Research Article

Biosorption of Mn (II) by *Spirogyra verrucosa* collected from Manganese Mine Water

S. R. Bansod[1*] and P. B. Nandkar[2, 3]

[1]Department of Botany, Shri Shivaji Arts, Commerce & Science College, Akola, Dist. Akola (M.S.), India.

[2]Department of Botany, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur (M.S.)India.

Abstract

Mining industries frequently generates acid mine drainage (AMD) either by its operating or abandoned mines which are often characterized by an elevated levels of certain heavy metals, sulphate, low pH and some other toxic impurities in mine water creates environmental and ecological problems. Present study planned to suggest role of alga *Spirogyra verrucosa* in Manganese (Mn) removal by biosorption process from the mine water of Manganese mines of Nagpur District, Vidarbha Region, Maharashtra. The biosorption of Mn(II) ions from aqueous solution by using dead green algal (*S.verrucosa*) biomass was investigated by studying effect of pH, temperature, quantity of biosorbent, contact time as well as initial metal ion concentration. The optimized values obtained with respect to these parameters clearly indicates that pH 5, temperature 30°C, biosorbent quantity 1.0 gm/l, contact time 120 min. and initial metal ion concentration 50mg/l were the basic requirement for the biosorption of Mn(II) ions by dead algal biomass. Also, the biosorption kinetic and isotherm modeling applied to the equilibrium data for biosorption of Mn(II) ions onto alga reveals the fitness of the pseudo-second-order rate expression (R^2=0.994) as well as the suitability of Langmuir (R^2=0.859) and Freundlich (R^2=0.761) isotherm models with an indication of the applicability of this metal ion-dried algal system for removal of Mn(II) ions in a monolayer biosorption as well as heterogenous surface conditions. However, comparatively biosorption equilibrium was better described by Langmuir isotherm model with monolayer biosorption capacity of *S.verrucosa* biomass 21.80 mg/g. Also, the maximum removal 40.66 mg/g (80.20%) of Mn(II) ion by alga under optimized conditions promises the potential use in mine water treatment technology.

Introduction

With the progress of industrialization and human activities, the threat of the discharge of waste and wastewater containing heavy metals to environment by various industries has now tremendously increased (Volesky, 2001). Mining industries frequently generates acid mine drainage (AMD) either by its operating or abandoned mines which are often characterized by an elevated levels of certain heavy metals, sulphate, low pH and some other toxic impurities in mine water (Modis *et al.,* 1998) and can cause pollution of surface and ground water as well as surrounding land if not controlled in due course of time.

Environmental contamination due to heavy metals leads to the phenomenon of accumulation in food chain and becomes a permanent burden on ecosystems (Bailey *et al.,* 1999) causing serious hazard to human health and other forms of life. However relevant national and international standards and guidelines have been prepared by various agencies for the purpose of environmental
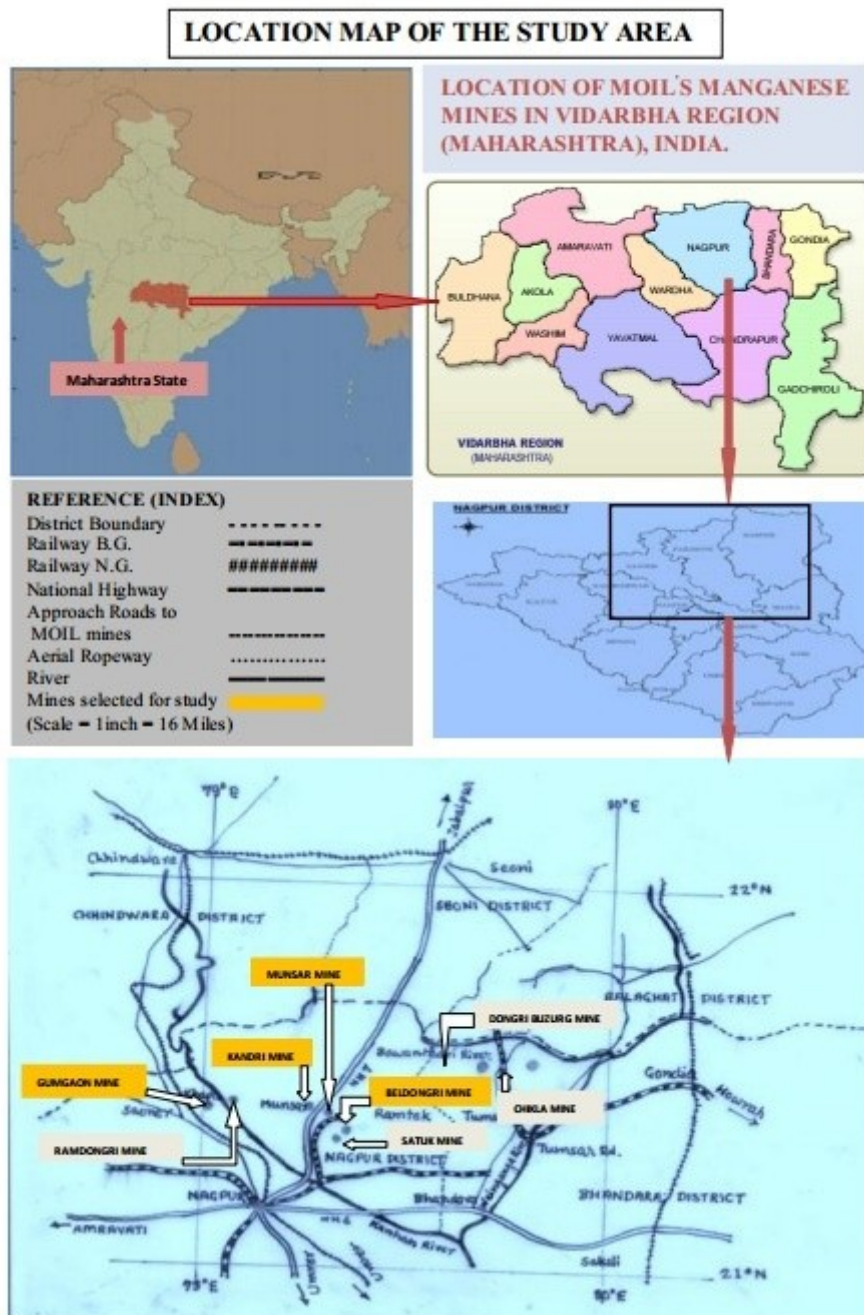
Map 1. Location map of the study area (Source: www.google.com, www.moil.nic.in)

protection with respect to the metal bearing effluents discharge in to water bodies and natural streams. Different technologies on assessment of acid mine drainage were proposed by several researcher (Moreno *et al.,* 2001; Mohan and Chander, 2001; Brenner, 2001 and Saha *et al.,* 2002; Morgan *et al.,* 2004).

Conventional technologies currently available for removal of heavy metals are quite expensive and not much effective (Volesky, 2001) and also generates toxic byproducts (Aksu *et.al.,* 1998) questioning their environmental friendly applications as well as techno-economic feasibility (Sandau *et al.,* 1996). Therefore efficient, inexpensive and environment friendly technologies are in urgent need to control heavy metal contamination in wastewaters at discharge point to acceptable or permissible level (Matheickal and Yu, 1996). Biosorption seems to be a novel, competitive, effective and cheap approach to fulfill the requirements (Volesky, 2001) and has certain advantages than the conventional type of technologies used so far (Kratochvil and Volesky, 1998; Ahalya *et al.,* 2003). Many microorganisms like algae, bacteria, fungi and yeast has been used in biosorption process to remove metal ions because of their remarkable advantages over conventional methods (Arica *et al.,* 2001) and capability to bind with metal ions from aqueous solutions as well (Dursun, 2006; Wang and Chen, 2006; Volesky, 2007).

The present investigation was undertaken to assess and optimize Mn (II) sorption capacity of alga *Spirogyra verrucosa* (Guiry and Guiry, 2014)
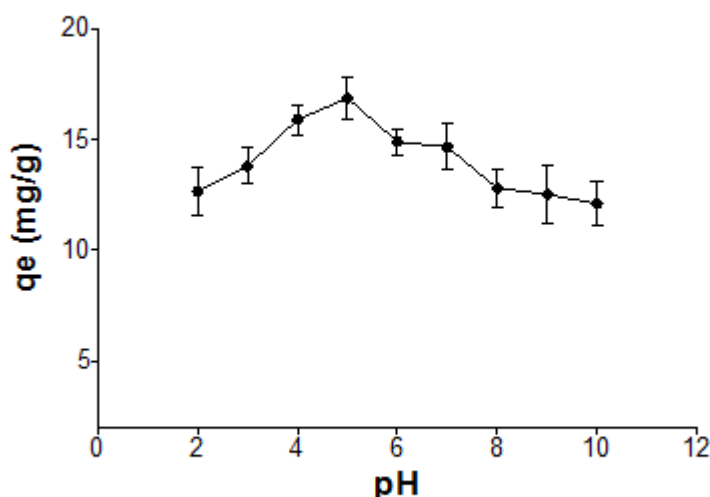
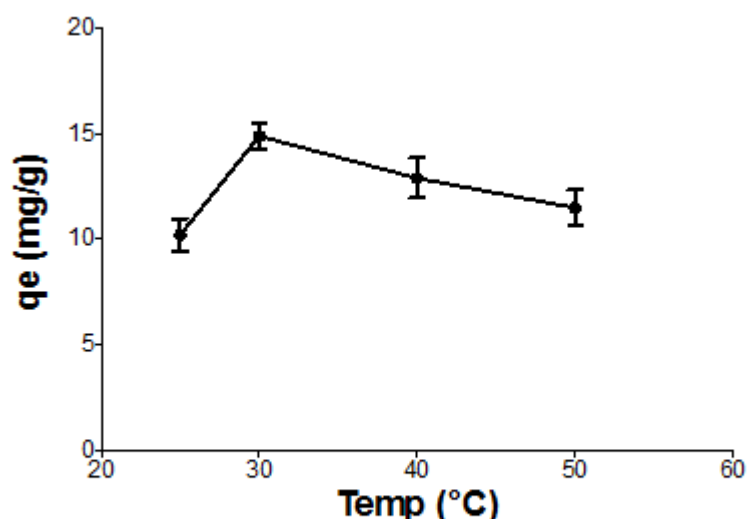Fig: 1.Effect of pH on equilibrium Mn (II) sorption capacity of *Spirogyra verrucosa*
(n=3 ± SD).

Fig.: 2. Effect of temperature on equilibrium Mn (II) sorption capacity of *Spirogyra verrucosa*.Data points are mean of three independent experiments (Mean ±SD).

collected from Mn contaminated (Bansod and Nandkar, 2015) Manganese mine water. However, many algal systems have been used in order to remove metal ions from different contaminated sites although there is lack of information available on the biosorption of metal ions by algal biomass from Manganese mine water. Optimization of pH, contact time, temperature, biosorbent quantity and initial metal ion concentration of Mn(II) sorption capacity of alga was studied. Suitability of both Langmuir and Freundlich adsorption isotherm for equilibrium isotherm modeling between unadsorbed and adsorbed Mn(II) ions was studied. Kinetic study was also applied to the Mn(II) ion biosorption data

for the validity of rate expression model. Findings of the investigation would be helpful during planning and strategy development in designing mine water treatment system for the mining sites in near future.

2. Materials and Methods

2.1. Collection of algal material

Four Manganese mines (Kandri, Mansar, Beldongari and Gumgaon) of MOIL (Manganese Ore India Limited) Nagpur District, Vidarbha Region, Maharashtra, India (Map 1) were selected and surveyed for algal material collection from open pit pond mine water. In present investigation
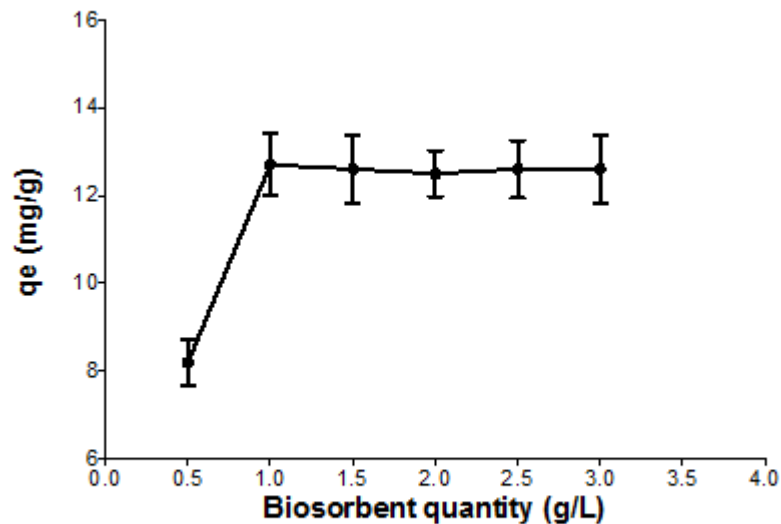
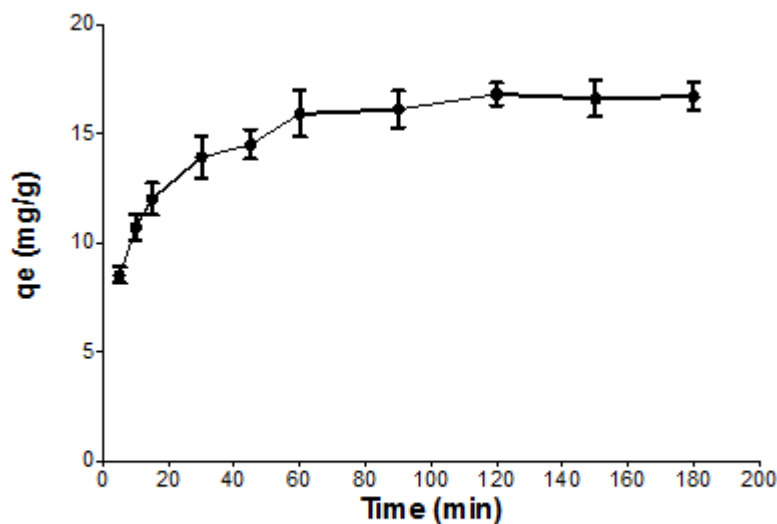Fig. 3. Effect of biosorbent quantity on equilibrium Mn (II) sorption capacity of *Spirogyra verrucosa* (n=3 ± SD).

Fig. 4. Effect of contact time on equilibrium Mn (II) sorption capacity of *Spirogyra verrucosa* (n=3 ± SD).

alga *S. verrucosa* was found to be present abundantly forming mats on the mine water which contains an elevated level of Manganese concentration and hence used as a biosorbent.

2.2. Preparation of biosorbent

The harvested algal biomass from mine water was initially washed thoroughly with distilled water to remove all the extraneous material attached to it and placed on a filter paper/ blotting paper to reduce the water content before treating the biomass with 0.02 M HNO_3. Then it was dried overnight at 50°C until a constant weight was obtained and the final weight of the biosorbent was recorded. The biosorbent were

then crushed and passed through a 300 nm sieve to attain uniform particle size and used for further studies.

2.3. Preparation of synthetic solution

Synthetic stock solution of Manganese was prepared by dissolving 3.076 grams of $MnSO_4$ $7H_2O$ (Analytical grade) in 100 ml of double distilled water to obtain concentration of 1000 mg/l as a stock solution and serial dilutions from of this stock solution were prepared to obtain10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/l concentration of Mn(II) ion solution. The desired pH were maintained by using buffer solutions (KCl-HCl buffer for pH 2, citric acid- sodium
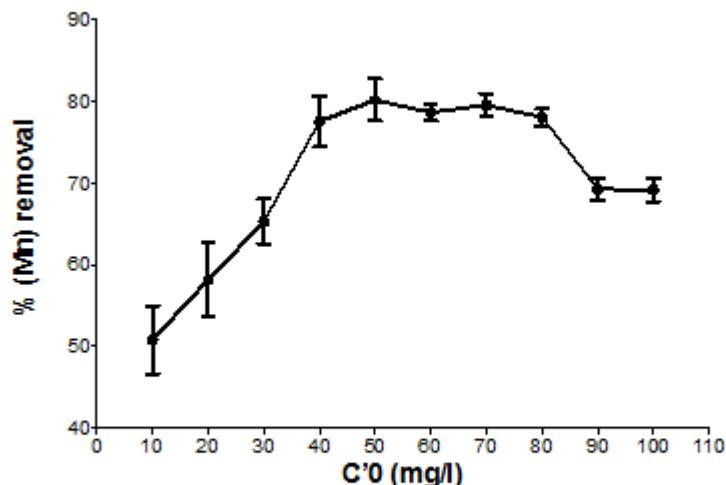
Fig. 5. Equilibrium adsorption quantities and % removal of Mn (II) ions at different concentration by *Spirogyra verrucosa* (n=3 ± SD).
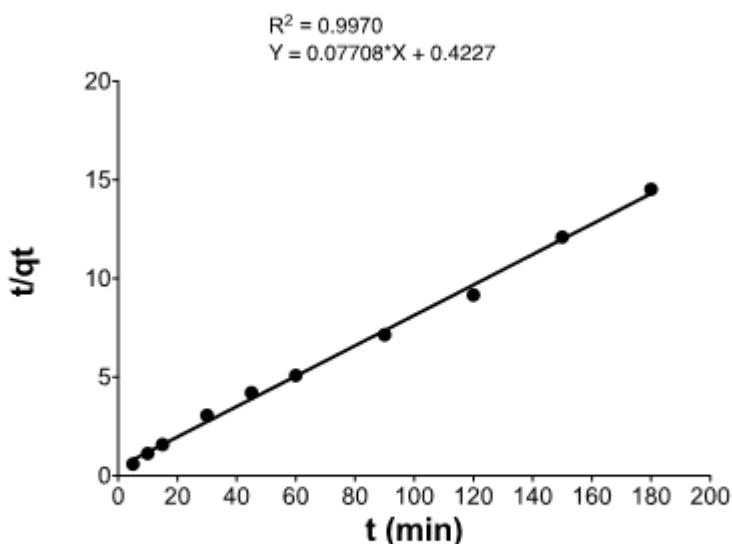

Fig. 6. Pseudo-second order kinetic plot of biosorption of Mn (II) ions onto *Spirogyra verrucosa.*

citrate buffer for pH 3-5, Na_2HPO_4-NaH_2PO_4 buffer for pH 6-8 and glycine-NaOH buffer for pH 9-10) in all experiments.

2.4. Batch mode studies

The experiments for the batch mode studies were carried out in 250 ml Erlenmeyer flasks with dry algal biomass of 0.5 g /100ml aqueous solution. The flasks filled with Mn(II) ion concentrations ranging from 10 mg/l to 100 mg/l were kept at 25°C on a rotary shaker at 200rpm. Evaluation of the maximum biosorption capacity of the alga was carried out on optimization of pH (2-10), temperature (25-50°C), contact time (5-180 min.) by using 100ml of 20mg/l concentration of Mn(II) metal ion with an algal biomass dose of 0.5g (dry weight) per flask except for optimization of biosorbent quantity and initial metal ion concentration the range of algal dose (0.5-3 g) and initial metal ion concentration (10-100mg/l) were used respectively. Blanks were also considered for each treatment in the experiments.

2.5. Metal Analysis

All the samples were tested for metal ion concentration by using Atomic Absorption Spectrometer (AAS) at Department of Chemistry, Laxminarayan Institute of Technology, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur.

Table 1. Mean (n=3 ± SD) of equilibrium biosorption quantities and % removal of Mn (II) ions at different concentration by the algal biomass *Spirogyra verrucosa*.

| C'$_0$ (mg/l) | C$_0$ (mg/l) | *Spirogyra verrucosa* | |
		qe (mg/g)	% removal
10	9.04 ±1.26	4.59 ±0.65	50.80 ±7.25
20	19.2 ±0.62	11.17 ±1.51	58.20 ±7.88
30	29.4 ±0.75	19.19 ±1.40	65.30 ±4.76
40	39.6 ±1.85	30.72 ±2.16	77.60 ±5.46
50	50.7 ±0.72	40.66 ±2.26	80.20 ±4.46
60	61.3 ±1.57	48.24 ±1.08	78.70 ±1.76
70	69.6 ±2.10	55.40 ±1.73	79.60 ±2.49
80	78.4 ±1.34	61.23 ±1.47	78.10 ±1.88
90	89.2 ±1.05	61.81 ±2.00	69.30 ±2.24
100	102 ±3.00	70.58 ±2.55	69.20 ±2.50

C'$_0$ = Initial calculated Mn(II), C$_0$ = Initial estimated Mn(II)

Table.2. Pseudo-second order kinetic constants for the biosorption of Mn (II) ions by the algal biomass *Spirogyra verrucosa*.

| Biosorbent | Mn(II) | | | |
	q$_{eq}$ Exp. (mg/g)	q$_{eq}$ Cal. (mg/g)	K$_2$ (g/mg min.)	R^2
Spirogyra verrucosa	14.9	14.49	0.010	0.994

Table.3.Langmuir and Freundlich Isotherms' constants for the biosorption of Mn (II) ions by the algal biomass *Spirogyra verrucosa*.

| Biosorbent | Mn(II) | | | | | |
| | Langmuir parameters | | | Freundlich parameters | | |
	q$_{max}$ (mg/g)	b (L/mg)	R^2	n	K$_f$	R^2
Spirogyra verrucosa	21.80	48.52	0.859	1.75	89.94	0.761

2.6. *Mathematical Modeling and Interpretation of Data*

The data collected as a result of biosorption studies were tested by conventionally used Langmuir and Freundlich isotherms for adsorption. In addition, kinetic examination was also carried out for the validity of rate expression model.

2.7. *Statistical analysis*

The data obtained in triplicate were analyzed by SPSS statistical package (Window version 17) and Microsoft software Excel 2007 and represented as mean values with standard deviation in figures and tables.

3. Results and discussion

Biosorption of Mn(II) was studied by considering the importance of pH, temperature, contact time, biosorbent quantity and initial metal ion concentration as an influencing factors in the process. The biosorption data were fitted to different isotherms and kinetic models.

3.1. *Effect of pH on Mn(II) biosorption*

The removal of Mn(II) ions by alga was found to be pH dependent at an initial calculated metal ion concentration of 20mg/l. Acidic pH range (4-6) was favored by alga for equilibrium Mn(II) sorption and maximum biosorption 16.8 mg/g was recorded at pH 5.0 (Fig. 1). Decrease in biosorption of Mn(II) ions by alga was observed at increased pH values. However, not such variations were noted in Mn(II) concentration of blanks readings (without alga) as a control.

Biosorption of metal ions have been reported pH dependent in several studies (Sheng *et al.,* 2004, Romera *et al.,* 2006). Maximum biosorption of metal ions at low pH range (4-6) seems to be contributed by positively charged algal surface and generation of isoelectric point for algal biomass at pH 5.0 (Crist, *et al.,* 1981) as well as
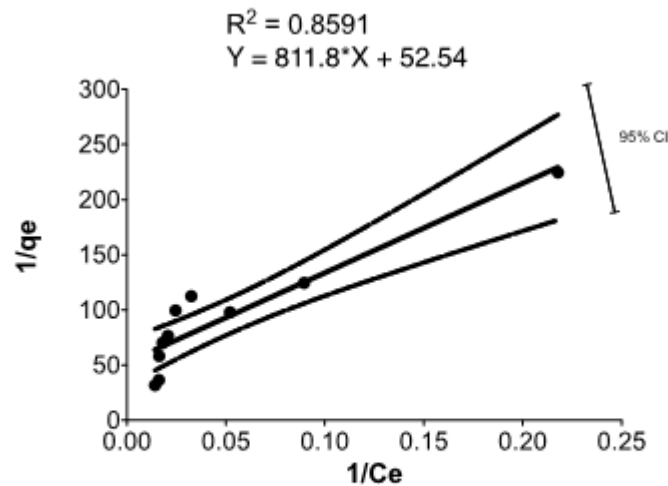
Fig. 7. Langmuir adsorption isotherm for biosorption of Mn (II) ion onto *Spirogyra verrucosa*. Solid line shows the linear relationship between the mass of adsorbate (Mn) adsorbed and ratio of amount of final adsorbate /total mass of adsorbate adsorbed. Dotted line showed the 95% confidence interval.
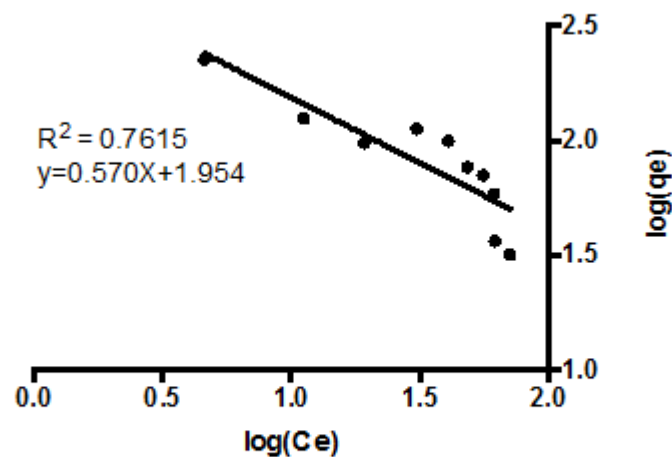

Fig. 8. Freundlich adsorption isotherm for biosorption of Mn(II) ion onto *Spirogyra verrucosa*

protonation of certain functional groups, binding sites surrounded with H^+ ions resulted in to attraction of metal ions towards algal surface at greater extent (Donmez and Aksu, 2002). However, there was decrease in biosorption at increased pH range (5-7) which might be due to precipitation of Mn(II) ions to Mn $(OH)_2$ at higher pH level. Many algal species especially chlorophycean members have been reported for its biosorption capacities in the pH range 2.0 to 6.0 for metal ions (Han *et al.,* 2006; Deng *et al.,* 2007; Gupta and Rastogi, 2008).

3.2. Effect of Temperature

The temperature has been found to affect the biosorption. In present investigation extent of Mn

(II) ion biosorption by *S. verrucosa,* has been recorded maximum 14.9 mg/g at 30°C (Fig. 2) and lower at 25, 40 and 50°C. The decreased adsorption at lower temperature can be due to shrinking of the surface whereas elevated temperatures can be attributed to exothermic characteristics of the biosorbent. Adsorption equilibrium alters in a very specific way because of temperature change either due to exothermic or endothermic nature of a process. The effect of temperature at a specific pH on the adsorption isotherm of metal ions by sorbent was explained by Shen and Duvnjak (2004). Similar findings were reported in other studies on removal of heavy metals also (Park *et al.*, 2005 and Guzel *et al.,* 2008).

3.3. Effect of Biosorbent Quantity

The biosorption capacity and biomass concentration of biosorbents was found to be directly proportional to each other (Aydin *et al.*, 2008, Dundar *et al.*, 2008) but the amount adsorbed decreases per unit mass of biosorbents. In present investigation, better Mn(II) metal ion uptake (12.7 mg/g) was recorded at 1gm/l concentration (Fig. 3) as compared to 0.5 gm/l, 2 gm/l, 2.5 gm/l and 3gm/l, per unit mass by the alga. Suitable reason for this type of trend might be due to the effect of a partial aggregation at increased concentration of biosorbent, which reduces availability of the effective surface area required for the biosorption of metal ions (Gupta *et al.*, 2001). Increased biosorbent quantity also increases the availability of biosorption sites or functional groups (Tunali *et al.,* 2006; Gupta and Rastogi, 2008).

3.4. Effect of Contact Time

Exposing biosorbent in terms of contact time for the sorbate is of great importance in the biosorption mechanism. In present investigation, equilibrium of the solution was generally achieved in 120 min. (Fig. 4) by alga for the sorption of Mn (II) ions. Initially rapid adsorption of Mn(II) ions was recorded during the first 5 to 30 min. by algal biomass, slowing down considerably after the first 90 min.. This was probably due to large number of vacant surface sites available at initial level for adsorption which might be unavailable or difficult to be occupied after some time because of forces among the solute molecules of the solid and bulk phase. Also dominance of intraparticle diffusion process over adsorption may have been result in the diminishing removal of metal ions with increasing time (Deo and Ali, 1993; Volesky, 2003). Similar finding on equilibrium time (120 min.) for sorption of metal ions was reported on green filamentous alga *S. condensata* (Onyancha *et al.*, 2008).

3.5. Effect of initial metal ion concentration

The initial metal ion concentration plays an important role in the process of biosorption. In present investigation, Maximun biosorption (40.66 mg/g) and percent removal (80.20 %) was recorded at 50 mg/l Mn(II) metal ion concentration by alga (Fig. 5 & Table 1). The probable reason for this could be the availability of number of ions for competition at the binding sites at a particular concentration. But the biosorption of Mn (II) ion did not increases considerably above the concentration of 50 mg/l and the percent removal of metal ions remained approximately constant or even showed slight decrease representing saturation of all binding sites available for adsorption on algal surface beyond a particular concentration.

3.6. Kinetic Studies

In order to evaluate the kinetic parameters for the biosorption studies of Mn(II) ions by dead algal biomass the pseudo-second order kinetic model (Ho and McKay, 1999) was employed with optimized concentration of algal biomass (1gm/l), initial Mn(II) ion concentration (20 mg/l),temperature (30°C) and time interval of 5, 10, 15, 30, 45, 60, 90, 120, 150, 180 min. (Fig. 4). Biosorption of Mn(II) ion increases with increasing contact time and equilibrium was attained at 120 min. indicates onset of desorption as there was no further increase in a biosorption observed with exceeded time.

According to the pseudo-second-order model the rate of occupation of biosorption sites is proportional to the square of the number of unoccupied sites. Determination of rate constants for biosorption of Mn(II) ions were done by using following equation (Ho and McKay, 1999).

$$\frac{dq_t}{d} = K_2 (q_{e-} \ q_t)2 \qquad \textbf{(Eqn. 1)}$$

Where, K_2 is equilibrium rate constant of pseudo–second order (g/mg min.), q_e and q_t are amount of metal ion sorbed (mg/g) at equilibrium and time t (min.), respectively. After being integrated and rearranged equation (Eqn. 1), following expression could be achieved:

$$\frac{t}{q_t} = \frac{1}{K_2 \ q_{eq}^2} + \frac{t}{q_{eq}} \qquad \textbf{(Eqn. 2)}$$

The rate constant values were calculated by plotting "t/qt" versus "t". Linear plot of "t/qt" versus "t" for the pseudo-second-order model for the biosorption of Mn(II) ions on to the algal biomass at 20 mg/l initial Mn(II) ion concentration as shown in Fig. 6 and the values of K_2, q_e and R^2 calculated from the plot were represented in Table 2. There was a good agreement observed in calculated value of q_e (14.49 mg/g) and experimental value of q_e (14.90 mg/g), as indicated by very high coefficient of correlation (R^2) value 0.994 recommends the validity of pseudo-second-order model to explain biosorption of Mn(II) ions by alga.

3.7. Equilibrium Isotherm Modeling

Langmuir model is based on an assumption that a monolayer sorption occurs at specific homogeneous sites of sorbate from the aqueous solution (Mashitah et. al., 2008). Therefore Langmuir isotherm was used to correlate the equilibrium data for the fitness of the isotherm.

The Langmuir isotherm is represented by the following equation (Langmuir, 1918):

$$q_e = q_e \cdot b \cdot C_e + (b + C_e) \qquad \textbf{(Eqn. 3)}$$

Where, q_e is the equilibrium constant of sorbate ion on surface of the biosorbent (mg/g), c_e is the equilibrium concentration of metal ion in solution (mg/l) and b is Langmuir's constant (L/mg). Linear plot of "$1/q_e$" versus "$1/q_e$" (Fig. 7) was obtained from the equilibrium data and the values of q_e, c_e and b were calculated from intercept and slope of the plot. The values obtained from Langmuir adsorption isotherm (Table 3) showed high regression correlation coefficients (R^2) 0.859 indicating the fitness of model for the biosorption of Mn(II) ions was taken place at the functional groups/binding sites available on the surface of the algal biomass which is regarded as monolayer biosorption. Also b value 48.52 (L/mg) and maximum capacity (q_{max}) 21.80 mg/g as revealed from the Langmuir isotherm defines the total capacity of the biosorbent for biosorption of Mn (II) ions by the alga.

The Freundlich model (Freundlich, 1906) was also applied to estimate the adsorption intensity of the adsorbent towards the sorbate. This theorem considers multi-layers adsorption on the sorbent surface. This model is represented by the equation given below:

$$q_e = Kf \, C_e^{1/n} \qquad \textbf{(Eqn. 4)}$$

Where, K_f is the Freundlich empirical constant relative to sorption capacity, C_e is the equilibrium concentration of metal ion in solution and $1/n$ is the empirical constant relative sorption intensity. The values of the above Freundlich parameters were derived from the intercept and slope of a linear plot of "$logq_e$" versus "$logC_e$" (Fig. 8). The high values of Freundlich empirical constant relative to sorption capacity (Kf) 89.94 and empirical constant relative sorption intensity (n) 1.75 along with regression coefficient (R^2) 0.761 showed high feasibility of Mn (II) ions adsorption on the algal surface (Table 3).

Based on the comparison with R^2 values obtained from both model, the equilibrium data was found to be fitted well to the Langmuir model rather than Freundlich model and also indicates the applicability of this metal ion-dried algal system for removal of Mn(II) ions in a monolayer biosorption as well as heterogenous surface conditions (Kiran *et al.*, 2007; Pahlvanzadeh *et al.*, 2010).

Thus, present chlorophycean green filamentous alga *S. verrucosa* was found to show better biosorption capacity (40.66 mg/g) for the removal of Mn(II) ions. The present study seems to agree with the trend shown by similar biosorption studies previously conducted for heavy metals and other cations by using green filamentous alga *S. verrucosa* (Gupta *et al.*, 2001; Shuja and Azzizullah, 2006) and Spirogyra Species (Gupta *et al.*, 2006; Bishnoi *et al.*, 2007; Gupta and Rastogi, 2008; Matei *et al.*, 2015).

4. Conclusion

The purpose of the present study was to find out the biosorption capacity of filamentous green alga, *S. verrucosa* collected from Manganese mine water. The dead algal biomass was taken under investigation for the removal of observed Manganese concentrations in mine water and to propose low cost eco-friendly biosorbents for mine water treatment. The findings were based on biosorption capacity, equilibrium modeling and kinetic studies. Experiments were carried out in order to examine the effect of initial solution pH, temperature, initial metal ion concentration, biosorbent dosage and contact time. The values of these parameters obtained on performing batch mode studies revealed that pH 5, temperature 30°C, biosorbent quantity 1.0 gm/l, contact time 120 min. and initial metal ion concentration 50mg/l were the optimum requirement for the biosorption of Mn(II) ions.

The biosorption kinetic and isotherm modeling applied to the equilibrium data for biosorption of Mn(II) ions onto alga reveals the fitness of the pseudo-second-order rate expression (R^2=0.994) as well as the suitability of Langmuir (R^2=0.859) and Freundlich (R^2=0.761) isotherm models with an indication of the applicability of this metal ion-dried algal system for removal of Mn(II) ions in a monolayer biosorption as well as heterogenous surface conditions. However, comparatively biosorption equilibrium was better described by Langmuir isotherm model with monolayer biosorption capacity of *S.verrucosa* biomass 21.80 mg/g. Also, the maximum removal 40.66 mg/g (80.20%) of Mn(II) ion by alga under optimized conditions.

Thus, the present study concludes that *S. verrucosa* could be employed as a low-cost and eco-friendly biosorbent as a substitute to the expensive methods used at present for the removal of Mn (II) ions from acidic mine water (AMD) with special emphasis on manganese mine water. This may also help in the development of subsequent eco-friendly mine water treatment technologies in the application of biosorption at industrial scale.

Authors' contributions

SRB and PBN conceived the idea. SRB designed the experiments, performed the survey of mines, collected

samples, analyzed the data and interpreted the results. SRB wrote the manuscript, PBN finalized and approved the final content of the manuscript. Both SRB and PBN commented on and revised the manuscript.

Acknowledgement

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