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Research Article

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Simultaneous removal of Ni(II) – Cd(II) metal ions from wastewater by biosorption process using modified *A. barbadensis miller* leaves powder .

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Abstract

This study addresses the use of waste *A. barbadensis Miller* as bio-adsorbent after chemical modification with (Na_2CO_3) **[MABL]** residue powder henceforth) for the simultaneous removal of Cd(II) and Ni(II) ions from wastewater. The equilibrium biosorption data was obtained at different experimental and initial metal ion concentration conditions (C_0=10–100mg/l, Contact time=120 min, temp=30°C, MABL dosage of 0.6 g/l at pH 6.). The biosorption capacity for Cd (II) was higher than that for Ni(II) for the binary metal solutions. The maximum removal of 84.45 % was attained which is an effective removal percentage of Ni(II) and Cd(II) in battery industry wastewater The competitive extended Freundlich model represents the binary biosorption equilibrium data satisfactorily and adequately. This study proves that MABL is an effective and low-cost bio-adsorbent for the removal of heavy metals simultaneously from wastewater.

Keywords : Biosorption; Modified *A,barbadensis miller* leaves (MABL); Multi-component isotherms; Cadmium(II); Nickel(II)

1. Introduction

Heavy metals and toxic pollutants arising from industrial effluents are a prominent source of environmental pollution.which is increasing significantly day by day in the water bodies. Contaminated heavy metal effluents discharging into natural water reservoirs arise from various industries, including mining, smelting, refining ores, fertilizer industries, electric board manufacturing, tanneries, batteries, and paper industries [1]. Typically, Heavy metals are chemical elements that have relatively high density, highly water-soluble and are toxic or cancerous even at low concentrations and very harmful to human and aquatic lives [2]. Cadmium (Cd(II)) and nickel (Ni(II) ions are frequently encountered together in industrial wastewaters (e.g. from mine drainage, plating plants, paint and ink formulation units, and porcelain enameling. Cadmium and Nickel from battery industries are also one of the major

source of water pollution. Cadmium also occurs in nature in the form of cadmium sulfide (CdS), causing kidney malfunction at overdoses, spilling proteins in the urine disrupting protein metabolism etc. [3-4]. Nickel is also a common environmental pollutant that is considered toxic (e.g. in concentrations of 15 mg/l), especially to activated sludge bacteria, and its presence is detrimental to the operation of anaerobic digesters used in wastewater treatment plants[4-6]. Exposure to high levels of Cd(II) and Ni(II) even for short periods of time causes nausea, vomiting, and diarrhea [5-6]and it is a suspected human carcinogen on long-term exposure. Nickel and Cadmium may also cause bone defects (osteocalcin, osteoporosis) in humans and animals. The average concentration of Ni(II) and Cd (II) found in the plating plant effluent is in the range of 0.17-1.36 mmol/Land 0.13-0.18 mmol/ L respectively. The Ministry of Environment and Forests (MOEF), Government of India has set Minimal National Standards (MINAS) of 0.0018 and 0.0341 mmol/L, respectively for Cd (II) and Ni (II) for safe discharge [6-7].

Several techniques used to remove heavy metal ions from aqueous streams include ion-exchange, reverse-osmosis, electrocoagulation/precipitation and biosorption. Biosorption is one of the best implementable methods at the industrial scale for the removal of heavy metals. Biosorption is an effective, economical, and feasible technique, that does not require additional chemicals. As a result, there is lot of interest in scientific community recently to use natural bio adsorbents including agro-wastes, leaves residue etc [7-9] .

A. barbadensis miller is the biological name of the commonly used perennial medicinal plant aloe vera. This belongs to the family of Liliaceae and is found almost everywhere in India [10-12]. As a result of growing interest of use of Aloe vera (*A. barbadensis miller leaves*) as a wonder drug and cosmetic, many industries using Aloe vera have emerged -worldwide including India. In turn, they produce considerable solid residue throughout the year from processing of the Aloe vera. In India, *A. barbadensis miller* leaves waste-based sorbents market stood at $ 28.70 million in 2019 and expected to reach $ 46.22 million by 2025. Aloe vera rind is a solid waste and is abundantly generated by the industries with no further use [13-15]. Chemical pretreatment to biosorbents is generally done to enhance the chemical surface heterogeneity, to enhance the number and dispersion of the functional groups available for binding with the metal, and/or to alter the surface morphology etc. Various chemicals are used for this purpose and for this study Na_2CO_3 was selected based on the bio -adsorption capacity. The efficiency of the Na_2CO_3 treatment to dried *A. barbadensis Miller leaves* powder **(MABL)** is already established and has been documented elsewhere [11-17]**.** Most of the work reported

in the literature involves single- component biosorption of heavy metal ions [4-8]. As stated earlier, industrial effluents contain several metals requiring simultaneous removal of two or more metals. To the best of our knowledge simultaneous removal of Cd (II) and Ni (II) ions by Modified *A. barbadensis miller* leaves residue (MABL) has not been reported so far.The main objectives of the present work are :

- To Study the feasibility of using MABL as a bio- adsorbent for the simultaneous removal of Cd (II) and Ni (II) metals ions from aqueous solution.
- To generate experimental data on biosorption equilibrium for the binary system containing Cd (II) and Ni (II).
- To develop the isotherm model applicable to non- competitive (extended Langmuir and extended Freundlich) biosorption of these metal ions.

2 Materials and Methods

2.1. Preparation of bio-adsorbent

Juneja Ayurveda and Herbal Industry, located in New Delhi, India, provided the bio-adsorbent *A. barbadensis Miller* (ABL) leaf residue. Dust and other contaminants were eliminated by washing the raw biomass material two or three times with distilled water. The *A. barbadenesis miller* leaves of were autoclaved for 20 to 30 minutes. During the steam heating, the sample was dried in an oven at 80 °C for 24 hours after being cleaned twice or three times with distilled water to remove color. A grinder was used to grind the dry material, and it was then sieved to a mesh size of 100 -150 microns. ABL Powder was pretreated with 0.1 M Na_2CO_3 chemical solutions for 12 hours at room temperature while being stirred at 150 rpm. After this process, the modified *A. barbadensis Miller* leaves (MABL) suspension was filtered and repeatedly cleaned with distilled water until the pH stabilized. This bio-adsorbent was then kept in a desiccator for further usage after being oven-dried for 24 hours at 80 °C.

2.2 Preparation of adsorbate

All the chemicals utilized in this investigation was of Analytical Reagent (AR) grade and had a purity level of above 99%. 2.743 g of cadmium nitrate ($Cd(NO_3)_2.4H_2O$) (Thomas Baker, India) was dissolved in the 1000 ppm of Cd (II), and 4.9538 g of Ni (II) in the form of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 1000 ml of double distilled water to prepared the stock solution . 0.1 M HCl and 0.1 M NaOH were used to balance of the solution's original pH. The final concentrations of metal ions were analyzed using Atomic Absorption Spectrophotometer (AAS 4141, ECIL, India), at a wavelength of 228 for Cd (II) and 217 nm for Ni(II) and using an air–acetylene flame. The binary mixtures of Ni(II) and Cd(II) ions of

different concentrations were prepared from their stock solutions. The concentrations of metal ions solutions were varied from 20 ppm to 100 ppm.

2.3 Biosorption Experiments

Batch operation was adopted to investigate the interaction between modified *A.barbaradensis miller* and a binary mixture of Ni (II) and Cd (II) ions. The simultaneous biosorption of the metallic cations from the binary mixture was investigated at experimental conditions: temperature 30ºC, pH 6.0, stirring spee 100 rpm, contact time of 120 minutes and MABL dose of 0.6 g /l. The initial Ni (II) concentrations were changed from 0 to 100 mg/L at each initial Cd(II) ion concentration and the concentration of one metal ion was varied in the range of 20-100 mg/l and the other metal ion was kept fixed at 20mg/l in one set of binary mixture. Similarly in other sets of binary mixtures, the concentrations were varied. The equilibrium uptake of Ni (II) decreases with the increasing initial cationic concentration up to 100 mg/L at all Cd (II) ions. A similar trend was observed for the uptake of Cd (II) ions in the absence and presence of Ni (II) ions.

2.4 Mono-component and Binary-Component Isotherm Equations

The equilibrium the characteristics of adsorption have been described by different isotherm equations, including Freundlich and Langmuir. The Freundlich isotherm [16] is derived by applying an inference that the surface is heterogeneous and that the heat of adsorption circulates unevenly over it. While in the Langmuir theory [17], the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent adsorbate (mg/l) and qe is the equilibrium adsorbate loading onto the adsorbent (mg/g) at high liquid-phase concentrations of the adsorbate. Langmuir and Freundlich isotherms can be expressed by equations 1 and 2.

Langmuir Isotherm:, $$\frac{1}{q_e} = \frac{1}{q_m \ K_L C_e} + \frac{1}{q_m} \qquad (1)$$

Freundlich Isotherm: $$\log qe = \log K_F + \frac{1}{n_f} logCe \qquad (2)$$

Where qe is adsorption capacity at equilibrium, qm is maximum adsorption capacity (mg/g)

K_L is the Langmuir adsorption constant (l/mg) related to the energy of adsorption,

K_F is the Freundlich constant (l/mg$n^{-1)}$ and (1/n) is the heterogeneity factor. A minimization

procedure can be adopted to solve Eq. (5) by maximizing the correlation coefficient between the predicted values of qe from Eq. (5) and the experimental data using the solver add-in function of the MS excel.

Binary-Component Isotherm Equation

For multi-component mixture biosorption in aqueous solution, two isotherm models namely Extended Langmuir and Extended Freundlich are generally employed [6].

Extended Langmuir Isotherm

The extended Langmuir isotherm model presented in equation (3) was formulated to explain multicomponent adsorption systems by expanding the mono-component Langmuir adsorption isotherm model. The fundamental theory of this model is that each sorbent active site is the same and equally accessible to every adsorbate.Hence, all the adsorbate molecules in the multicomponent system are adsorbed on the same adsorbent active surface sites and there is no interaction between the molecules adsorbed. The model further presupposes that the adsorption energy at the adsorbent active sites is uniform A simple theoretical treatment in case of multicomponent is the extension of the Langmuir equation, by neglecting interactions and assuming that the only effect is the reduction of vacant surface area available for the biosorption. Thus, the Langmuir Isotherm Equation for the biosorption of the binary mixture of Cd (II) and Ni (II) ions is given by equation 3

$$q_{e,i} = \frac{q_{max} K_i C_{e,j}}{1 + \sum_{j=1}^{N} K_j C_{e,j}} \qquad (3)$$

Where $q_{e,i}$ is the individual biosorption yield, q_{max} is the maximum biosorption yield, and $C_{e,j}$ is the equilibrium concentration in mg/L. Here, the values of q_{max} and Ki can be obtained from the optimized fitting of the Langmuir Isotherm Equation to the data that is obtained from the single component equilibrium biosorption.

Extended Freundlich Isotherm

The mono-component Freundlich equation can be applied to binary systems to develop extended Freundlich isotherm model. The model is used for heterogeneous systems when interaction is happening among the adsorbed molecules. Multicomponent system can be represented as equation 4 and 5.

$$q_{e,1} = \frac{K_{F,1} C_{e,1}^{n1+x1}}{C_{e,2}^{x2} + Y1 C_{e,1}^{Z2}} \qquad (4)$$

$$q_{e,2} = \frac{K_{F,2} C_{e,2}^{n2+x2}}{C_{e,2}^{x2} + Y2 C_{e.1}^{z2}} \quad \textbf{(5)}$$

Here, the constants n_1, n_2, and K_{F1} & K_{F2} are the same as used for Freundlich isotherm for single component and the other six parameters (X_1, Y_1, Z_1 and X_2, Y_2, Z_2) are determined using non-linear regression technique on multicomponent data.

The $q_{e,i}$, individual biosorption yield (Ad_i, %) and the total biosorption yield (Ad_{total}, %) can be calculated by using the following equations.

$$q_{e,i} = \left(\frac{C_{o,i} - C_{e,i}}{W}\right) V \quad \textbf{(6)}$$

$$\mathrm{R}\% = 100 \left(\frac{C_{0,i} - C_{e,i}}{C_{0,i}}\right) \quad \textbf{(7)}$$

$$\%\ \boldsymbol{R(Total)} = \sum \frac{C_{o,i} - C_{e,i}}{C_{o,i}} * \mathbf{100} \quad \textbf{(8)}$$

Where, **V** is the volume of the adsorbate containing solution (l) and W is the mass of the bio-adsorbent (g). $C_{o,i}$ is the initial concentration (mg/l) and $C_{e,i}$ is the equilibrium concentration (mg/l).

2.5. Determination of Multi Component Isotherm Parameters

All isotherm parameters of all the multi-component models can be determine using the MS Excel 2010 for Window by minimizing Marquardt's percent standard deviation (MPSD). MPSD has also been used to test the adequacy and accuracy of the fit of various isotherm models to the experimental data.

$$\mathrm{MPSD} = 100 * \sqrt{\frac{1}{n_m - n_p} \sum_{i=1}^{n} \left(\frac{q_{e,exp,i} - q_{e,cal,i}}{q_{e,exp,i}}\right)^2} \quad \textbf{(9)}$$

3 Result and Discussion

3.1 Effect of initial pH

The pH of the solution has significant effect on the adsorption process on adsorbents. This is due in part in the hydrogen ion as a strong competing adsorbate and in part in the metal ions' chemical speciation under the influence of the pH of the solution.

The concentration of the hydrolyzed cadmium species depends on the cadmium concentration, and the solution pH. It is evident that the Cd(II) are the only ionic species present in the solution for pH < 6. It is obvious that in the alkaline range precipitation plays main role in removing the Cd(II) ions attributed to the formation of precipitate of $Cd(OH)_2(S)$. Similarly, showed that Ni(II) are the only ions present in the nickel solution at pH < 6. This is also confirmed in the present study and those of other investigators [18,19]. During the adsorption run, the pH changes quickly and then remain constant. For an experimental run, the effect of pH is shown in Fig. 1 Variation of pH with time for the removal of Cd (II) and Ni (II) by MABL contact time =120 min , T = 30 ◦C, C_0 = 100mg/l, MABL dosage = 0.6 g/l. for Cd(II) and Ni (II) . This increase in pH during the sorption process because of the simultaneous and, perhaps, competitive adsorption of the metal cations and H+ ions onto MABL. Between pH 6 and 8.5, the majority of Cd is present as $Cd(OH)^+$. The effect of pH^0 on the removal of individual Cd (II) and Ni (II) ions by MABL is shown in Fig.1.The removal of metal ions is found to increase with an increase in the pH from 3 to 6. The maximum uptake of metal ions was obtained at about pH 6.

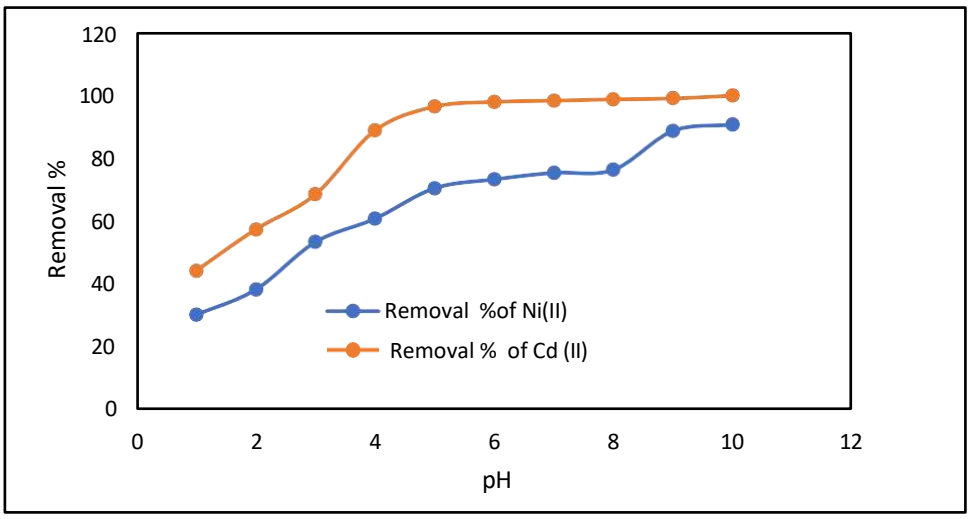


Fig1 . Effect of pH on removal efficiency

3.2 Effect of contact time

Aqueous metal ion solutions with Co= 100 mg/l were kept in contact with the MABL for 120 min. Accordingly, all the batch experiments were conducted with a contact time of 120 min under vigorous shaking at 150 rpm. Fig. 2 present the adsorptive removal of Cd(II) and Ni(II) and their uptake by MABL. The rate of cation removal is found to be very rapid during the initial 20 min, and thereafter, the rate of metal ions removal decreases considerably. No

significant change in metal ion removal is observed after about 120 min During the initial stage of sorption; a large number of vacant surface sites are available for adsorption. After a lapse of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the adsorbate molecules on the solid surface and in the bulk phase. Besides, the metal ions are adsorbed into the mesopores that get almost saturated with metal ions during the initial stage of adsorption. Thus, the driving force for mass transfer between the bulk liquid phase and the solid phase decreases with the passage of time. Further, the metal ions have to traverse farther and deeper into the pores encountering much larger resistance. This results in the slowing down of the adsorption during the later phase of adsorption.

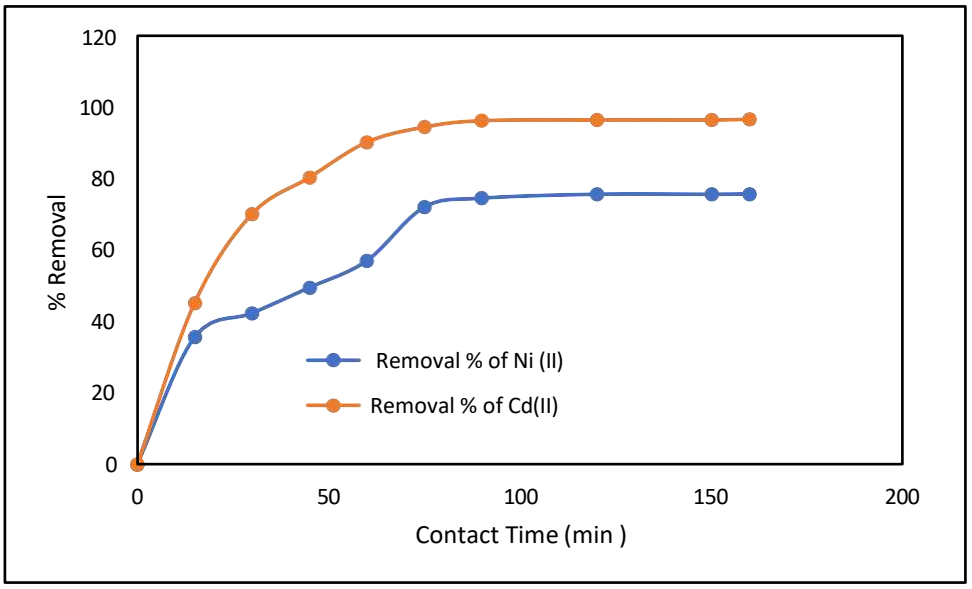


Fig 2: Effect of Contact Time on removal efficiency

3.3 Effect of dose

Effect of adsorbent dose and particle size on the removal of Cd(II) and Ni (II) with MABL was studied at different dose (0-2.5 g/L) keeping Cd(II) and Ni(II) concentration (100 mg/L), stirring speed (150rpm), pH (6) and contact time (120 min) constant. The results as shown in Fig. 3 indicate that increase in adsorbent dose result in a higher removal of Cd(II) and Ni (II). Maximum removal was observed at adsorbent dose of 2 g/L. The increase in the percentage removal with increase in the adsorbent dosage is due to the increase in the number of adsorption sites. for both Metal ions optimum dose of 0.6 g/l was found. This may be attributed to overlapping or aggregation of adsorption sites resulting in decrease in total adsorbent surface area available to metal ions and an increase in diffusion path length.

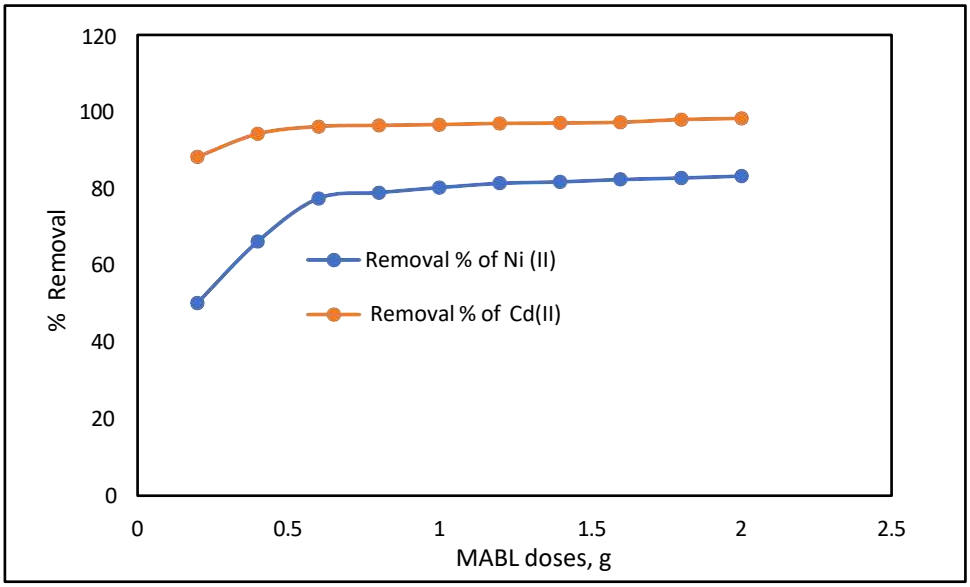


Fig 3. Effect of adsorbent doses on removal efficiency

4. Binary biosorption study on Ni (II) and Cd (II)

The biosorption yields and the removal percentage of heavy metals has been obtained for the two component [Cd(II) and Ni (II)] optimum value of solution at pH 6, determine all sample in the given Table1. The biosorption capacity of MABL for Cd (II) is generally greater than that for Ni (II). Increasing metal Concentration results in decrease in percentage removal of the metal ions in both the cases. In contrast, when the initial ion concentration was increased from 20 to 100 mg/l, the loading capacity of MABL increased from ~1 mg/g to 4.96 mg/g for Ni (II) and from 1.66 to 16.59 mg/g for Cd (II). The initial concentration provides the necessary driving force to overcome the resistances to the mass transfer of Cd (II) and Ni (II) ions between the aqueous phase and solid phase.

Table.1: Comparison of individual and total bio sorption equilibrium uptakes and yields found at different Cd (II) concentrations in the absence and presence of Ni (II) in increasing concentrations from MABL.

Co, mg/l, Ni(iI)	Co, (mg/l) Cd(II)	Ce , (mg/l), NI(II)	Ce ,mg /l, Cd(II)	% R, Ni (II)	% R, Cd(II)	qe(mg/g), Ni(II)	qe(mg/g) , Cd(II)	Total %R
0	0	0	0	0	0	0	0	0
10	0	2.08	0	79.2	0	1.32	0	39.6
20	0	4.34	0	78.3	0	2.61	0	39.15
30	0	6.81	0	77.3	0	3.86	0	38.65
50	0	11.8	0	76.4	0	6.36	0	38.2
100	0	24.4	0	75.6	0	12.6	0	37.8
0	10	0	0	0	0	0	1.66	50
10	10	3.08	0.03	69.2	99.7	1.15	1.66	84.45
20	10	6.34	0.1	68.3	99	2.27	1.65	83.65
30	10	9.75	0.13	67.5	98.7	3.375	1.64	83.1
50	10	17.8	0.29	64.4	97.1	5.36	1.61	80.75
100	10	100	0.34	0	96.6	0	1.61	48.3
0	20	0	0	0	0	0	3.33	50
10	20	4.26	0.03	57.4	99.85	0.95	3.32	78.62
20	20	8.94	0.12	55.3	99.4	1.84	3.31	77.35
30	20	13.92	0.26	53.6	98.7	2.68	3.29	76.15
50	20	50	0.34	0	98.3	0	3.27	49.15
100	20	46.6	0.41	53.4	97.95	8.9	3.26	75.67
0	30	0	0	0	0	0	5	50
10	30	5.37	0.03	46.3	99.9	0.77	4.99	73.1
20	30	11.04	0.07	44.8	99.76	1.49	4.98	72.28
30	30	30	0.28	0	99.06	0	4.95	49.53
50	30	28.75	0.35	42.5	98.83	3.54	4.94	70.66
100	30	58.7	0.46	41.3	98.46	6.88	4.92	69.88
0	50	0	0	0	0	0	8.33	50
10	50	6.37	0.06	36.3	99.88	0.605	8.32	68.09
20	50	20	0.13	0	99.74	0	8.31	49.87
30	50	19.89	0.23	33.7	99.54	1.685	8.29	66.62
50	50	34.3	0.36	31.4	99.28	2.616	8.27	65.34
100	50	70.2	0.47	29.8	99.06	4.96	8.25	64.43
0	100	0	0	0	0	0	16.66	50
10	100	10	0.05	0	99.95	0	16.65	49.97
20	100	20	0.12	0	99.88	0	16.64	49.94
30	100	30	0.14	0	99.86	0	16.64	49.93
50	100	50	0.27	0	99.73	0	16.62	49.86
100	100	100	0.46	0	99.54	0	16.59	49.77

The individual and total biosorption equilibrium uptakes by MABL and the yields of Cd (II) and Ni (II) ions at different initial concentrations of Ni (II) ions are also listed in the above Table 1. From Fig 4 & 5 represent the Comparison of Percentage of removal of Cadmium (II) varying with Nickel (II) (0-100 ppm) and percentage of removal of Nickel (II) varying with Cadmium (II) (0-100 ppm) respectively. From 6 and 7 Comparison of the equilibrium biosorption of Nickel (II) ion at varying concentrations of Cadmium (II) ion and Cadmium (II) at varying concentration of Nickel (II) ions respectively.

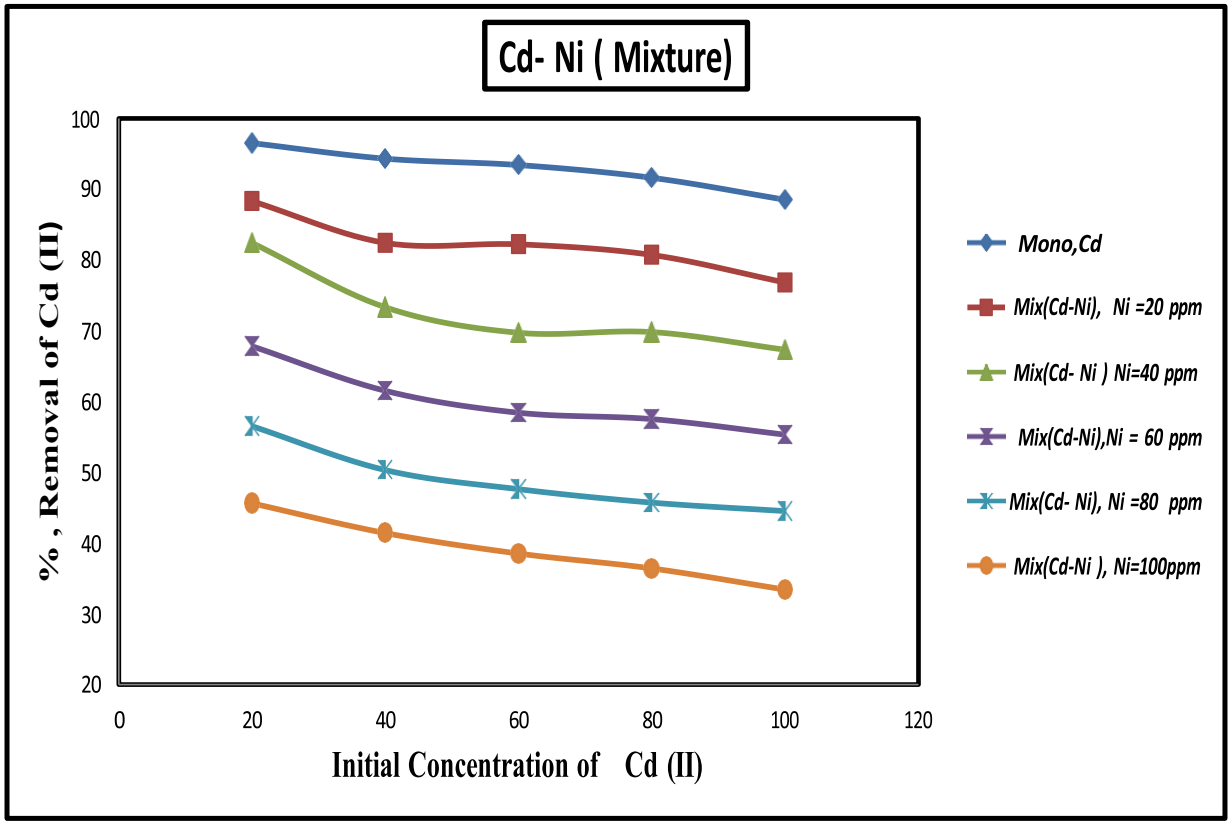


Fig 4. Comparison of Percentage of removal of Cadmium (II) varying with Nickel (II) (0-100 ppm).

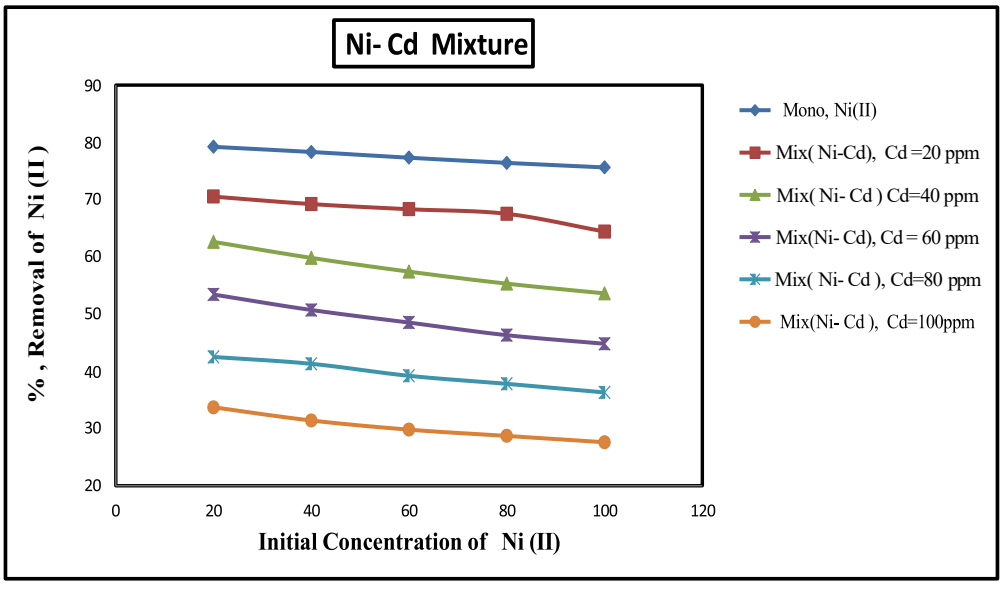


Fig 5. Comparison of percentage of removal of Nickel (II) varying with Cadmium (II) (0-100 ppm)

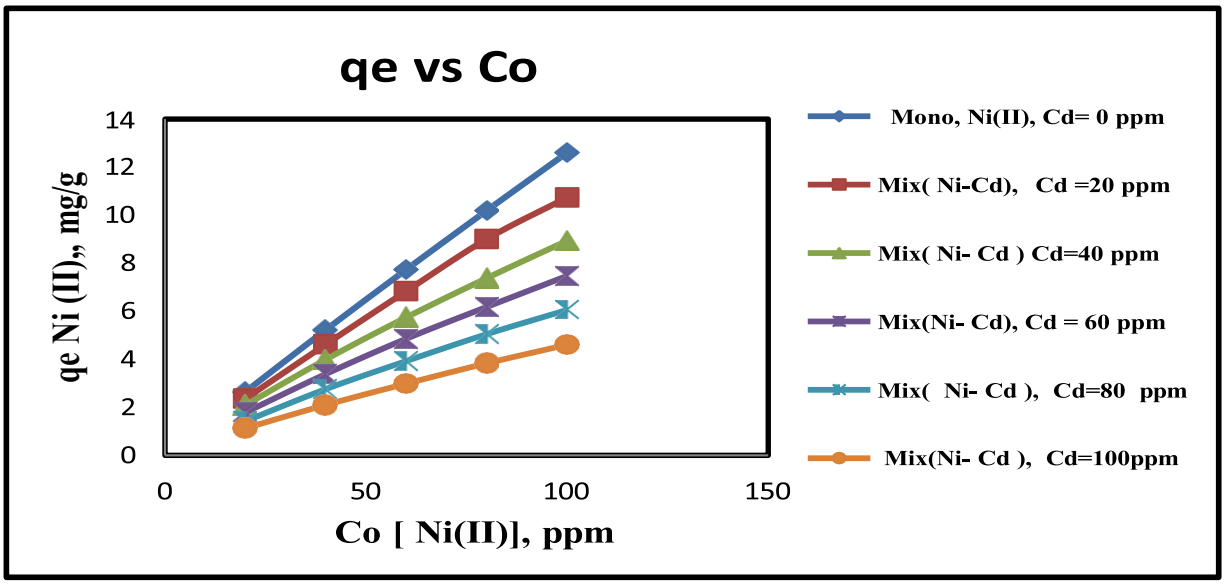


Fig 6. Comparison of the equilibrium biosorption of Nickel (II) ion at varying concentrations of Cadmium (II) ion. pH = 6, t = 120 min, T = 30° C, Co[Cd(II)] = 10-100 mg/l, and MABL dosage = 0.6 g/l

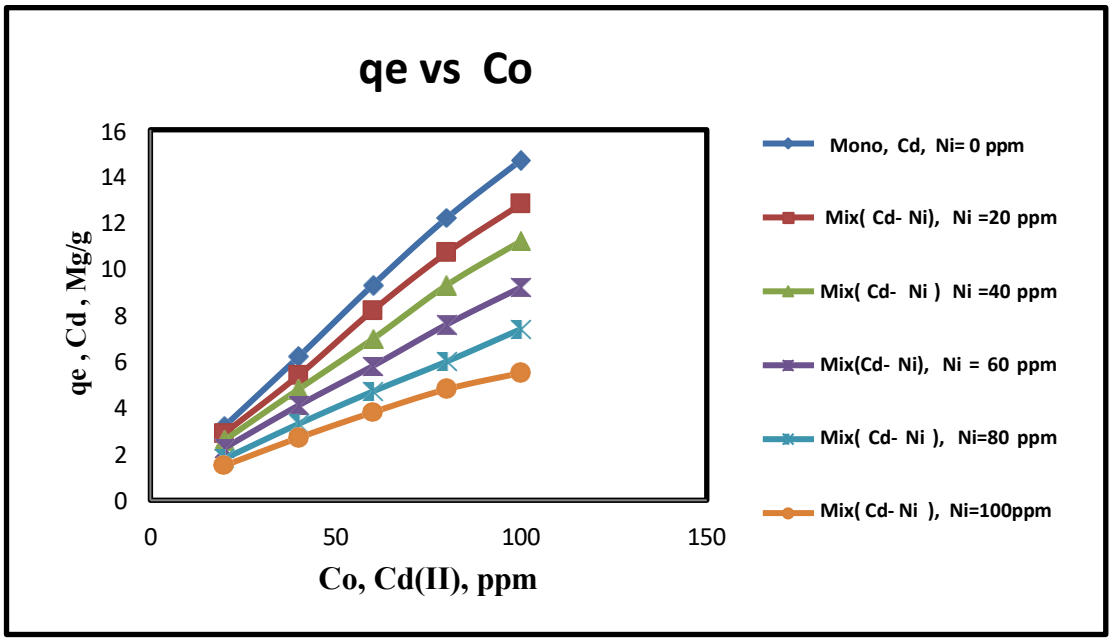


Fig 7. Comparison of the equilibrium biosorption of cadmium (II) ion at varying concentrations of nickel (II) ion. pH = 6, t = 120 min, T = 30^0C, Co[Cd(II)] = 10-100 mg/l, and MABL dosage = 0.6 g/l.

In general, a mixture of different adsorbates may exhibit three possible types of behavior: synergism (the effect of the mixture is greater than that of each of the individual adsorbates in the mixture), antagonism (the effect of the mixture is less than that of each of the individual adsorbates in the mixture) and noninteraction (the mixture has no effect on the adsorption of each of the adsorbates in the mixture). The combined effect of the two components, viz., Cd(II)

and Ni(II) seems to be antagonistic. To analyze the antagonistic adsorption interaction of the two metal ions, the adsorption yields of the single and binary component systems were also compared.

From Table 1, it was observed that the total maximum adsorption yield equal to 84.45 % for the total metal concentration of 200 mg/l containing equal (100 mg/l) concentration of Cd(II) and Ni(II) in the mixture [Ad Tot% = 84.45= 100 × [69.2 mg/l Cd(II) + 99.7 mg/l Ni(II) ion)/200 mg/l initial total concentration]]. However, the total experimental adsorption yield was 49.77 % for metal ion concentration of 200 mg/l consisting of 100 mg/l each of Cd(II) and Ni(II) ions [Ad Tot% = 49.77= 100 × [(99.54 mg/l Cd(II) + 0 mg/l Ni(II) ion)/200 mg/l initial total concentration].

This shows that the binary solution exhibited inhibitory (antagonistic) adsorption for each metal, thereby resulting in a lower sorption yield. The uptake of Cd (II) ions in the absence and presence of Ni (II) ions in the range of 10–100 mg/l concentrations was also studied. Fig. % and 6 depicts the variation of Ni(II) uptake at equilibrium with increasing initial Ni(II) concentrations (from 0 to 100 mg/l) at a constant initial Cd(II) concentration (10–100 mg/l) at pH0 6.0. Similar adsorption patterns have been observed both in the single component (Ni(II) ion) and the binary (Cd(II)–Ni(II) ion) systems; Ni(II) ion equilibrium uptake increases with increasing initial Ni(II) ion concentration up to 100 mg/l. Increase in Cd(II) concentration decreases the equilibrium uptake of Ni(II) ion

The above fig 4,5,6,7 give us a relative and diagrammatic viewpoint of the test parameters that have been detailed in the Table 2 and helps in providing a detailed pictorial insight as to how the experimental parametric data compare to each other at the varying degrees of Initial Concentration of the metallic ions in the binary system.

Generally, when cationic adsorbates are mixed together, three possible types of behavior might be exhibited as per scientific beliefs and findings:-

a) Antagonism – The extent of biosorption of the mixture is less than the rate of adsorption of a single component.

b) Synergism – Synergism is the phenomenon when the extent of biosorption of a mixture is significantly higher and more than that of a single component system.

c) Neutral Interaction – When the mixture has no influence, either positive or negative in the process of biosorption of the different adsorbates in the mixture.

In this case, among the three established behaviors of Antagonism, Synergism and Neutral Interaction, there seems to exist an Antagonistic biosorption in the combined mixture of Cd (II) and Ni (II) ions. .This is far lower than that obtained in case of single ion [either Ni (II) or Cd (II)].

4. Binary Equilibrium study on Ni (II) and Cd (II)

For binary systems of Ni (II) and Cd(II) ions , the pH value of the mixture was kept at 6, to avoid precipitation of Cd (II), therefore, single and binary equilibrium studies were carried out to determine the best suitable isotherm for binary system at experimental condition of Temp= 30^0C, MABL dose = 0.6 g, rpm =150, and pH=6.

4.1. Single Component biosorption Isotherm

Table 2 enlists the individual Langmuir and Freundlich biosorption isotherm parameters for Cd (II) and Ni (II) obtained from the fitting of experimental data along with regression coefficient, R^2. The equilibrium biosorption data of Cd (II) and Ni (II) ions singly onto the MABL are found to be best represented by Freundlich isotherm.

Table2: Isotherm parameters values for the removal of Cd (II) and Ni (II) ions by MABL.

Langmuir Constants			
Adsorbate	K_L(l/mg)	q_m(mg/g)	R^2
Cd (II)	0.05	5.26	0.91
Ni (II)	0.02	2.94	0.75
Freundlich Constants			
Adsorbate	K_F((mg/g)(mg/l)^1)	N_f	R^2
Cd (II)	1.24	0.48	0.98
Ni (II)	0.94	0.89	0.93

Thus the experimental data represented in the table and regression coefficients listed in the table, depicts that the Freundlich isotherm model best represents the data at equilibrium biosorption. At a constant pH level of 6, the value of $n < 1$ indicates that both the metal ions are favorably adsorbed by MABL.

4.2. Binary Biosorption System Model

The data of binary mixture biosorption onto MABL have been fitted to the Extended Langmuir and Freundlich isotherm models described by Eq. 3 and 4 respectively. The parametric

values of the two models for binary biosorption systems are given in Table 3. The MPSD values for both the cases are given in Table 3.

Table .3: Multi Component Isotherm Parameter Values for the simultaneous removal of Ni (II) and Cd (II) by MABL.

Adsorbate	Extended Langmuir Model		Extended Freundlich Model		
	Ki	Q_{max}	Xi	yi	zi
Cd (II)	0.108	3.42	0.732	0.738	0.892
Ni(II)	0.112		0.703	0.275	1.147
MPSD	30.5		11.25		

The Extended Freundlich model best fitted the experimental data with the lowest MPSD value 11.25 in comparison to Extended Langmuir MPSD value of 30.5.

5. Comparative study of biosorption using real battery waste water and stimulated waste water

In addition to Ni (II) and Cd (II) ions, real wastewater from industry may contain a variety of organic and inorganic materials. These material may have synergistic, antagonistic or neutral effect on the removal of target metal ions. Therefore, for making the present research studies more meaningful and useful for the industry, the present studies were also done on real wastewater from manufacturing site of Ni-Cd batteries industry

The wastewater was collected from Ni-Cd battery manufacturing (HBL power System Ltd, Delhi) industry. This wastewater was tested for some physical and chemical characteristic in the laboratory. These are pH, = 2.3; Color = Grayish -dark; Ni (II) = 58.2 ppm, Cd (II) = 43.4 ppm , studies were done in both batch at Temp=303K. COD = 560 mg/l , TDS = 20650 mg/l , TSS = 2800 mg/l , Turbidity = 3NTU The standard unit of turbidity is that produced by one part of finely divided silica in a million parts of distilled water. The allowable turbidity limit in water is 5 to 10 NTU. And the turbidity data helps in determining the special treatment requirement for water before being used for water supply.

Batch experiments were conducted to ascertain the feasibility of MABL biosorbents for the removal of Ni(II) , Cd(II) and Ni – Cd ions from battery industry [HBL power system

limited (Battery manufacturer in Delhi)] **eff**luent. Experiments were performed on the effluent at the optimized conditions (for each metal ion) as were for simulated solution of binary mixture.

Simulated wastewater having same concentration of Cd (II) & Ni (II) as in real wastewater was also prepared & removal of metal ions from this simulated wastewater was also studied for the comparison purposes. The data from simulated wastewater and real wastewater were analyzed for percentage removal of Ni (II) and Cd (II) ions. The Percentage removal data in three condition are tabulated as Table 4 and Fig8 It is clear from theses tables that for given optimized environmental conditions. The percentage removal of both Ni (II) and Cd (II) ions from real wastewater decreased as compared to simulated wastewater. Also, the percentage removal was quite low in both ions cases as compared to their single ion case. It can be concluded that percentage removal of Ni (II) and Cd (II) were not-only affected by each other, but also affected by the presence of other competing entities in real wastewater. Therefore, it can be concluded that more quantity of bio-adsorbent shall be required to achieve similar removal in real wastewater.

Table 4: Percentage removal of Ni (II) and Cd (II) ions in Battery Industrial effluent

	Biosorption Conditions						
Heavy metals	pH	dose MABL (g)	Metal ion Con, (mg/l)	Time (Min)	Temp (K)	RPM	**%R**
Ni	6	0.6	58.2	120	303	150	45.5
Cd	6	0.6	43.4	120	303	150	52.3

Where IM = Initial Metal ions Concentration

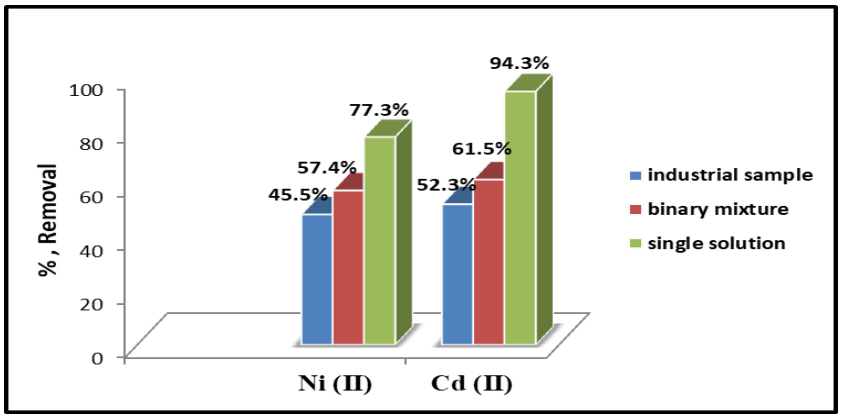


Fig 8 Comparison Graph between Industrial sample, Binary mixture and single solution [% Removal of Cd (II) & Ni (II)]

It is evident from these figures that the percentage removal of both Ni (II) and Cd (II) ions from real wastewater was consistently less than that for simulated wastewater at any time . Again This may be due to the presence of other impurities present in the real wastewater. However, the findings suggest the bio-adsorbent has the potential to remove not only Ni(II) and Cd(II), but also other impurities also.

2.7 Mechanism of the MABL on the Cd ions

The biosorption mechanism occurs in chemisorption through a chemical interaction between the Ni (II) - Cd (II) being adsorbed with the MABL, which is previously exposed to certain chemical modifications in this case to produce such surface functional groups according to FTIR (i.e. acidic functional groups such as Alcohol, Aldehyde , Nitril , and Alkyl halide) shows in Fig 9 . These functional groups thus retain the absorbed substance much more firmly in biosorption, that requires much more energy to release it [13,11], which is result of the electrostatics attraction due to the covalent bonding .

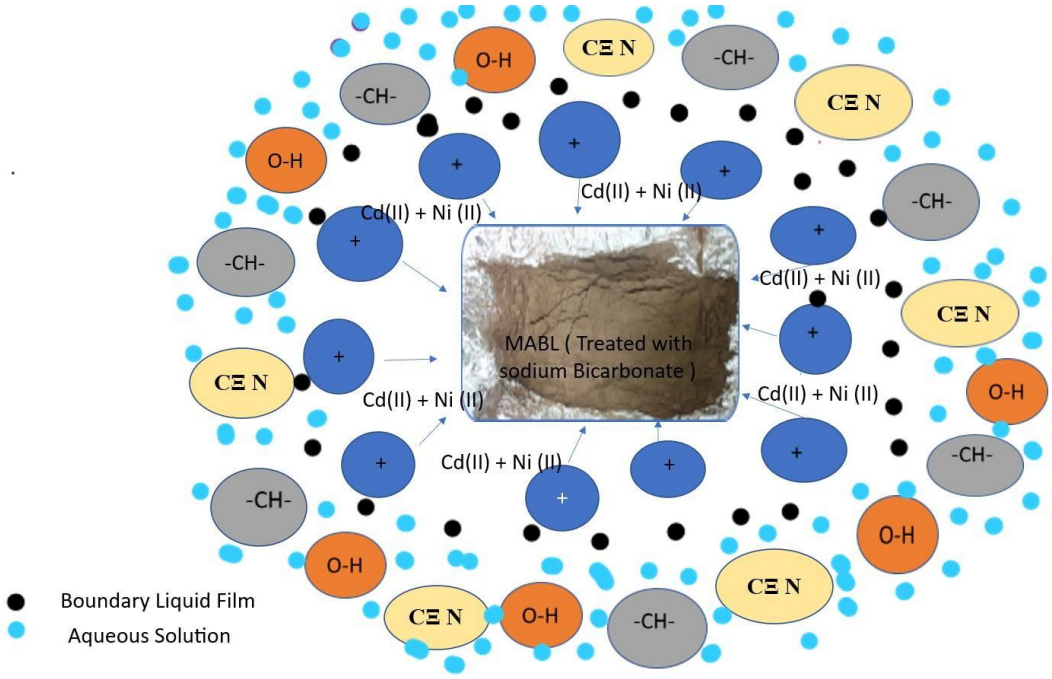


Fig 9.: Proposed Mechanism by interaction of the functional group in the Biosorption Process

5. Conclusion

MABL is an effective bio-adsorbent for the simultaneous removal of Cd (II) and Ni (II) metal ions from the aqueous solution. Binary biosorption for both Cd (II) and Ni (II) metal ions from aqueous solution was studied at pH 6 as Cd (II) and Ni(II) ions form precipitates beyond 7. In the binary metal mixtures, the affinity of the MABL for Cd(II) ions was greater than that for Ni (II) for single as well as binary solution under the same experimental conditions. Behavior in binary mixture was found to be antagonistic. The extended Freundlich biosorption model was found suitable to model the binary mixture experimental biosorption equilibrium data. Finally, this work highlights the important influence of the initial concentration of the interfering metal ions that result in both inhibitory and enhancing effects on metal adsorptions. This work opens the way for further research to better understand the exact adsorption mechanism of heavy metal adsorption onto MABL from multicomponent real systems.

Abbreviations

ABL	*A.barbadensis Miller leaves*
AR	Analytical reagent
MABL	Modified *A.barbadensis Miller leaves*
MPSD	Marquardt's percent standard deviation
AAS	Atomic absorption spectroscopy
Temp	Temperature
Time	Contact time
USEPA	United States Environmental Protection Agency
Cd (II)	Cadmium
Ni (II)	Nickel
Min	Minute
l	Liter
M	Molecular weight
C_0	Initial metal concentration
Ce	Final metal (or residual/equilibrium) concentration
m	Dry weight of biomass (dose)
q_e	Equilibrium uptake of metal
q_m	Maximum metal uptake or maximum adsorption capacity (mg/g)
V	Volume of liquid
K_L	Langmuir constant (empirical constant) (L/mg)
K_F	Freundlich capacity factor (mg/g) (L/ mg) $^{1/n}$
n_f	Freundlich intensity parameter (dimensionless)

C_e	Equilibrium concentrations (mg / L)
C_i	Initial Concentration of Ni (II) (mg/ L)
Ea	Activation energy (kJ/mol)
I	Intercept of the plot reflects the boundary layer effect
K_c	Distribution factor of bioadsorbent (Dimensionless)
R_L	Separation factor (Dimension less Constant of Langmuir Isotherm)
R	Ideal gas constant (8.314 J mol^{-1} K^{-1})

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Shweta conducted the research, analyzed the data, and wrote the paper; others authors followed the experiences, and OK analyzed the data; all authors had approved the final version.

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Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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