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Biosorption of Mercury (II) from Aqueous Solutions by *Zygnema fanicum* Algae

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Abstract: The ability of *Zygnema fanicum* algal biomass to remove Hg (II) is investigated. The mercury biosorption process is studied through batch experiments at different temperatures with regard to the influence of contact time, initial mercury, shaking, concentration and pH. Batch equilibrium tests showed that at pH 8.5 the maxima of mercury absorption rate (80%) obtained. By increasing initial concentration, absorption rate increases (increases up to 7.5 mg L^{-1} after that it is almost constant). Time contact has a direct effect on biosorption up to 60 min after that it is almost constant or desorption occurred. Temperature has no significant effect on absorption rate.

Key words: Algae, heavy metals, adsorption, isotherm, qio lake

INTRODUCTION

Mercury is one of the most toxic heavy metals released in the environment (Shaolin and David, 1997; Zilloux *et al*., 1993).

Mercury is readily accumulated by organisms. The major effects of mercury poisoning are neurological and renal disturbances as well as impairment of pulmonary function (Manohar *et al*., 2002; Saglam *et al*., 2002). This metal is released to the environment from anthropogenic activities that include agriculture, battery production, fossil fuel burning, mining and metallurgical processes, paint and chloralkali industries and wood pulping (Boening, 2000). In addition activities such as solid waste combustion, industrial developing and petrochemical activities discharge mercury to environment especially aquatic ecosystem (WHO, 1998). Finding an effective method of heavy metals removal is an important issue.

Adsorption as a treatment process has been found to be an economically feasible alternative for metal removal. Activated carbon is one of the most well known adsorbents (Bello *et al*., 1999; Budinova *et al*., 2003; Gómez-Serrano *et al*., 1998) but the high cost of the process has limited its use.

The use of inexpensive biological materials, such as bacteria, fungi and algae, for removing and recovering heavy metals from contaminated industrial effluents has emerged as a potential alternative method to conventional techniques, which may be expensive and ineffective (Kratochvil *et al*., 1997; Wilde and Benemann, 1993). The uptake of metals by biomass can take place actively, by means of a metabolic activity dependent process (bioaccumulation) or by means of a passive and usually rapid (several minutes) metabolism-independent process called biosorption (Godlewska-Zykiewicz and Kozowska, 2005). The mechanism and kinetics of mercury biosorption on algal biomass depends on the experimental conditions particularly medium pH and mercury concentration (Zeroual *et al*., 2003).

The variety of materials tested includes bark, chitin, lignin, modified wool and seaweeds (Bailey *et al*., 1999). They can be used for the effective removal and recovery of several species from wastewater streams. Algae as a proper alternative has been considered for heavy metals removal (Volesk, 2003; Lodeiro *et al*., 2005).

This research aimed to perform an experimental study on mercury removal from synthetic mercurial wastewater using *Zygnema fanicum* Algae originated from Qio Lake (Khoramabad Iran).

MATERIALS AND METHODS

Organism identification and preparation: This study was conducted (in Khoramabad city Iran, 2006) on synthetic wastewater containing mercury. Two kinds of natural and pure algae were used. Natural algal mass was taken from Qio Kohram Abad Lake. A photomicroscope equipped with a camera and loop set lamella were used. Identification of algae was possible by direct observation on the lamella. Immobilization materials such as gelatin was used to immobile their movements. Woods Hole MBL Medium was used for algal growth. The alga was washed twice with running water and once with deionized water. The washed biomass was oven-dried at 60°C for 24 h,

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crushed with an analytical mill, sieved (size fraction of 0.5-1 mm) and stored in polyethylene bottles until use (Herrero *et al*., 2005).

To determine viability of algae, Evans blue solution (5%) was used.

Stock solution preparation: 0.1354 g $HgCl_2$ dissolved in (70 cc distilled water + 1 cc HNO_3) made up to 700 cc (1 cc = 1 mg Hg)

Adding sulfide agents to medium: Sulfide agents such as Na_2S, $FeSO_4$ have a large application in heavy metals precipitation because of their sever affinity. In other hand on the surface of biological absorbent (such as algae) agent groups such as carboxyl, amide, thiol, phosphate and hydroxide that make complex with metal ions.

Because of this reason in present study, chemical agents frou sulphate, menionin and added to the culture. It was hypothesized that these agents enter to the cell structure and make more accumulation on the surface of algae cell resulting in more removal.

Absorption test: Determined amount of algal mass in temperatures 25, 4 and 37°C and pH values 7, 4, 8.5 and Hg(II); concentrations 10, 100 and 1000 ppb, contact times 1, 5, 10, 20, 40, 60 and 80 min was used. After expiring contact time, samples were filtered by Waltman filter (0.45 micron). pH was lowered by HNO_3, then absorption test carried out by Hg solution 1000 ppb in two condition: mixing and non-mixing on natural pure algae.

Experimental procedures should be brief but complete enough to be repeated; procedures published previously should be cited in references.

RESULTS AND DISCUSSION

Separated algae from the lake (Qio Lake of Khoramabad) were Aspergilla, *Zygnema fanicum* and Oedogonium. In order to measure Hg (II) values in samples, using standard solutions absorption, standard curve was plotted (Fig. 1). Slope and correlation coefficient showed the linear relation between absorption and concentration also high sensitivity of the procedure. Table 1 shows the absorption and concentration of Hg standard solutions.

Effect of pH on Hg (II) biosorption: Solution pH values have a significant influence on mercury uptake by Zygnema Fanicam Researches showed that pH is an important factor in heavy metals biosorption (Volesk, 2003; Wase and Forster, 1997). Maximum absorption (60.46%) occurred at pH 8.5. By increasing contact time

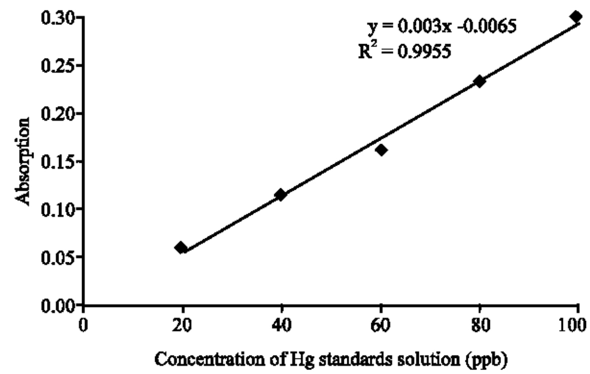

Fig. 1: Calibration curve. Concentration of mercury standard solution versus rate of absorption

Table 1: The absorption and concentration of Hg standard solutions

Absorption	Concentration of Hg standards (ppb)
0.000	Blank
0.085	20
0.115	40
0.163	60
0.234	80
0.299	100

the absorption has increased until contact time 80 min not only absorption not increased but also desorption has occurred (Fig. 4). This can be justified due to absorbent nature in different pH values. Algal cell wall has many agent groups. Dependency of Hg removal to pH probably depends on type and state of agent-groups and chemistry of Hg in solution.

As seen from Fig. 2 the mercury uptake at lower pH values is smaller. Between pH values 4.0 and 7.2 the metal adsorption increases, attaining values that remain almost constant for higher pH value (pH 8.5).

As a general rule, the pH influence on metal uptake by some biomasses is closely related to the ionic states of the cell wall functional groups as well as to the metal speciation in solution. In the case of Hg biosorption, the pH dependence is slightly different to that observed for other metals. As an example, Cd (II) also presents an S shape curve but the maximum uptake is reached at pH 4.5 (Lodeiro *et al*., 2004). It can well be assumed that cadmium is present in its free ionic form, Cd^{2+}, all along the pH range studied. Therefore, the cadmium biosorption depends on the protonation or deprotonation of the cell wall functional groups, mainly carboxylic groups (Rey-Castro *et al*., 2004). On the contrary, the mercury biosorption process is not only affected by the acid-base properties of the cell wall but also by the metal chemical speciation, which is rather more complex than that of Cd (II) and hence, it may play an important role.

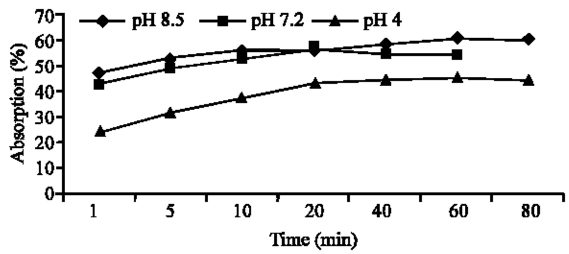

Fig. 2: Effect of pH on efficiency of absorption rate (condition: temperature 25°C, initial concentration of Hg 1000 µg L^{-1}, algae dose 3 g L^{-1}, without shaking)

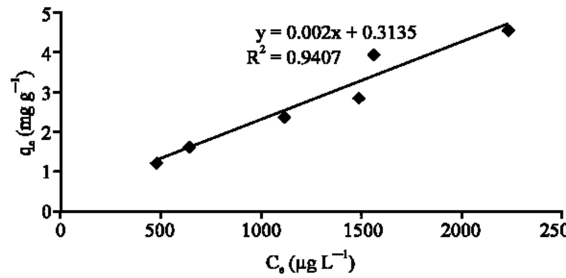

Fig. 3: Hg (II) sorption isotherms based on the Freundlich model, using *Zygnema fanicum* temperature = 25°C; pH = 8.5, mixing 100 rpm and contact time 40 min)

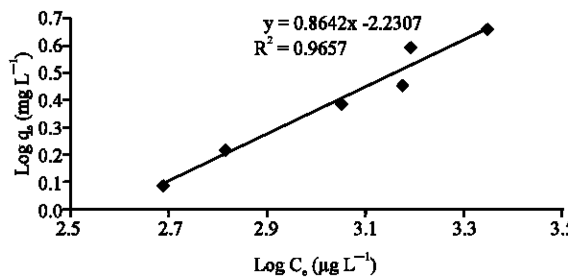

Fig. 4: Hg (II) sorption isotherms based on the Langmuir model, using *Zygnema fanicum* (temperature = 25°C; pH = 8.5, mixing 100 rpm and contact time 40 min)

Adsorption isotherms

Langmuir and Freundlich isotherms: The quantification of the biosorptive/bioaccumulative features of a biosorbent must be established for proper evaluation (Vecchio *et al*., 1998). There are several isotherms equations used in the literature to reach that objective.

The two most frequently used are the Langmuir and Freundlich models (Acar and Malkoc, 2004; Gazso, 2001). The Langmuir model is valid for modeling monolayer adsorption onto a homogeneous surface with constant adsorption energy; the Freundlich equation posits a heterogeneous surface and considers that molecules attached to a surface site will have an effect on the neighboring sites (Volesky, 1990). The biosorption data from different initial concentrations were analyzed in terms of both Langmuir and Freundlich equation at pH = 8.5 and 25°C, mixing rate 100 rpm contact time 40. The Freundlich isotherm equation (r^2 = 0.9657) seemed to describe better the adsorption process of Hg (II) by the *Zygnema fanicum*. than the Langmuir equation (r^2 = 0.9407). Equations (Fig. 3, 4) and the applicability of both Langmuir and Freundlich isotherms implied that both monolayer adsorption and heterogeneous surface conditions exist under the experimental conditions used here, with the latter process prevailing.

Effect of temperature: Figure 5 shows the effect of temperature and contact time on Hg absorption efficiency by natural algae. This shows that differences of Hg absorption in three mentioned temperatures (4, 25 and 37°C), was not significant statistically (Interval Confidence 95%). Absorption rate increased to 60 min after that it is not only increased but also constant or small desorption has occurred. With regard to Fig. 3 maximum Hg removal occurred in 4°C (54.09), 25°C (53.84%) and 37°C (53.25%). Temperature had not effect on balance time. This can be because of independency of such mechanisms to energy (such as dead algal cell

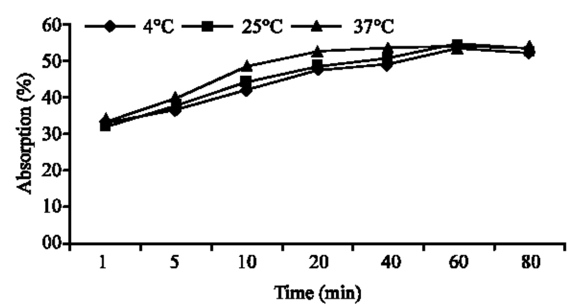

Fig. 5: Effect of temperatures (4, 25 and 37°C on Hg absorption rate (condition: temperature 25°C, initial concentration of Hg 1000 µg L^{-1}, algae dose 3 g L^{-1}, without shaking)

mass), that the nature of absorption is often physicochemical process (Yagmur *et al*., 2002).

Effect of initial concentration: The effect of nine different initial concentrations of Hg (II) on the biosorption of this metal by *Zygnema fanicum* was evaluated. By increasing initial concentration to 6.5 mg L^{-1} Hg, absorption rate has increased. After that it is almost constant (Fig. 6).

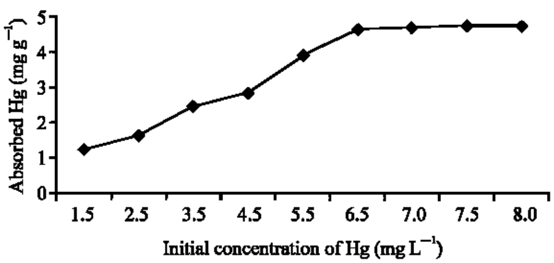

Fig. 6: Effect of initial Hg concentration on absorption by natural algae (temperature 25°C, pH 7.2, mixing rate 100 rpm, contact time 20 min, algal dose 3 g L^{-1}

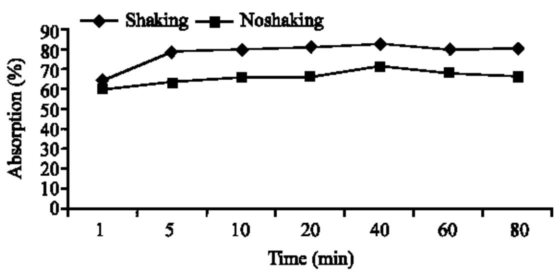

Fig. 7: Effect of mixing on Hg efficiency by *Zygnema fanicum* (mixing rate 100 rpm, temperature 25, initial Hg concentration 100 μg L^{-1}, pH 8.5 algal dose 1 g L^{-1})

These results agree with the results obtained by both inorganic (Echeverrıa *et al*., 2003) and organic (Acar and Malkoc, 2004) sorbents. It is possible that a higher ionic strength of Hg (II) provokes more mercury sorption (Say *et al*., 2001).

Effect of initial concentration on absorption (Fig. 4) by mixture of algae showed increasing in absorption. In other word, the maximum capacity of Hg absorption by natural algae increased up to 7.5 mg L^{-1} the maximum absorbed Hg is 4.7 mg g^{-1}.

Effect of shaking: Shaking is an important factor for not only homogenizing the environment but also increasing effective contact. At present research absorption rate evaluated. Results showed that mixing rate has a considerable effect on absorption rate. It increased the absorption (to 5 min), after that, it is almost constant (Fig. 7).

CONCLUSION

Results from this study confirm that *Zygnema fanicum* used here is a suitable biosorbent for Hg(II) ions and that, in terms of percentages of mercury biosorbed, this process was more efficient for higher concentrations of Hg. This is an important fact because; it can be use for concentrations higher than 6.5 mg L^{-1} (4.7 mg g^{-1} can be expected).

This study shows that *Zygnema fanicum* was found to be an effective biosorbent for mercury removal. The mechanism and kinetics of mercury biosorption on algal biomass depends on the experimental conditions particularly time, pH and mercury concentration. The present work demonstrates that mercury can be effectively removed from the mercurial solution by batch biosorption process. Research on Removal of other heavy metals by this alga should be considered.

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