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Full Length Research Paper

Batch studies on the removal of Ni (II) from aqueous solution by *Azolla filiculoides*

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There are many plants which have the ability to accumulate large amounts of heavy metals and one of them is the aquatic fern, *Azolla filiculoides*. Toxic metals constitute a serious health risk because they accumulate in soils, water and organisms. One of the methods for removing these pollutants from water and soil is the use of plants. The aim of this study was to test the ability of *A. filiculoides* to adsorb Ni from polluted waters. The maximum uptake of nickel ions by the collected *A. filiculoides* biomass under the optimal conditions was approximately 45.32 mg/g dry *Azolla*. Desorption experiments indicated that EDTA was an efficient desorbent for recovery from nickel ions.

Key words: Nickel, *Azolla filiculoides,* wastewater, biosorption.

INTRODUCTION

Toxic metals are extensively used in various industries such as the semiconductor industry. Many studies have shown that the heavy metals contained in the waste streams from the industries are highly toxic and can seriously damage the aqueous environment. Different methods including chemical and biological methods have been used for the removal of heavy metals from wastewater. Chemical methods, such as precipitation, evaporation, electroplating, ion exchange and membrane processes, are limited in practical application due to the high costs and the voluminous sludge (Spearot and Peck, 1984; Matheickal and Yu, 1999).

Biosorption, one of the biological methods, is an attractive method for the removal of heavy metals from aqueous solutions, since the efficiency in reducing the concentration of heavy metal ions to very low levels is high and the biosorbent materials are usually inexpensive and eco-friendly ((Volesky, 1994). Many biomaterials produced from bacteria, fungi and plants have been tested for removal of heavy metals from wastewater.

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Among the organisms used for biosorption, water ferns (*Azolla* spp.), an inexpensive, readily available source of biomass, can be used effectively for biosorption. Benaroya et al. (2004) showed that *Azolla filiculoides* growing in metal-laden water accumulated 1.8 g Pb/g.

Antunes et al. (2001) demonstrated 99.9% removal of Au with an optimum concentration of 5 g *A. filiculoides*/l. These high metal recoveries support the application of *Azolla* in recovery of residual Au from wastewater. Heavy metal removal by biosorption has been extensively investigated during the last several decades (Aksu, 2001; Ahmady-asbchin et al., 2009; Davis et al., 2003; Kapoor et al., 1993; Wang, 2006; Wang, 2002). Esmaeili et al. (2008) employed activated carbon prepared from *Gracilaria* and obtained more that 90% removal of Cu from waste water. Adsorbent materials (biosorbent) derived from suitable biomass of both the living and dead can be used for the effective removal and recovery of heavy metal ions from wastewater streams (Muraleedharan et al., 1995). The biomasses include bacteria (Ozdemir and Ozturk, 2003), fungi (Fourest et al., 1994), yeast (Volesky et al., 1993), marine algae (Kaewsarn, 2002) and others. Wang (2006) reuse of biosorbents, selection of good and cheap support materials for biomaterial immobilization, improvement of reuse methods, and enhancement of properties

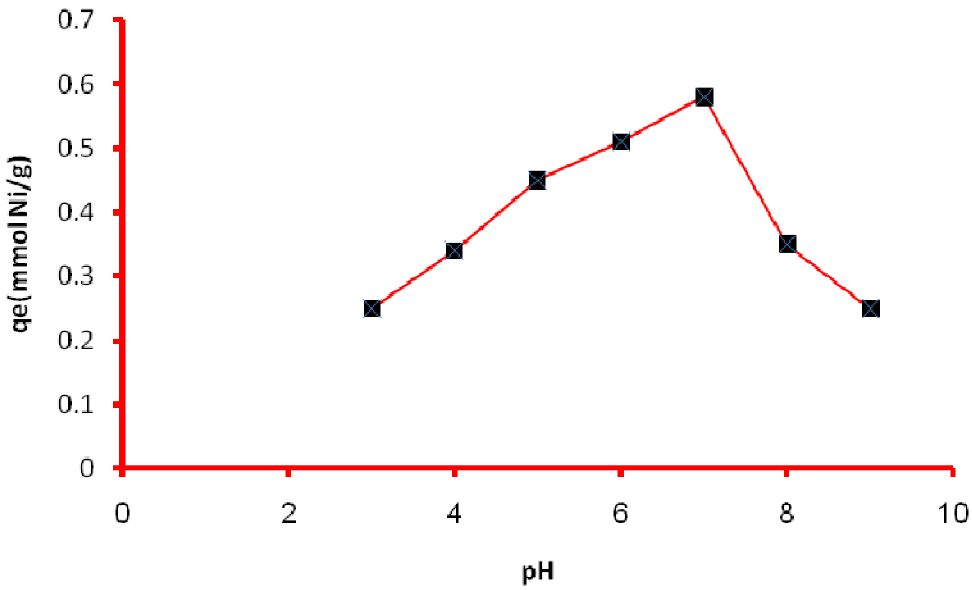

Figure 1. Effect of pH on the nikcel ions biosorption by *A. filiculoides.*

of immobilized biosorbents such as pore ratio, mecha-nical intensity and chemical stability are also important factors for application. The aim of this study was to investigate the effects of initial metal ion concentration, contact time, concentration of algal biomass and pH on biosorption of Ni ions by the *A. filiculoides* biomass; and the binding mechanism of che-mical groups occurring in the aquatic fern, *A. filiculoides* that were responsible for Ni ions biosorption.

MATERIALS AND METHODS

Preparation of *Azolla* biomass

The raw biomass *Azolla* was collected from the surface of Asbchin Wetland in the south shores of Caspian Sea, west Mazandaran province, the north part of Iran. One gram 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 to 1 mm size particles was used for biosorption experiments. Nickel 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 were carried out at room temperature (25 ± 1°C). The initial pH was adjusted with 1 M HCl or 1 M 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 was made between 0.1 g dried biomass and a 100 ml nickel solution (3 mmol/L). After copper 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 ions after desorption. The nickel ions stock solutions were prepared by dissolving their corresponding analytical grade salts of $NiCl_2$ $6H_2O$ (Merck) in distilled water.

Biosorption experiments

A series of nickel 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 adjusted by HNO_3 or NaOH. The *A. filiculoides* was added to the solutions while being shaken at 1500 rpm in the orbital shaker. All experiments were performed at room temperature of 25 ± 1°C.The pH was frequently measured and adjusted accordingly by HNO_3 or NaOH. 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 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 Ni ions biosorption on *A. filiculoides* was studied at room temperature by varying the pH of the solutions. Figure 1 shows that the biosorption of nickel ions increased up to pH 7.8. The decrease of biosorption levels by lowering pH is due to competition between protons and metal ions for capturing same sites, in which at low pH, metal ions are 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

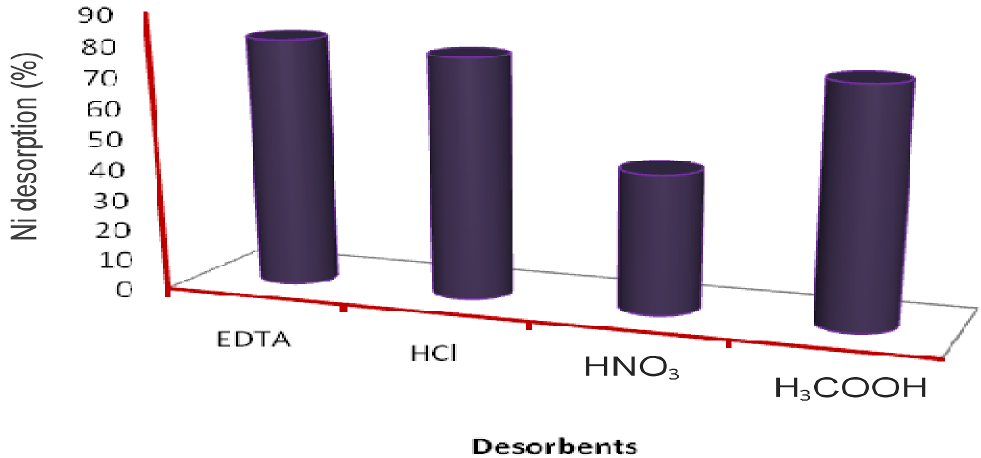

Figure 2. Nickel ions recovered by different desorbents.

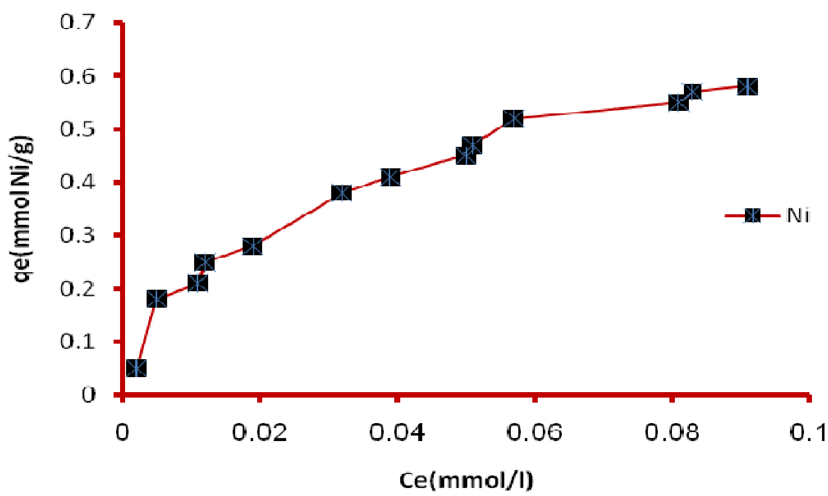

Figure 3. Sorption isotherm of nickel ions in demonized water.

majority of heavy metals were precipitated at pH values of over 8 for nickel ions.

Desorption experiment

Figure 2 shows the percentage of nickel 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; Arica et al., 2003):

$$\text{Recovery}(\%) = \frac{(Desorbed)}{(Adsorbed)} x100 \qquad 1$$

Where, 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 (m_o–m_e) for each recovery process; m_o and m_e are the heavy metals mass in the aqueous solution, before and after the biosorption, respectively.

The high recovery percentage of Ni 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 7.8. The experimental results were corrected with the Langmuir isotherm model. The Langmuir adsorption isotherm is probably the most widely applied adsorption isotherm. This model is valid for monolayer sorption onto a surface with a finite number of identical sites which are

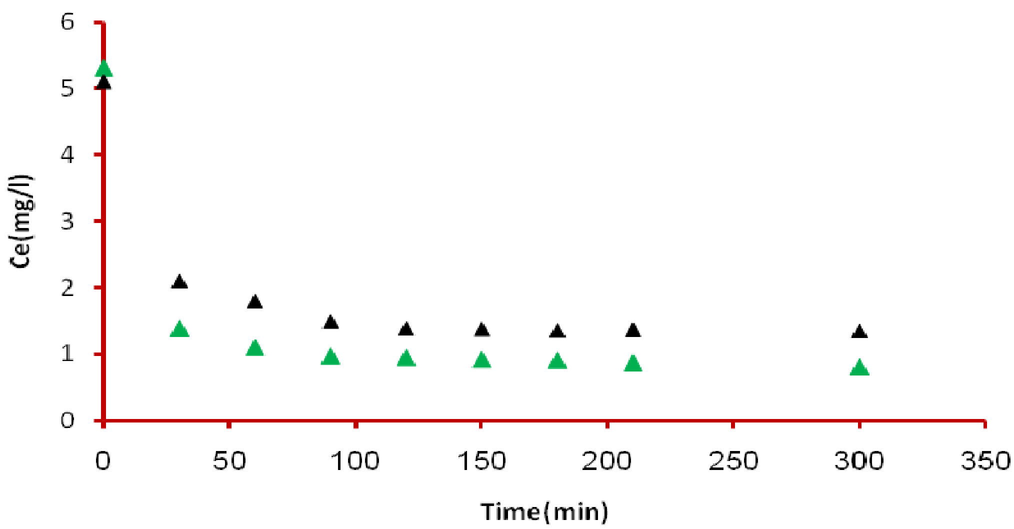

Figure 4. The adsorption kinetic of nickel ions at pH 7.8 and 25°C in demonized water (▲) and tap water (▲) ($C_e = C_f$ final or equilibrium concentration of nickel ions).

homogeneously distributed over the sorbent (Xiangliang et al., 2005).

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

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*, was followed in the same time with nickel adsorption. This release depends on the initial nickel ions concentration of the solution, which could lead to a fixation mechanism by ion exchange.

As a result of the isotherms of nickel ions adsorption and calcium, sodium and magnesium desorption were practically similar, nickel 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 that of Na^+.

Kinetic experiments

Figure 4 shows the kinetics of nickel adsorption onto the *A. filiculoides*, at 25°C, pH 7.8, in deionized and tap water; the contact times to reach the mass balance were obtained at 300 min. This time was obtained by batch reactor studies. Moreover, for similar experimental conditions, a light reduction in the Ni fixation capacity was observed in the case of tap water and probably due to a competition of fixation between the ions initially present in this natural water and Ni (II).

Conclusion

This study indicates that the aquatic fern, *A. filiculoides*, which is widely available at a low cost, can be used as an efficient biosorbent material for the removal of nickel ions from wastewater. The adsorption isotherm of nickel ions by dried *A. filiculoides* pieces could be adequately described by the Langmuir isotherm model. The maximum adsorption capacity was 45.32 mmol/g for nickel ions. Desorption experiments proved that EDTA were an efficient and practical desorbent 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 *A. filiculoides* was pH 7.8 for nickel ions since it combined the best characteristics for the lowest chemical precipitation and the highest biosorption. With the 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 ions from wastewater.

ACKNOWLEDGEMENT

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