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ORIGINAL ARTICLE

The Biosorption of Heavy Metal from Aqueous Solution by Fem Azolla *Filiculoides*

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ABSTRACT

Metals toxic constitute a serious health risk because they accumulate in soils, water and organisms. One of the methods of removing these pollutants from water and soil is the use of plants (Phytoremediation). There are many plants which have the ability to accumulate large amounts of heavy metals. The adsorption of heavy metals onto *Azolla filiculoides* was investigated from aqueous solutions in the batch biosorption experiments. The aim of this study was to verify the ability of *Azolla filiculoides* to fix Ni and Zn from polluted waters. The maximum uptake capacities of the collected *Azolla filiculoides* from the Asbchin Wetland west of Mazandaran in the north part of Iran at the optimal conditions for Ni and Zn ions were approximately 45.32 and 49.27mg/g dry *Azolla* respectively. Desorption experiments indicated that Ethylene diamine tetra acetic acid EDTA were efficient desorbents for recovery from nickel ions.

Key words: metals toxic, *Azolla filiculoides,* wastewater, biosorption 3

Introduction

Metals toxic are used in various industries such as the semiconductor industry .As a result, waste streams from the industries contain metal ions. Many studies have shown that they are highly toxic and can seriously damage our aqueous environment. The different methods are used for the removal of heavy metals as important contaminants in water and wastewater. In the chemical methods, to effectively decrease of heavy metals to acceptable levels require a large excess of chemicals, which increase the costs because of generating the voluminous sludge [10]. On the other hand, a number of methods exist for the removal of heavy metals from liquid waste when they are present in high concentrations. These include methods such as precipitation, evaporation, electroplating, ion exchange and membrane processes [9].

In the meantime, biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of industrial wastewater. The major advantages of biosorption technology are their effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials [11]. Among the organisms used for biosorption, water ferns (Azolla spp.) are an inexpensive, readily available source of biomass. Benaroya et al. [3] showed that *A. filiculoides* growing in metal-laden water accumulated 1.8 g Pb/g. These high metal recoveries support the application of Azolla in recovery of residual from wastewater. Heavy metal removal by biosorption has been extensively investigated during the last several decades [1,3,5,8]. Esmaeili et al. [6] employed activated carbon prepared from *Gracilaria* and obtained more that 90% removal of Cu from waste water. The initial binding and exchange of heavy metal ions to insoluble constituents in the *Azolla* matrix most probably involves cell wall charged groups (such as carboxyl and phosphate). Pectin and Cellulose are important polysaccharides constituent of

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plant cell walls, made of fragments of polygalacturonic acid chains, which interact with Ca^{2+} and Mg^{2+} (as the important exchanged ions with heavy metals) to form a three dimensional polymer by (–COO) 2Ca and or (–COO) 2Mg bindings as the ion exchanging bases [7]. K^+ and Na^+ are mostly present in *Azolla* cell as soluble salts [4].

The aim of the present study was to characterize the nature and binding mechanism of chemical groups occurring in the aquatic fern *A. filiculoides* that were responsible for nickel and zinc ions biosorption. The initial binding and exchange of heavy metal ions to insoluble constituents in the *Azolla* matrix most probably involves cell wall charged groups (such as carboxyl and phosphate).In addition the effects of initial metal ion concentration, contact time, concentration of algal biomass and pH.

Materials and methods

Preparing of Azolla:

The raw biomass *Azolla* was collected from the surface of Asbchin Wetland in the southern shores of Caspian Sea, west of Mazandaran province, the north part of Iran. 1 g. of *Azolla* was washed three times with deionised water and was air-dried in sunlight. The dry biomass was milled and an average of 0.5-1 mm size particles was used for biosorption experiments. Nickel and zinc solutions of different concentrations (0.01 to 0.44 mmol/L) were prepared by adequate dilution of the stock solution with deionised water. All the adsorption experiments 4 were carried out at room temperature (25±1°C). The initial pH was adjusted with 1M HCl or 1M NaOH. Single-metal concentrations in the relevant samples were determined by an atomic absorption spectrophotometer (Chem., Tech, Analytical CTA 2000). The liquid phase was separated from the adsorbent by a filtration system using 0.45 μm membranes.

Desorption experiment:

For the desorption study, contact made between 0.1 g dried biomass and a 100 ml nickel and copper solution (3 mmol/L). After zinc and nickel ions sorption, the biomass was filtered, washed three times with distilled water to remove residual nickel ions on the surface, and kept in contact with the100 ml desorbent solution: HNO_3, HCl, EDTA, CH_3COOH and distilled water. The mixtures were shaken in a rotary shaker for 18 h. The filtrates were analyzed to determine the concentration of nickel and zinc ions after desorption. The nickel ions stock solutions were prepared by dissolving their corresponding analytical grade salts of $NiCl_2\ 6H_2O$ and $ZnCl_2$ (Merck) in distilled water.

Biosorption experiments:

A series of nickel and zinc biosorption experiments was conducted; the factors in the investigation included pH, temperature and adsorption capacity. The data were subsequently used for the model development as well as its validation. In the pH effect experiment, the desired solution pH was first adjusted by HNO_3 or NaOH. The *A. filiculoides* was added to the solutions while being shaken at 1500 rpm in the orbital shaker. The experiment was performed at room temperature of 25±1°C.The pH was frequently measured and adjusted accordingly by HNO_3 or NaOH. In the isotherm, experiments were carried out in bottle flasks filled with 1000 ml of water thoroughly mixed with 0.1 g of *A. filiculoides* at 25 ± 1°C. The initial concentrations of metal ions were ranged from 0.01 to 0.44 mmol / L. The initial pH was measured and if necessary, NaOH or HCl solution was added to reach an initial pH close to 5.5.

Results and discussion

Effect of pH on Biosorption:

The effect of pH on nickel and zinc ions biosorption on *A. filiculoides* is studied at room temperature by varying the pH of heavy metals solution. Figure 1 shows the biosorption of nickel ions were increased up to pH 5.5. The decreasing of biosorption levels by lowering pH can be explained due to competition between protons and metal ions for the capturing same sites, which at low pHs, metal ions do not successful. The higher the pH value, the higher the dissociation since free sites for the binding of nickel ions can be produced; however, the majority of heavy metals precipitate at pH values over 8 for nickel ions. 5

Desorption experiment:

Fig.2 shows the percentage of nickel and zinc ions released by *A. filiculoides* pieces after treatment with different desorbents. It was observed that the percentage of desorption using distilled water was almost negligible.

The recovery percentage is obtained from the following relation (Zhao et *al*., 1999 and Arica, *et al*., 2003):

$$Recovery(\%) = \frac{(Desorbed)}{(Adsorbed)} * 100 \qquad \text{Eq: 1}$$

that the "desorbed" is the concentration and/or the mass of metal ions after the desorption and the adsorbed is equal to (Co–Ce) and/or (mo–me) for each recovery process. mo and me are the heavy metals mass in the aqueous solution, before and after the biosorption, respectively.

The high recovery percentage of Ni and Zn ions by EDTA allows the recycling of ions from the biomass in industry.

Biosorption Isotherms:

Figure 3 shows the nickel ions uptake isotherms at pH 5.5. The experimental results were corrected with the Langmuir isotherm model. The Langmuir adsorption isotherm is probably the most widely applied adsorption isotherm. This model which is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the sorbent (Xiangliang et al. 2005).

$$q_e = \frac{b.q_{\max}.C_e}{1+b.C_e} \qquad \text{Eq: 2}$$

where q_e is the amount of metal ions adsorbed (mg/g), C_e is the equilibrium concentration (mg/L), q_{max} is the maximum adsorption capacity and b is an affinity constant.

The release of calcium, sodium and magnesium initially fixed onto the *A. filiculoides*, has been followed in the same time of nickel adsorption. This release depends on the initial nickel ions concentration of the solution, which could lead to a fixation mechanism by ion exchange.

Because the isotherms of nickel and zinc ions adsorption and calcium, sodium and magnesium desorption were practically similar, nickel and zinc ions seemed to be exclusively adsorbed by an ion exchange mechanism. The study of heavy metals recovery shows that the ability of proton in the exchanging and recovery is more than Na+. 7

Kinetic experiments:

Figure 4 shows the kinetics of Nickel and zinc adsorption onto the *A. filiculoides*, at 25 °C, pH 5.5, in deionized water; the contact times to reach the mass balance were obtained at 300 min. This time obtained by batch reactor studies. Moreover, for similar experimental conditions, a light reduction in the Zn fixation capacity was observed in the case of deionized water. In this study of tap water a light reduction in the Zn and Ni ions and probably due to a competition of fixation between the ions initially present in this natural water and Ni (II) and Zn (II).

Discussion:

This study indicates that the aquatic fern *Azolla filiculoides*, which is widely available at a low cost, can be used as an efficient biosorbent material for the treatment of nickel and zinc ions in wastewater. The adsorption isotherm of nickel and zinc ions by dried *Azolla filiculoides* pieces could be adequately described by the Langmuir isotherm model. The maximum adsorption capacity was 0.78 and 0.75 mmol/g for nickel and zinc ions respectively. Desorption experiments proved that EDTA were an efficient and practical desorbents for the recovery of metals ions from the biomass. The pH value that was selected for the experiments on the biosorption of metals ions by *Azolla filiculoides* was pH 7.5 for nickel ions and 6.7 for zinc since it combined the best characteristics for the lowest chemical precipitation and the highest biosorption. With advantages of high metal biosorption and desorption capacities, the biomass of *Azolla* is a promising application as a cost-effective biosorbent material for the removal of nickel and zinc ions from wastewater.

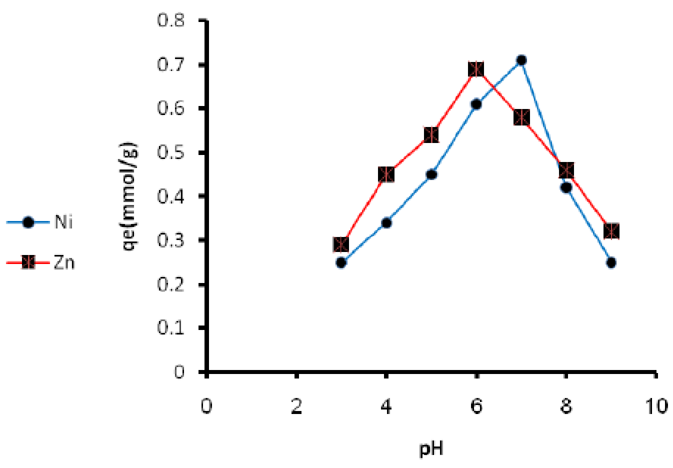

Fig. 1: Effect of pH on the nikcel and zinc ions biosorption by *A. filiculoides*

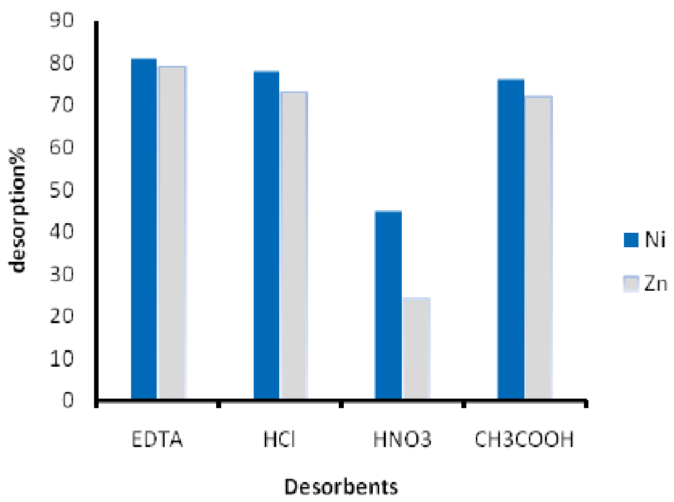

Fig. 2: Nickel and zinc ions recovered by different desorbents 6

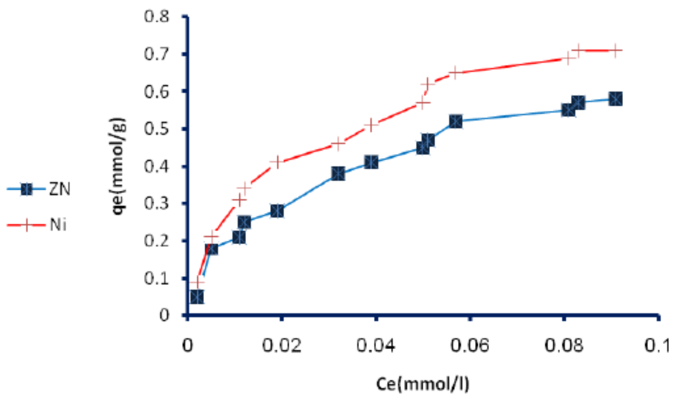

Fig. 3: Sorption isotherm of nickel and zinc ions in deionized water.

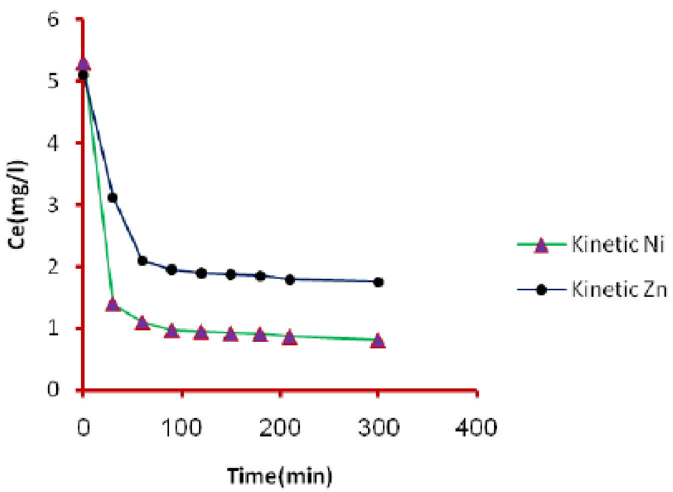

Fig. 4: The adsorption kinetic of nickel and zinc ions at pH 5.5 and 25°C in deionized water

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