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Removal of lead(II) from aqueous solution using heartwood of *Areca catechu* powder

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ABSTRACT

Removal of lead(II) from aqueous solution was studied using the powder of heartwood of *Areca catechu* as a new biosorbent under batch method at room temperature. Various sorption parameters such as contact time, initial concentration of lead(II) ion, effect of pH and amount of the biomass on the adsorption capacity of the biosorbent were studied. The adsorbent was effective for the quantitative removal of lead(II) ions in acidic conditions and equilibrium has been achieved in 25 min. The equilibrium adsorption data were fitted to Langmuir and Freundlich adsorption isotherm models and the model parameters were evaluated. The kinetic study showed that the pseudo-second order rate equation better described the biosorption process. The FT-IR spectra of the adsorbent before and after treatment with lead(II) solution indicated that hydroxyl, carboxyl, amide and amine groups were major binding sites with the metal. This method is quite feasible, economic, time saving, and low cost.

1. Introduction

Contamination of the environment by heavy metals is a growing concern because of health risks on humans and animals [1,2]. Most of the toxic metal pollutants are waste products of industrial and metallurgical processes and in particular, the effluents from tanning industries. According to the WHO, the metals of most immediate concern are Al, As, Cd, Cr, Co, Cu, Fe, Pb, Mg, Hg, Ni, and Zn.

There are several techniques, which have been utilized to reduce heavy metal ion content in effluents, namely lime stone precipitation, ion exchange, adsorption on activated carbon, membrane processing and electrolytic methods [1]. Most of these methods have been found to be limited since they often involve high capital and operational cost and may also be associated with the generation of secondary wastes. Of these techniques, activated carbon adsorption appears to be particularly competitive and an effective process for the removal of heavy metals at trace level [3]. A good number of studies have been reported for metal ion removal by using different bioadsorbents. In this regard, low cost biosorbent such as neem-leaf powder [4], *phaseolus vulgaris* [5], Canadian albicans [6], macro fungus [7], pine bark [8], *ficus religiosa* leaves [9], green algae [10], citrus peel [11], bael leaves [12], *moringa oleifera* bark [13] etc. have been utilized for the removal of lead and other heavy metals from wastewater.

Lead was chosen for biosorption studies with regard to their wide use in the industry and the potential pollution impact. Lead is released into the aqueous system from paper and pulp industries, lead smelter, boat and ship fuels, battery manufacturers and ammunition industries. Lead can contaminate the environment by anthropogenic sources as well as natural geochemical processes. It can accumulate along the food chain and is not amenable to biological degradation [14]. Lead exposure causes weakness in fingers, wrists and ankles. The effects of lead toxicity are very wide ranging and include impaired blood synthesis, hypertension, severe stomach-ache, and brain and kidney damage and even can cause miscarriage in pregnant women. The consistent pattern of lower IQ values and other neuropsychological deficits among the children exposed to higher levels of lead pollution have been reported [15].

In the present study, the ability of the heartwood powder of *Areca catechu* (betel-nut tree) (HPAC) to eliminate Pb(II) ion from synthetic wastewater and the effect of various parameters such as contact time of biosorbent and sorbent, pH of the metal solution, initial metal ion concentration and different biomass amount have been investigated. Equilibrium modeling was carried out using Langmuir [16] and Freundlich [17] adsorption isotherm. The nature of the sorption process has been evaluated with respect to its kinetic aspects.

2. Materials and methods

2.1. Preparation of the heartwood powder of *A. catechu* (HPAC)

A healthy and matured *A. catechu* (betel-nut tree) is collected from Bakhrapara village of Bongaigaon district of Assam, India and the heartwood of the same is carefully separated. The heartwood of *A. catechu*, which is soft and spongy, is cut into small pieces and washed with tap

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water and then with double distilled water to remove dust and other impurities. The small cut pieces of heartwood of *A. catechu* are sun-dried for seven days and dried again in an electric oven at 70 °C for 48 h. The dried materials are grounded in a laboratory blender and made into fine powder. The finely divided powder of the heartwood of *A. catechu* is then shorted in desiccator and used for biosorption studies.

2.2. Metal solution

All chemicals and reagents used for experiments and analyses were of analytical grade. Stock solution of 1000 mg/L of Pb(II) was prepared from Pb $(NO_3)_2$ (E. Merck, Mumbai, India) in double distilled water that contained few drops of 0.1 N HNO_3 to prevent the precipitation of Pb(II). The solution was diluted as required to obtain the working solution. The initial pH of the working solution was adjusted to 5.0 by an addition of the 0.1 N HNO_3 or 0.1 N NaOH solutions except for the experiment examining the effect of pH. Fresh dilutions were used for each study.

2.3. Methods of adsorption studies

Batch adsorption experiments were carried out by shaking the flasks at 120 rmp for a fixed period of time using a mechanical shaker. Following a systematic process, the adsorption uptake capacity of Pb(II) in batch system was studied in the present work. The data obtained in batch mode studies was used to calculate the equilibrium metal adsorptive quantity by using the following expression:

$$q_e = \frac{(C_o - C_e)V}{m}$$

where q_e is the amount of heavy metal ion adsorbed onto per unit weight of the biomass in mg/g, V is the volume of solution treated in liter, C_o is the initial concentration of metal ion in mg/L, C_e is the equilibrium metal ion concentration in mg/L and m is the biomass in g.

2.3.1. Effect of contact time

Batch biosorption experiments were carried out at different contact times (5, 10, 15, 20, 25, 30 and 35 min) at an initial concentration of 20 mg/L of Pb(II) ion solution at pH 5.0, the HPAC dose concentration is 0.5 g in 100 ml of solution in 250 ml conical flask at room temperature (29 °C ± 2 °C). The samples were then agitated in a mechanical shaker at 120 rmp at a regular time interval and filtered through Whatman 42 filter paper and the filtrates were analyzed using flame atomic absorption spectrometry (Model: Perkin Elmer 3110). Each determination is repeated three times and the results given were the average values.

2.3.2. Effect of initial metal ion concentration

Equilibrium experiments were carried out by contacting 0.5 g of HPAC with 100 ml of Pb(II) ion solution of different initial concentrations (10 mg/L–70 mg/L) at pH values of 5.0 at room temperature. A series of such conical flasks were shaken for 25 min at a speed of 120 rpm at room temperature (29 °C ± 2 °C). The samples were filtered and the filtrates were analyzed as mentioned before.

2.3.3. Effect of biosorbent concentration

Batch adsorption tests were done at a different concentration of HPAC from 0.1 g to 0.6 g at a 100 ml solution of 20 mg/L of Pb(II) ion at pH 5.0, for a contact time of 25 min at room temperature (29 °C ± 2 °C). The samples were then agitated and filtered and the filtrates were analyzed as mentioned before.

2.3.4. Effect of solution pH on biosorption

The effect of pH on the adsorption capacity of HPAC was investigated using a 100 ml solution of 20 mg/L of Pb(II) ion for a pH range of 2.0 to 7.0 at 29 °C. Experiments could not be performed at higher pH value due to hydrolysis and precipitation of lead ions. Flasks were agitated on a shaker for 25 min to ensure that the equilibrium was reached. The mixtures were then filtered and the concentration of metal in the filtrates was measured.

2.4. FT-IR measurements

FT-IR spectra for both free HACP and Pb(II) loaded HPAC were obtained by KBr pellets methods operated on FT-IR spectrophotometer (Brucker, Vector 22) to investigate the functional groups present in the biomass and to look into possible Pb(II) binding sites.

3. Result and discussion

3.1. Effect of contact time

The effect of contact time on Pb(II) biosorption on HPAC was studied and the results were shown in Fig. 1. From Fig. 1, it was found that the adsorption quantity of Pb(II) ion on HPAC increases as the contact time increased. The biosorption of lead onto HPAC was rapid for the first 5 min (88%) and equilibrium was nearly reached after 25 min (97%). Hence, in the present study, 25 min was chosen as the equilibrium time. Basically the removal rate of sorbate is rapid, but it gradually decreases with time until it reaches equilibrium. The rate in percent of metal removal is higher in the beginning due to the larger surface area of the adsorbent being available for the adsorption of the metals [18]. It is also relevant that, since active sorption sites in a system have a fixed number and each active site can adsorb only one ion in a monolayer, the metal uptake by the sorbent surface will be rapid initially, slowing down as the competition for the decreasing availability of active sites intensifies by the metal ions remaining in the solution [19].

3.2. Effect of initial metal ion concentration

Biosorption experiments with HPAC were conducted for solutions containing 10 mg/L to 70 mg/L Pb(II) ion. As seen in Fig. 2, at lower concentrations of Pb(II) ion (10 mg/L–40 mg/L), biosorption was completed in about 5 min, but at higher concentrations it took about 25 min. At lower concentrations, all metal ions present in the solution would interact with binding sites and then facilitated about 99% adsorption. At higher concentration, more Pb(II) ions are left unabsorbed in the solution due to the saturation of binding sites. This appears due to the increase in the number of ions competing for available binding sites in the biomass [20].

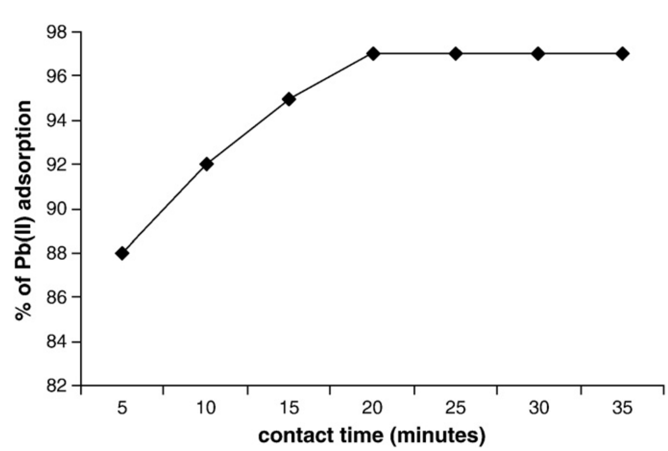

Fig. 1. Effect of contact time on Pb(II) adsorption on the heartwood powder of *Areca catechu* (HPAC), 100 ml single metal solution, pH = 5.0, initial metal ion concentration (C_o) = 20 mg/L, biosorbent amount = 0.5 g, and temperature = 29 °C.