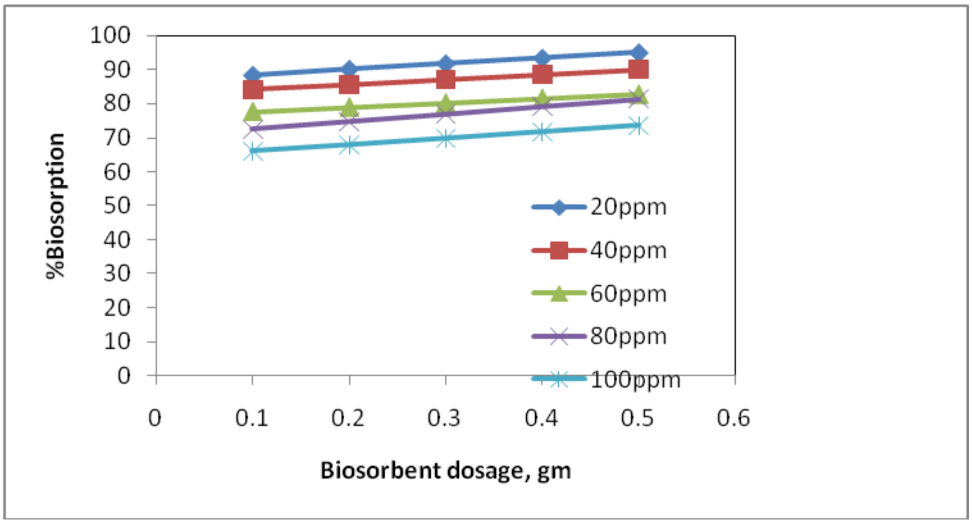

Fig. 4: Effect of Biosorbent dosage on arsenic removal by *turbinaria vulgaris sp.* for 20, 40, 60, 80, 100 mg/l metal and 0.1 to 0.5 g/30 ml of biosorbent concentration.

3.5 Equilibrium modeling:

A. Langmuir Isotherm

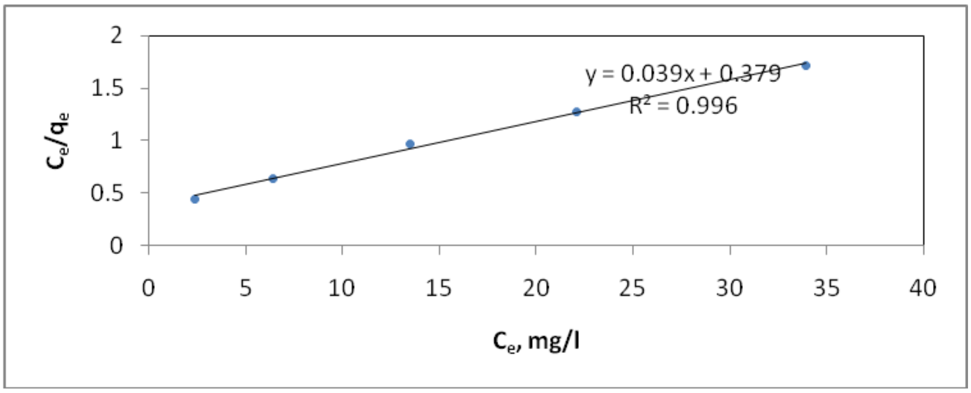

Fig. 5: Langmuir biosorption isotherm at 0.1g/30ml of biosorbent concentration.

Equilibrium studies are carried out to predict maximum arsenic removal by turbinaria vulgaris. Experiments were conducted at 20mg/l by fixing other parameters as constant. Langmuir and Freundlich models were used in establishing equilibrium relation between arsenic ions biosorbed onto the turbinaria vulgaris (q_e) and residual arsenic ions in solution (c_e). Langmuir isotherm has been extensively used for dilute solutions in following linear form[3]

$$\frac{C_e}{q_e} = (\frac{C_e}{a}) + \frac{1}{ab} \qquad (1)$$

where, 'a' is maximum metal uptake per unit mass of adsorbent to form complete monolayer and 'b' represents the affinity of binding sites. The plot of (c_e/q_e) against (c_e) indicates the applicability of this model. From the graph equilibrium data were well fitted by Langmuir model.

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B. Freundlich Isotherm

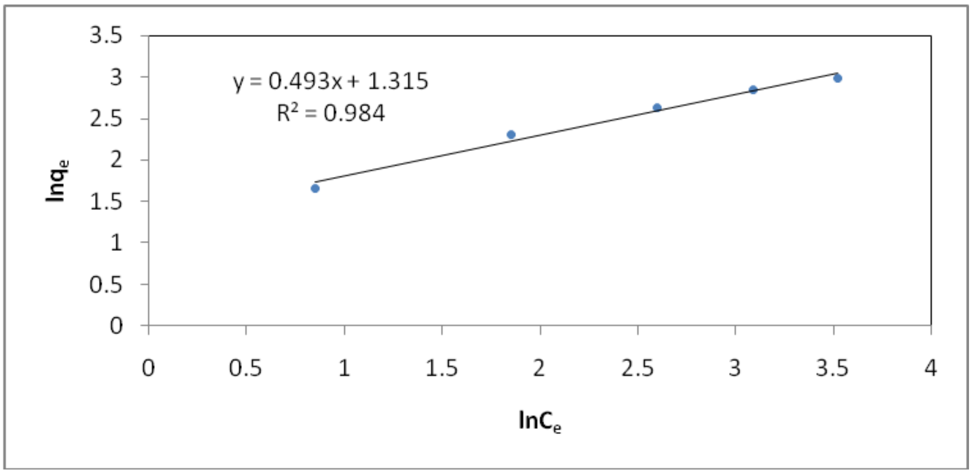

Fig6: Freundlich biosorption isotherm at 0.1g/30ml of biosorbent concentration

Freundlich model can be described by the equation given below[4]

$$q_e = K_f C_e^{1/n} \qquad (2)$$

where, the value of k_f and n are indicators of biosorption capacity and intensity. The linear plot of log (q_e) against log (c_e) describes the fitness of the this model.

3.6 Kinetic modeling

A. The Pseudo First-Order Lagergren Equation

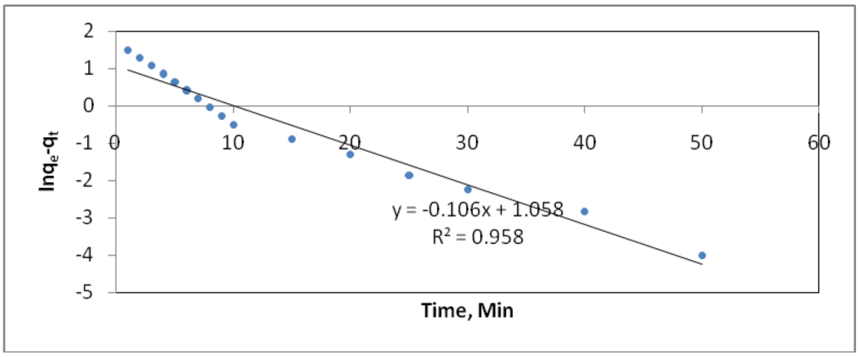

Fig. 7: pseudo first order for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

Lagergren equation or pseudo-first order reaction is mathematically expressed as[5]

$$\frac{dq}{dt} = K_1(q_e - q_t) \qquad (3)$$

where q_e is the amount of metal ion adsorbed on biosorbent at equilibrium (mg g^{-1}), q_t the amount of metal ion adsorbed on biosorbent at time ‘t’ (mg g^{-1}) and k_l is Lagergren constant (min-1). Integrating the above equation and transforming to log scale

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (4)$$

Linear plot of log(q_e _ q_t) against time indicates whether this kinetic model is applicable or not for biosorption process.

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B. The Pseudo-Second Order Equation

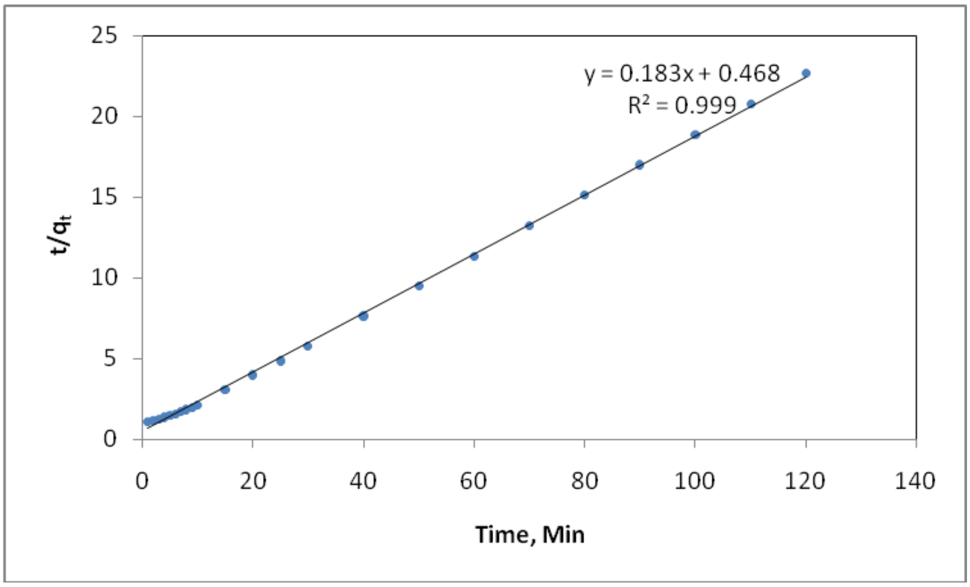

Fig. 8: pseudo second order for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

3.7 The pseudo second order equation is expressed by the following equation[6]

$$\frac{dq}{dt} = K_2 (q_e - q_t)^2 \qquad (5)$$

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^{\ 2}}\right) + \frac{t}{q_e} \qquad (6)$$

Where q_e = amount of adsorbed metal ion on biosorbent at equilibrium (mg g^{-1}), q_t = amount of adsorbed metal ion (mg g^{-1}) on biosorbent at time'tʼ, k_2 = second order rate constant (g mg^{-1} min^{-1}). A linear plot of t/q vs. t indicates whether this model of biosorption is applicable for this case or not.. From the graph kinetic data were well fitted by pseudo second order model.

IV. CONCLUSION

Biosorption potential of biomass prepared from turbinaria vulgaris sp. for the removal of arsenicfrom aqueous metal solutions was investigated. Batch mode experiments were conducted by varying one parameter at a time to find out effect of individual process parameter and it was found that the process is strongly affected by following independent factors i.e., initial metal ion concentration, biomass dosage and the pH of the solution. Turbinaria vulgaris sp. was found to be very competent in removing arsenic ions (88.31%) and also the maximum removal rate was achieved within 60 min of contact time at optimum pH of 4. The equilibrium data was well described by Langmuir model. Biosorption kinetic data were fitted with the pseudo-second-order kinetic model.

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