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BIOSORPTION OF HEAVY METALS BY PRETREATED BIOMASS OF A.BARBADENSIS MILLER LEAVES RESIDUE

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ABSTRACT

The biosorption potential of chemically pretreated herbal biomass of A.barbadensis Miller leaves residue for Cd(II) and Ni(II) ions from aqueous solution . Biomass was pretreated with different types of alkaline/salts (NaOH, Na_2S, Na_2CO_3, NaCl & KOH), acids (HCl, $H_2C_2O_4$ & H_2SO_4) . Pretreatment of biomass with Na_2CO_3 and NaOH were proved to increase or maintain adsorption efficiency and capacity in comparison to untreated biomass. Pretreatment with $NaHCO_3$, NaCl and $CaCl_2$ significantly reduce (10-40%) metal efficiency of the adsorbent. Whereas, acid treatments resulted in drastic loss (80%) in metal uptake efficiency of the biomass. Amongst various pretreatments, Na_2CO_3 could be used efficiently for the removal of Ni(II) and Cd(II) ions from aqueous solution using A. barbadensis miller leaves residue.

Keywords : A. barbadensis Miller leaves powder ; Bioadsorption; Cadmium; Nickel; Pretreatments.

I. INTRODUCTION

Environment pollution by toxic metal ions, particularly as a result of industrialization, is increasingly being associated with public health in an urban setting, as toxic metals not only lead to contamination of aquatic life but also cause harm to people's health, even at low concentrations[1]. In recent years, there has been a growing concern with environmental protection. This can be achieved either by decreasing of pollutants invasion to the environment or by their removal from contaminated media [2].Among these toxic metals, cadmium and Nickel is of considerable environmental and health significance because of its increasing mobilization and human toxicity. The major sources for the intoduction of cadmium in water are nonferrous metals smelting and refining, manufacturing processes related to chemicals and metals, and domestic wastewater[3]. These metals ions are also exposes human health to severe risks, as it can provoke cancer, kidney damage, mucous membrane destruction, vomiting, bone damage as well as affect the production of progesterone and testosterone[4]. Consumption of rice containing high concentration of cadmium led to a surge in the Itai – Itai disease in japan in 1955 [5]. Cadmium Cd(II) and nickel Ni(II) ions are frequently encountered together in industrial waste water from electroplating, batteries , paint , porcelain enamelling). Ni (II) Concentration in the effluent wastewaters varies from ranges between 10 and 80 mg / l and Cadmium ions Cd (II) concentration from plating plant around 15 -20 mg/l. [6].

Several methods have been widely applied for the removal of toxic metal ions such as precipitation, ion exchange, reduction, electrochemical treatment, reverse osmosis, solvent extraction, membrane filtration [7].

These methods have a high cost, generate secondary pollutants, or are simply incompetent.

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Biosorption has emerged as a promising method, with such advantages as high efficiency even with low metal concentrations , low cost , no additional nutrients requirements, easy operation, potential metal recover . Various physical (heat treatment, autoclaving, freeze drying, and boiling) and chemical (acids, alkali and organic chemicals) pretreatment protocols have been developed to convert the viable cells into nonviable[8].According to many reserchers, the chemical pretreatment methods may provide better results in the list of number of pretreatment protocols owing to change in cell wall chemistry of the biosorbent have reported that alkaline (caustic) treatment could enhance metal binding by biomass[9]. Acid-washing process have better results over other treatments as this treatment may dissolve polysaccharide components in the outer cell wall layer of the biosorbent, thus producing additional binding sites [10].

In present Study A. barbadensis Miller Leaves powder i.e Aloe Vera residue is a Selected as a bioadsorbent , This plant which belongs to the family of Liliaceae and is generally succulent with a roll of elongated. This plant has very long age, which found a lot in India (11). Aloe leaf consists above 75 nutrients and 200 active compounds, including 20 minerals, 18 amino acids, and 12 vitamins like A, B1, B2, B12, E and C. (12). Now a days so many herbal industries in india so much amount waste after extraction of juice and gel. However, effect of chemical pretreatments is the important parameters for the successful application of biosorption by the biosorbent. Therefore, current investigation was designed to investigate the biosorption potential of pretreated biomass of *A. barbadensis Miller leaf powder* for removal of Cd(II) and Ni(II) from aqueous solution.

II. MATERIALS AND METHODS

1.1. Bioadsorbent

The raw biomass of A. barbadensis Miller leaves residue was collected from different herbal industries in New Delhi . The biomass were washed with distilled water to remove extraneous materials and dried at 80 ^{0} C over night . The dried biomass was then used in this work.

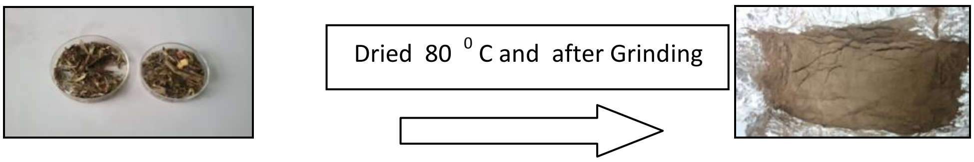

Fig 1. A.barbadensis Miller leaf (ABL)Residue Converted into Dried powder form for use of Different Chemical pretreatments

1.2 Adsorbate

All the chemicals used in the study were of analytical reagent (AR) grade. Nickel Nitrate {$Ni(NO_3)\cdot 6H2O$} was procured from M/S Qualigens Fine Chemicals, Mumbai. Cadmium Nitrate {$Cd(NO_3)4H_2O$}, Stock solutions of Cd(II) and Ni(II) were made by dissolving exact amount $Ni(NO_3)\cdot 6H_2O$ and $Cd(NO_3)4H_2O$ of in double distilled water, respectively.

II. PRETREATMENTS OF BIOMASS

A.barbadensis Miller leaves residue powder biomass was subjected to different chemical treatments. The acid and base of same normailities (0.1 N) were used for pretreatments (Table 1). In each pretreatment, the biomass was slowly stirred in the chemical solution for a certain period of time. After each pretreatment biomass was washed with double distilled water till pH of the washing solution reached a neutral range (6-7). Finally

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pretreated biomass was dried in an oven at 80 ± 1°C for 24 hours. The biomass was then passed through 150 µm mesh sieve of to obtain particle sizes of less than 0.5-1 mm diameter. The dried biomass was preserved in airtight jar to be used in biosorption tests. Simple oven dried biomass was also utilized in biosorption test experiments to assess and compare the potency with chemically pretreated biomass.

III. BATCH BIOSORPTION EXPERIMENTS

Bioadsorption experiments were conducted using separate solutions containing Ni(II) and Cd(II) added in the form of $Ni(NO_3)_2.6H_20$ and $Cd(NO_3)_2.4H_2O$ respectively. Batch biosorption experiments were conducted by adding the 2 g of biomass in the reaction mixture measuring 100 mL with final adjustment of pH at 5.0 (0.5N NaOH and 0.5N HCl was used to adjust pH). The reaction mixture biomass were agitated in orbital shaker at 150 rpm for three hours at 30 ± 1°C. After that time, the mixture was filtered through Whatman filter paper No.1 and the residual metal ion concentrations were determined using Atomic Absorption Spectrophotometer (AAS 4141) ECIL, India at wave length of 217 nm using air acetylene flame.All the experiments were run in triplicates and control experiments were conducted with simple oven dried biomass (without any treatment).

The amount of metallic ion biosorbed per gram of biomass (q) and the efficiency of biosorption (R) were calculated using the following equations:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$\% \ Removal \quad (R) = \frac{(Co - Ce)}{Co} \times 100 \quad (2)$$

where, Ce = initial concentration of the metallic ion (mg L^{-1}); C_0 = final concentration of metallic ion (mg L^{-1}); M = dried mass of the biosorbent in the reaction mixture (g); V = Volume of reaction mixture (mL).

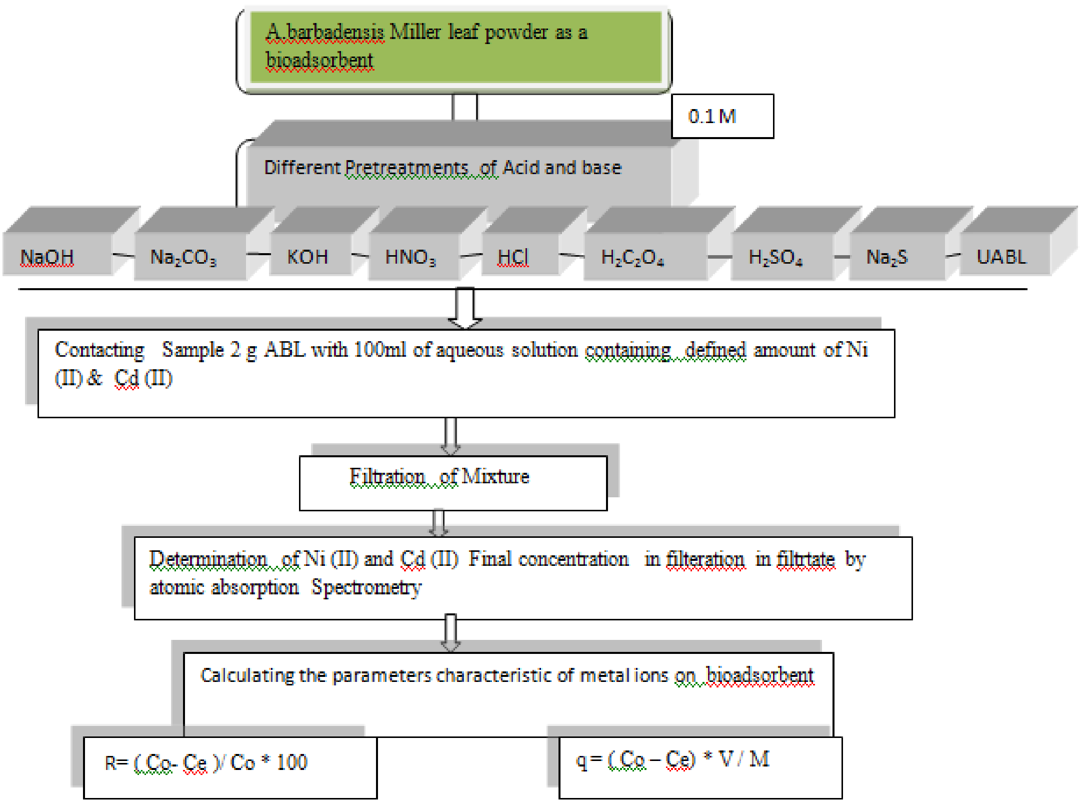

Fig.2. Flowsheet of Bioadsorption Process to removal of Cd(II) & Ni(II) ions with Different Pretreatments.

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IV. RESULTS

Batch experiments were employed to assess the biosorption potential of pretreated *A.barbadensis miller leaves powder* biomass while untreated biomass (UABL) was taken as control. The effect of pretreatments on biosorption of Ni(II) ion by *A. barbadensis Miller leaves* is show in Fig. 1(a). The results showed that biomass pretreated with Na_2CO_3 (0.1N) exibited the maximum biosorption efficiency (83.2 %) and capacity (4.16 mg g^{-1}) for Ni(II) as compared to control and rest of pretreatments. The biosorption efficiency of 75.5% (~3.77 mg g-1) recorded for biomass pretreated with NaOH (0.1N). Rest of chemical pretreatments to the biomass resulted in significant reduction in adsorption efficiency and capacity . However, the highest reduction of ~ 26% to 10.7 % in biosorption potential was dominant in case of HCl and H_2SO_4 pretreated biomass. Consequently trend of biosorption for Ni(II) ions was recorded to follow the sequence of Na_2CO_3 > NaOH ≥UABL (Table 1).

Table 1. Comparative analyses of biosorption potential of *A. barbadensis Miller Leaves powder* for metal ions. Biosorption efficiency R (%) and Adsorption Capacity q(mg/g).

Treatments	%R, Cd (II),	%R, Ni (II),	q, Cd (II)	q, Ni (II)
NaOH	94.3	75.5	3.91	3.775
Na_2CO_3	98.2	83.2	4.91	4.16
Na_2S	90.6	70.2	3.715	3.51
KOH	89.6	61.5	3.63	3.075
HNO_3	25.7	23.5	1.285	1.175
HCl	28.8	26.7	1.44	1.335
$H_2C_2O_4$	18.3	7.8	0.915	0.39
H_2SO_4	21.9	10.3	1.095	0.515
Untreated , ABL	88.8	60.2	4.44	3.01

For Ni(II) similar trend of various employed pretreatment was observed as mentioned for Cd(II). Alkali pretreatment

[Na_2CO_3 (0.1 N)] showed significantly greater adsorption efficiency (98.2%) as compared to UABL (Fig. 1b). Biomass pretreated with NaOH (0.1N) showed efficiency (94.3 %) having capacity of ~4.91 mg g^{-1} as was recorded in UABL. The verified biosorption potential was significantly higher than the other given treatments.

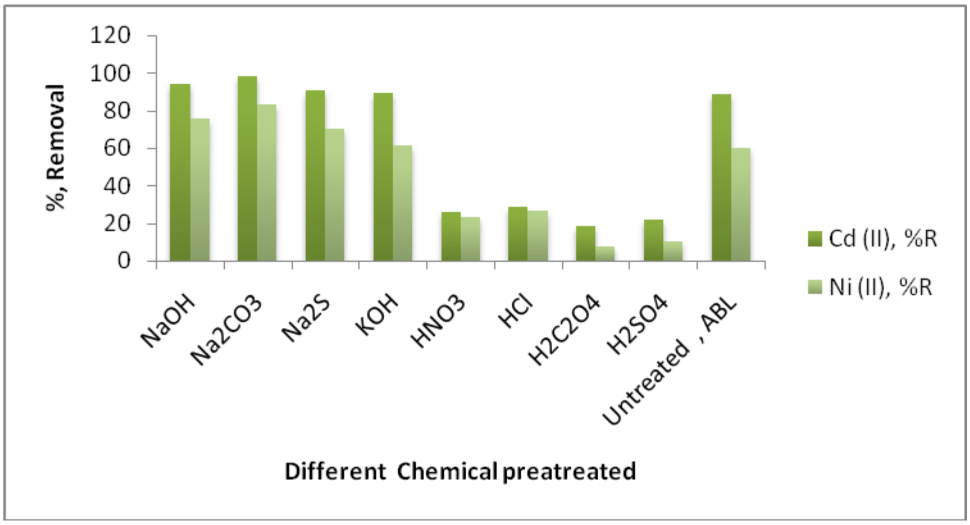

Fig. 3 . Graph Between % removal Vs Different Chemical Pretreatments For Cd (II) & Ni(II)

The most of the non significant treatments but was reduced nearly 25% in contrast to maximum (98.2%) recorded potential. Chemical treatments like HCl (0.1 N) and H_2SO_4 (0.1 N) maintained lowest extent of biosorption capacities of 1.22 mg g^{-1} and 1.44 mg g^{-1}, respectively for Cd(II) ion removal in comparison with other pretreatments. The tendency of pretreated biomass of *A.barbadensis miller leaf residue* for maximum removal of Cd (II) was categorized as: Na_2CO_3 > NaOH ≥ UABL (Table 1).

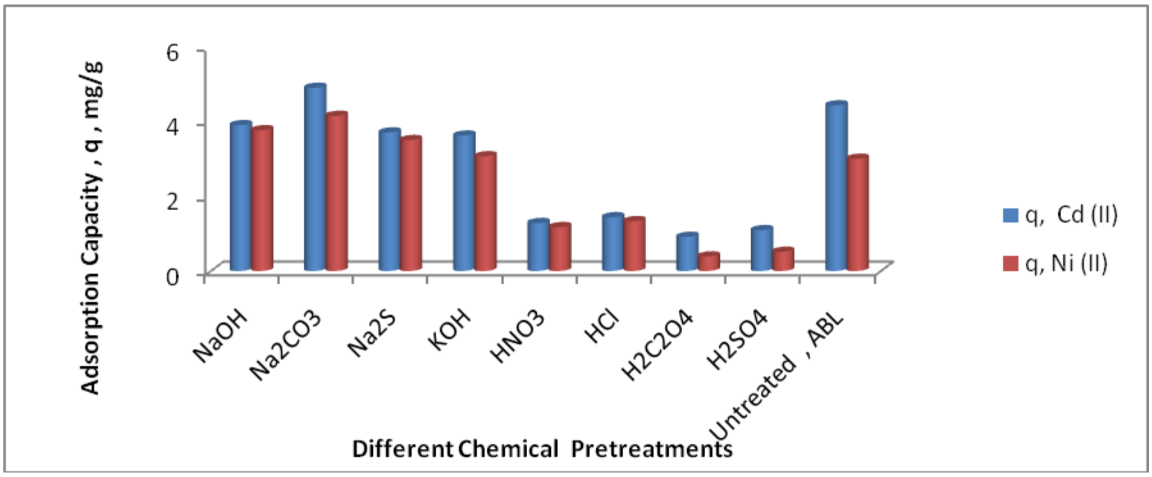

Fig. 4. Graph Between Adsorption capacity VS Different chemical pretreatments for Ni(II) & Cd(II)

V. DISCUSSION

In present investigation, biomass of *A. barbadensis miller leaves* was pretreated with different bases and acids of same normality and was evaluated for Cd(II) and Ni(II) removal from aqueous solution. Assessments revealed that the A.barbadensis miller leaves powder biomass exposed to alkaline supplements/salts exhibited significantly higher and parallel biosorption efficiency in comparison to untreated biomass.Whereas most of the pretreatments induced reduction in uptake efficiency and capacity of the adsorbents as compared to control (untreated biomass). Whereas, physical and chemical treatments can be use to enhance the metal uptake capacity of the biomass, which led to removal, hiding or exposing chemical groups that binding or exchange with the adsorbed metal ions [13]. In current research work, an increase in biosorption of Cd(II) and Ni(II) ions was noticed as a result of alkali pretreatments particularly Na_2CO_3 and NaOH. Similar enhancement in metal uptake capacity of the A.barbadensis Miller leaf powder biomass regarding alkali pretreatment was recorded by [14]. It could be due to chemical modifications of the cell wall components. The modification of biomass probably destroys autolytic enzymes that cause putrification of biomass and remove lipids and proteins that mask the reactive sites [15]. The deproteination should theoretically reduce metal retention. Reduction in adsorption efficiency and capacity of adsorbent due to rest of alkaline/salts treatment (NaHCO3, detergent, NaCl and $CaCl_2$) could be results of more affinity of active chemical groups viz., HCO- 3, HSO- 4 & Cl- ions to the cell wall components of the adsorbent[16]. Presently the recorded reduction in sorption capacity of bioadsorbent for metal ions was evidenced due to acid pretreatment. It could possibly be explained in terms of H^+ ions binding to the biomass after acid treatment being responsible for the reduction in adsorption of heavy metals. This indicated that the acids destroyed the absorbing groups and their positive ions(H^+) may covalently bonded to the absorbing surfaceshave suggested that the higher the biomass electronegativity the greater would be the attraction and adsorption of heavy metal cations[17]. Thus, the remaining H^+ ions on the acid pretreated biomass may change the biomass electronegativity, resulting in a reduction in bioadsorption cdapacity.

VI. CONCLUSION

The present study concludes that chemically pretreated biomass of *A. barbadensis Miller leaves residue* exhibited greater, same or less adsorption capacity and efficiency than that of untreated biomass, The bioadsorbent could be effectively utilized to remove Cd(II) and Ni(II) by pre treating it with Na_2CO_3.

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