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Characterization of chemically modified biosorbents from rice bran for biosorption of Ni(II)

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ABSTRACT

The current study explains the effect of chemical pretreatments on rice bran (RB) for the removal of Ni(II) from aqueous solution. Among the pretreated RB biomasses, NaRB, HARB, CaRB and SARB showed much improvement in adsorption capacity. The kinetic data was analyzed in term of pseudo first-order and pseudo second-order expressions. The Langmuir and Freundlich isotherm models were applied to the equilibrium data and defined very well the Langmuir isotherm model. The maximum biosorption capacity of NaRB, HARB, CaRB and SARB for Ni(II) was found to be 153.6, 149.4, 144.0 and 140.0 mg/g, respectively. The results from the sequential adsorption–desorption cycles showed that it was possible to reuse the biosorbent. Among the desorbents studied, HNO_3 with desorption efficiencies equal to 68.2 and 67.4%, for NaRB and HARB, respectively, at the end of three cycles, was found to be the best desorbent.

1. Introduction

The pollution due to metal ions such as Ni(II) usually comes from several industrial processes such as electroplating, plastics manufacturing, Ni–cadmium batteries, fertilizers, pigments, mining and industries that involve metallurgy [1]. It is important to note that the regulations do not permit the concentration of nickel over 2 mg/L in effluents [2], while, the Ni(II) concentration in plating rinse can approach up to 2–900 mg/L. The effluent from several industrial process such as paint and pigment industry, porcelain enameling and copper sulphate manufacturing industries record Ni(II) concentrations that varies from 0 to 40 and 0.25 to 67 with an average concentration ~22 mg/L [3]. The Ni(II) concentration of these levels are seriously dangerous for human beings and other livestock due to the intrinsic carcinogenic nature of Ni(II) and their compounds [4]. Hence, it is essential to remove Ni(II) from water before domestic use. In this context, a number of conventional methods are practiced to remove Ni(II) from wastewater streams, such as *via* adsorption by using activated carbon [5]; chemical precipitation [6] and crystallization in the form of nickel carbonate [7]. In contrast to these conventional methods, the biosorption processes show many advantages such as being cost effective, selective and quite effective with an added feature to remove low concentrations of toxic metals from solutions [8]. The natural affinity of biological compounds for metallic elements could contribute to the purification of wastewater from toxic metals, a fact that has been proved in many cases and by many researchers [9–14].

In parallel developments, a huge wave of growing interest can be seen in abundant biomass types, which comes from the waste of large-scale industrial processes and agricultural waste materials [15,16]. In the later case, the major constituents of agricultural by-products are lignin and cellulose that contain several functional groups such as alcohols, aldehydes, ketones, carboxylic acid, phenolic and ether linkages. These groups have strong ability to bind toxic metal ions by utilizing an electron pair to form complexes in solution [17]. However, in order to use biomass for the removal of toxic metals from wastewater, they require some

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level of pre-treatment that helps to expose the binding sites. Therefore, in usual practice, several common chemicals such as mineral acids and alkalis, ethanol, some organic acids and acetone are commonly used for the pretreatment of biomass. In such cases, the extent of chemical pretreatment strongly depends on the cellular components of the biomass itself. In many instances, acidic pretreatment is found more successful; primarily due to the easy removal of impurities and ions that might block the binding sites [18].

At present, one of the largest sources of biomass from agriculture waste is rice bran (RB), which is the hard outer layer of rice grains. It is produced in large quantities during rice processing and is far in excess of any local uses (such as animal feed), thus frequently causing disposal problems. Since, RB is one of the largest produced biomass, it can be potentially used for the removal of toxic metals from wastewater. So far, only a few studies have been carried out that exploit RB for this purpose. Some of these studies include *in vitro* study for the determination of RB's capacity for Hg, Cd and Pb [19], bioscavenging of Cu(II) ion from aqueous solution [20,21], removal of mercury from waste water [22], biosorption of Cd(II), Cu(II), Pb(II) and Zn(II) from aqueous solutions [23], equilibrium studies for the sorption of chromium and nickel [24] and biosorption of nickel [25,26]. In most of these studies, the use of RB was fundamentally based on its granular structure, insolubility in water, chemical stability and local availability.

Since, the chemical pre-treatments can potentially modify the cell surface either by removing or masking the groups or exposing more metal ions binding sites, here we investigated the effect of inorganic bases, inorganic acids, organic solvents and inorganic salts on Ni(II) removal using RB as biomass. The major emphasis of the present study was to improve the biosorption capacity of RB for Ni(II) removal and in large perspective to contribute to the understanding and modeling of the equilibrium of biosorption process. For this purpose, various factors affecting the biosorption, such as treatment, pH of solution, initial metal ions concentration and time were investigated by the batch equilibration technique. Desorption studies to recover Ni(II) from the biosorbents using three different desorbents (acidic, basic and salt in nature) are also discussed.

2. Materials and methods

2.1. Chemicals and instruments

All chemicals were pro-analysis grade and were purchased from E. Merck Company (Darmstadt, Germany). Ni(II) working solutions were freshly prepared by diluting the stock solution (1000 mg/L).

The targeted metal ion [Ni(II)] concentrations were measured with an atomic absorption spectrometer equipped with an air-acetylene burner (Analyst 300, Perkin-Elmer, Waltham, USA). A pH meter (HM 30P, Analyticon Instruments Corporation, Springfield, USA) was used to check the pH of the metal ions containing solutions. Other instruments such as orbital shaker (PA 250/25. H, Adolf Kuhner AG, Birsfelden, Switzerland), Octagon siever (OCT-DIGITAL 4527-01, Endecotts Ltd, London, UK) and electric balance (AW 220, Shimadzu Kyoto, Japan) were also used during the course of study.

2.2. Rice bran collection and chemical pretreatment of rice bran

The biosorbent RB was collected from small rice processing mills situated in Sialkot and Hafizabad cities of Pakistan. The samples were washed thrice with distilled water to remove dust particles and then dried for one week at 70 °C. These samples were later crushed and sieved in order to select a fraction of untreated biomass with particle diameters 0.250 mm.

The chemicals used for pretreatments of RB were inorganic bases (sodium hydroxide, calcium hydroxide, aluminum hydroxide), inorganic acids (hydrochloric acid, nitric acid, sulphuric acid), organic solvents (formaldehyde, formic acid, acetic acid, methanol, acetic anhydride) and inorganic salt solutions (sodium carbonate, sodium bicarbonate). For inorganic acids/bases and inorganic salts pretreatments, 20 g of RB biomass was treated with 0.5 M of 200 mL solution of each chemical for 24 h in 500 mL conical flasks.

For formaldehyde treatment, pretreatment method of the sample was adopted from the 'Standard method' [27]. 5 g of this biomass was maintained in 500 mL of 0.5 M formaldehyde solution for 2 h with a stirring speed of 120 rpm at ambient temperature. The dried biomass was boiled in 0.1 M formaldehyde at 80 °C for 4 h and filtered through 0.45 μm millipore filter paper. The biomass after each treatment was washed with deionized water until the pH of the wash solution was in near neutral range (pH 6.8–7.2). For organic acid treatments, the chemical modification of RB was made according to the similar method previously described by Vaughan et al. [28]. 5 g ground RB was mixed with 0.5 M formic acid and 0.5 M acetic acid, respectively, and stirred for 30 min. The acid/RB slurry was placed in a stainless steel tray and dried at 60 °C in a forced air oven. After 24 h, the thermo-chemical reaction between acid and RB was preceded by raising the oven temperature to 130 °C for 90 min. After cooling, the modified RB was washed with distilled water until the pH of wash solution was in near neutral range (pH 6.8–7.2). The methanol and acetic anhydride treatment was made according to method described by Bai and Abraham [29]. After this the biomasses were dried at 60 °C for 24 h in a drying oven. Dried biomasses were ground in a mortar and pestle and sieved to obtain the particle size fraction ~0.250 mm.

The resulting biomasses were called inorganic bases treated biomasses as sodium hydroxide treated rice bran (NaRB), calcium hydroxide treated rice bran (CaRB) and aluminum hydroxide treated rice bran (AlRB); inorganic acids treated biomasses as hydrochloric acid treated rice bran (HARB), sulphuric acid treated rice bran (SARB) and nitric acid treated rice bran (NARB); organic solvents treated biomasses as formaldehyde treated rice barn (FRB), formic acid treated rice bran (FARB), acetic acid treated rice bran (AARB), methanol treated rice bran (MRB) and acetic anhydride treated rice bran (AAnRB); inorganic salts treated rice bran as sodium carbonate treated rice bran (NaCRB) and sodium bicarbonate treated rice bran (NabCRB).

2.3. Batch biosorption studies

After pretreatments, different parameters such as effect of pH (3–7, pH was adjusted by 0.1 M NaOH and 0.1 M HCl), effect of different initial Ni(II) concentrations and contact time were studied in batches. In all experiments, 100 mL solution of Ni(II) was taken in 250 mL conical flasks along with blank. 0.05 g pretreated biomass having particle size ~0.250 mm was added to each flask. These flasks were sealed with aluminum foil and agitated in orbital shaking incubator at 130 rpm at 30 °C for 24 h. After the completion of experiment, all samples were filtered using Whatman filter paper No. 42 and stored in plastic bottles to analyze Ni(II) before and after filtration.

2.4. Analysis of metal ion concentrations

The concentration of metal ions was measured with an atomic absorption spectrometer equipped with an air-acetylene burner (Analyst 300, Perkin-Elmer, Waltham, USA). The wavelength used for the analysis of the metal ion in this study was 232 nm. The instrument was calibrated within the linear range of analysis and a correlation coefficient of 0.99 or greater was obtained for the

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