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Short communication

Potential of NaOH pretreated *Mangifera indica* waste biomass for the mitigation of Ni(II) and Co(II) from aqueous solutions

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ABSTRACT

Mangifera indica biomass was chemically pretreated to evaluate its Ni(II) and Co(II) uptake capacity from aqueous solutions. The adsorption characteristics of Ni(II) and Co(II) by *M. indica* were found dependent on pH, chemical pretreatments, initial concentrations of the metals and time. The *M. indica* biomass was pretreated using HCl, HNO_3, H_3PO_4, NaOH, CH_3COOH, C_6H_6, HCHO and H_2O_2. The maximum Ni(II) and Co(II) uptake was 131.5 mg/g at pH 6 and 114.6 mg/g at pH 5, respectively at 30°C with NaOH pretreated *M. indica* biomass. The equilibrium adsorption data was better fitted to Langmuir adsorption isotherm model and pseudo-second order model.

1. Introduction

Boosted industrial activity during recent decades has led to the discharge of unprecedented volumes of metal infected wastewater, which is a serious cause of environmental deprivation. Heavy metals, due to their high toxicity, pose a serious threat to biota and the environment [1]. Toxic metals are group of pollutants, which are non-biodegradable and tend to accumulate in living organisms [2]. Ni(II) and Co(II) are two very noxious metals. In Pakistan, many industries such as vegetable ghee and stainless steel industries are responsible for Ni(II) and Co(II) contamination so it is very important to develop methods for the efficient removal of these toxic metals. Conventional techniques for removing dissolved metals include chemical precipitation, carbon adsorption, electrolytic recovery, ion-exchange, chelation and solvent extraction or liquid membrane separation [3,4]. These techniques are sometimes restricted because of technical or economic constraints as a result of high capital and operational cost. Biosorption is based on metal sequestering properties of certain natural materials of biological origin [5] and is an innovative technology that employs inactive and dead biomass for the recovery of metals from aqueous solutions. Different agricultural materials have been used in the biosorption of toxic metal ions from solution [5–22]. Moreover it has been found that by modifying agricultural by-products chemically or physically, their capacity can be increased.

This research work was carried out to examine the biosorption of Ni(II) and Co(II) from aqueous solutions using *M. indica* biomass. The effects of parameters such as pH, chemical pretreatments, initial metals concentrations and contact time were studied. The effects of kinetics of biosorption were systematically studied. The biosorption efficiency of the metals from loaded biosorbent was determined to further evaluate the feasibility of applying this biomass in practical Ni(II) and Co(II) removal processes. The selection of this biomass was made due to its easy availability in different parts of Pakistan with no cost. *M. indica* is extensively grown and effortlessly available. In addition recovering the metals from the biosorbent using some suitable ion exchanger, the biosorbent could be reused.

2. Materials and methods

2.1. *Mangifera indica* biomass

Different phyto parts of *M. indica* biomass were selected including leaves, bark and kernels. *M. indica* biomass used in this work was collected from Botanical Garden, University of Agriculture,

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Faisalabad, Pakistan. It was extensively washed with deionized and distilled water (DDW) to remove particulate material from their surface and oven dried at 60°C. Dried biomass was cut, ground using food processor (Moulinex, France) and then sieved through Octagon siever (OCT-DIGITAL 4527-01, Endecotts Ltd, London, UK). The fraction with 0.255 mm was selected for use in sorption tests.

To study the outcome of chemical pretreatments on the uptake capacity of the biomass, 20 g of every *M. indica* phyto part was treated with 200 mL of 1 M solution of HCl, HNO_3, H_3PO_4, NaOH, CH_3COOH, C_6H_6, HCHO and H_2O_2 for 24 h. The biomass was washed with DDW after each pretreatment procedure until a neutral pH was measured. The pretreated biomass was then dried in an oven at 60°C for 24 h, sieved again and then stored in desiccators until use for the biosorption studies. After pretreatments the resulting biomasses were named as hydrochloric acid treated *M. indica* (HAMi), nitric acid treated *M. indica* (NAMi), phosphoric acid treated *M. indica* (PAMi), sodium hydroxide treated *M. indica* (NaMi), acetic acid treated *M. indica* (AAMi), benzene treated *M. indica* (BMi), formaldehyde treated *M. indica* (FMi) and hydrogen peroxide treated *M. indica* (HPMi).

2.2. Batch biosorption studies

In all sets of experiments, fixed volume of Ni(II) and Co(II) solutions (100 mL) were thoroughly mixed with biosorbent having 0.1 g biosorbent dose and particle size 0.255 mm at 30°C and 120 rpm up to 24 h. To study the influence of pH, chemical pretreatments, initial metal concentrations and contact time, different conditions of pH (1–7) and (1–6) for Ni(II) and Co(II) respectively, initial metal concentration (25, 50, 100, 200, 400 and 800 mg/L), contact time (15, 30, 60, 120, 180, 240, 300 and 360 min) were evaluated. For adjusting the pH of the medium 0.1 N solutions of NaOH and HCl were used. The flasks were placed on a rotating shaker (PA 250/25. H. Adolf Kühner AG, Birsfelden, Switzerland) with constant shaking and the solutions were filtered through filter papers (Whatman No. 40, ashless). Preliminary tests were performed using an initial Ni(II) and Co(II) concentrations of 100 mg/L (initial pH 6 for Ni(II) and 5 for Co(II)).

2.3. Determination of the Ni(II) and Co(II) contents in the solutions

The concentration of Ni(II) and Co(II) in the solutions before and after the equilibrium was determined by an atomic absorption spectrometer equipped with an air-acetylene burner (AAnalyst 300, Perkin-Elmer, Waltham, USA) and controlled by Intel personal computer, having 0.2 nm slit width. The hollow cathode lamp was operated at 28 mA and the analytical wavelength was set at 232.0 nm and 240.7 nm for Ni(II) and Co(II), respectively.

The metal uptake q_e (mg metal adsorbed/g adsorbent) and % removal were calculated by Eqs. (1) and (2) respectively.

$$q_e = \frac{(C_i - C_e)V}{1000w} \tag{1}$$

$$\%\ \text{removal} = \frac{(C_i - C_e)100}{C_i} \tag{2}$$

where q_e is the metal uptake capacity (mg metal/g dry Mi), V is volume of the solution (mL), C_i is initial concentration (mg/L), C_e is final concentration in solution (mg/L) and w is mass of the sorbent (g).

3. Results and discussion

3.1. Effect of solution pH and pretreatments

Solution pH affects the solution chemistry of the metals [23]. A significant increase in Ni(II) and Co(II) uptake per weight of biomass was observed as the pH increased from 1 to 6 and 1 to 5 for Ni(II) and Co(II), respectively (Figs. 1 and 2). Maximum biosorption capacity of native and pretreated *M. indica* was observed at pH 6 for Ni(II) and at pH 5 for Co(II). At lower pH, due to the protonation of binding sites resulting from high concentration of proton, negative charge intensity on the sites is reduced which results in the reduction or inhibition for the binding of metal ions [24]. With increase in pH, there is increase in metal uptake, which may be due to the ionization of functional groups and an increase in the negative charge density on the cell surface. Beyond optimum pH values, the formation of hydroxide precipitates reduces the amount of free metal ions which accumulate to the biosorbent [17,25].

The chemical pretreatments play important role to enhance the adsorption capacity of the biomass by modifying the cell surface either by removing or masking the groups or exposing more metal binding sites [26,27]. Keeping this in mind we investigated the effect of different chemicals on Ni(II) and Co(II) removal using *M. indica* as biomass and the comparison of all pretreatments were shown in (Figs. 1 and 2). Uptake capacity of *M. indica* was increased after pretreatment with NaOH, HCl, H_3PO_4, HNO_3 and C_6H_6 but NaMi biomass showed the significant improvement compared to other pretreated biomasses. The possible explanation of improvement in the uptake capacity of NaMi, HAMi, HPMi and NAMi for Ni(II) and Co(II) is that acids pretreatment could rupture the biomass cells which could release polymers such as polysaccharides that have a high affinity toward certain metal ions and increase porosity and surface area for adsorption [17,26,28,29] and bases may remove the protein and lipid fractions of the biomass surface, thus may expose more metal binding sites and improve the adsorption capacity of biomass. Alkali treatment may also play a role in the exposure of certain chemical groups, which enhanced the binding of cationic metal contaminants or may destroy autolytic enzymes that cause putrefaction of biomass and remove lipids and proteins that mask reactive sites [18,30,31].

However the results in Figs. 1 and 2 indicated that AAMi, FMi and HPMi biomasses showed reduction in adsorption of Ni(II) and Co(II). Formaldehyde and acetic acid may cause cross-linking of adjacent hydroxyl groups in cell wall glucose and also reduction in surface area due to cross-linking. The reduced surface area and the high degree of cross-linking may inhibit effective interaction between metals and the specific binding sites, which resulted in reduction of adsorption [32].

As maximum sorption capacity was achieved with NaMi leaves, further experiments were performed with NaMi leaves at pH 6 and 5 for Ni(II) and Co(II), respectively.

3.2. Sorption isotherms

The apparent capacity of native and NaMi leaves for Ni(II) and Co(II) metals were determined at different Ni(II) and Co(II) concentrations. Fig. 3 clarifies the relation between sorption capacities and the metals ion concentrations. It was observed that Ni(II) and Co(II) uptake capacity increased as initial metal concentration increased up to 100 mg/L. Afterwards a decrease trend in sorption capacity was noted. This sorption characteristic indicated that surface saturation was dependent on the initial metal ion concentrations. At low concentrations, adsorption sites took up the available metal more quickly. Secondly, the ratio of the initial moles of metal ions to the available surface area was low at lower concentration and subsequently; the fractional sorption became independent of initial concentration. However, at higher concentration the available sites of sorption become fewer compared to the moles of metal ions present and hence, the percentage removal of metal would be dependent upon the initial metal ion concentration [33].