e-ISSN - 2348-2184
Print ISSN - 2348-2176

AMERICAN JOURNAL OF BIOLOGICAL AND PHARMACEUTICAL RESEARCH

Journal homepage: www.mcmed.us/journal/ajbpr

REMOVAL OF DIVALENT NICKEL IONS FROM SYNTHETIC WASTEWATER USING BROWN MUSTARD (*BRASSICA JUNCEA*) LEAVES BIOMASS

Chellappa Lingaraj and Malairajan Singanan*

PG and Research Department of Chemistry, Presidency College (Autonomous), Chennai – 600 005, Tamil Nadu, India.

Article Info

Received 29/11/2017
Revised 16/12/2017
Accepted 30/12/2017

Key words: Brown Mustard, Biomass, Nickel Removal, Synthetic Wastewater.

ABSTRACT

The adsorption of divalent nickel ions from synthetic wastewater by biomass of brown mustard (*Brassica juncea*) was investigated. The influence of contact time, initial metal ion concentration and temperature on metal ions removal has been studied. These variables had a considerable function in promoting the sorption process of Ni (II) ions using the biomass. The biosorption experiments were carried out with the initial concentration of Ni (II) as100 mg/L at the biomass dose rate of 2.5g/100mL. The equilibrium time was found to be of the order of 150 min for the maximum removal of 98.40 % of divalent nickel ions from synthetic wastewater.

INTRODUCTION

Heavy metals are frequently discharged by a number of industries and can lead to the contamination of freshwater and marine eco-system. Presence of heavy metals in natural and human-altered environments poses a higher risk to public health because of their toxic, non-biodegradable and bioaccumulation nature [1]. The removal of toxic heavy metal ions from wastewater has been widely studied in recent years, because they may be toxic to organisms including humans [2].

It is well known that many heavy metals are harmful to life. According to the World Health Organization (WHO) listing, the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead. These metals are significantly toxic to human beings and ecological environments [3].

Corresponding Author

Malairajan Singanan
Email: swethasinganan1966@gmail.com

Divalent nickel is toxic to most organisms for concentrations higher than 0.05 mg/L. It is carcinogenic in animals [4]. It is frequently encountered in raw wastewater effluent from industries, such as non-ferrous metal, mineral processing, electroplating, porcelain enameling, copper sulfate manufacturing, and battery and accumulator manufacturing process. According to the WHO guideline values, the maximum permissible concentration of nickel in drinking water is 0.02 mg/L. The accumulation of large quantities of Ni (II) in humans can cause a variety of negative health effects and leading to death [5]. Therefore, it is necessary to reduce the concentration of nickel in industrial effluent before it is discharged into the environment.

In order to remove toxic heavy metals like Ni (II) from water systems, some of the conventional methods have been used till date are electrolytic deposition, electro dialysis, electrochemical, evaporation, precipitation, ion exchange, reduction, reverse osmosis [6 – 8]. However, most of these methods are associated with high instrumental and operational costs [9]. Further, they may generate secondary wastewater that is more difficult to treat and disposal problems of solid wastes [10, 11].

Recently, adsorption has become one of the best alternative treatment techniques for wastewater overloaded with heavy metals. Basically, it is a mass transfer process by which an adsorbate is transferred from the liquid phase to the surface of the adsorbent and becomes bound by physical and/ or chemical interactions [12]. Moreover, it is a simple and versatile process and does not involve any extensive energy consumption [13, 14].

Adsorption by pure activated carbon (PAC) is more effective for metal ions removal from wastewater system. But the method becomes highly expensive for treatment of waste water [15]. Hence, new search for the low cost and environmentally friendly materials as adsorbents for the treatment of wastewaters is essential.

The main objectives of this article evaluation of the capability of the biomass generated from the very commonly cultivated brown mustard (*Brassica juncea*) a vegetable species in Tamil Nadu, India, for the removal of toxic heavy metal ion Ni (II) from synthetic wastewater as working model for its application of real industrial wastewater treatment. The effect of various important parameters such as pH, heavy metal concentrations and biomass dosages, contact time and temperature on the metal ion removal process is discussed.

MATERIALS AND METHODS

Preparation of the adsorbent

The brown mustard (*Brassica juncea*) plant leaves were collected from the local agricultural garden and repeatedly washed with double distilled water to remove the dust and other water-soluble impurities and dried at room temperature (30 ^oC). The plant material was ground using laboratory ball mill, then sieved to 1.0 – 3.0 mm size and stored in clean airtight polythene container for further use.

Preparation of the metal solution

A stock solution of 1000 mg/L of Ni (II) ion was prepared by dissolving 4.4783 g of $NiSO_4$ $6H_2O$ (Analytical grade substance supplied by Merck) and diluted to 1L. The working solutions of different concentrations were obtained by further diluting the stock solutions in distilled water. The desired pH of the adsorbate solution was adjusted using 0.1 N HCl or NaOH.

Biosorption process

Batch adsorption experiments were carried out by using series of iodine flask containing 0.5 to 4.0 g of biomass sample with 100 mL of synthetic solution of Ni (II) of the desired concentration of 100 mg/L at a constant temperature (30 ± 1^{o}C). The initial pH values of the solution were 4.5. The experimental flaks were agitated at a string speed of 250 rpm for a pre-determined time of 180 min. At the end of the agitation period, the solution was filtered off using Whatman No 40 filter paper. The progress of adsorption was assessed by determining the residual concentration of Ni (II) in filtrate by using atomic absorption spectrophotometer.

The percent removal of nickel ions and the amount of metal ion adsorbed from synthetic wastewater was calculated by the following equations:

$$q_e = \left(\frac{C_o - C_e}{w} \right) \times V \qquad (1)$$

$$\%\ \text{Removal} = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \qquad (2)$$

Where C_o and C_e are the initial and equilibrium concentrations of the adsorbate (mg/L), w is mass of biomass (g) and V is volume of the synthetic wastewater (mL) respectively.

Biosorption parameters

Optimization of level of pH, required contact time for establishing proper equilibrium, and the amount of biomass for best adsorption process is very much essential. Hence, systematically, the following steps were carried out.

The effect of pH on the biosorption of Ni (II) ions was carried out in the range of 2.0 to 6.5 g at the interval of 0.5 g. The initial concentration of the metal ions was kept at 100 mg/L at the desired experimental temperature and the amount of biomass was 2.0 g. For the purpose of optimization of amount of biomass, a series of experimental flasks were loaded with biomass in the range of 0.5 to 5.0 g at the interval of 0.5 g. The solution pH was kept at 4.5. By keeping the level of pH and amount of biomass as constant parameters, the equilibrium time was set from 30 to 180 min at the interval of 30 min. Role of temperature is also one of the important parameter on the biosorption process of mental ions on the adsorbent, so by considering the pH, equilibrium time, amount of biomass as constant and the working temperature is varied from 30 to 80 ^{o}C at the rate of 10 ^{o}C for the accomplishment of best biosorption.

To illustrate the influence of different amount of metal ions concentration on biosorption process, the biosorption experiments were carried out using the initial concentration of Ni (II) ion 10, 25, 50 and 75 mg/L respectively. In all the above experiments, properly 5 ml of aliquots were taken from the suspension and the concentration of Ni (II) ion is determined by using AAS. The data obtained were analyzed and standard deviations of the statistical tests were carried out using the program of analysis of variance (ANOVA) by using SPSS program.

RESULT AND DISCUSSION

Characterization of biomass sample

The characterization of biomass is very much essential to ascertain the proper adsorption capacity of the adsorbents in any metal ion removal process. The important physico-chemical properties of the brown mustard (*Brassica juncea*) are presented in Table 1.

Effect of pH

It is well known that the pH of the aqueous solution is one of the influential parameter on the biosorption of metal ions by biosorbents [16]. The pH of the solution affects the protonation of the functional groups present in the biosorbent and also the metal ion solution chemistry. Therefore, in order to establish the effect of pH on the adsorption of Ni (II) ions, the batch equilibrium studies were carried out in different pH values. The analytical result are presented in the Figure 1 and shows that the amount of divalent nickel ions removed from aqueous solution as a function of pH at a concentration of 100 mg/L. The amount of Ni (II) ions removed from solution increases rapidly from pH 3.5 to pH 6. It is estimated that, the maximum removal of 98.40 % of nickel ion was established at the pH 4.5. At low pH, there was clear competition for sorption sites between Ni (II) and protons. Above pH 6, the rate of removal of nickel ions from the solution by the brown mustard biomass started decreasing which indicates the hydroxylation and precipitation of Ni (II) at higher pH.

Effect of amount of biomass

A study on the influence of amount of adsorbent is an important parameter in the adsorption process because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. The effect of adsorbent dose on the percent removal of Ni (II) at an initial concentration of 100 mg/L is presented in Figure 2. The results reveal that, the increase in Ni (II) ion from 30.25 % to 98.40 % with the required optimum dose of 2.5 g/100 mL. Beyond the optimum dose the removal efficiency did not change with the adsorbent dose. Removal of Ni (II) ion with an increase in the amount of biomass is due to the increase in surface area and adsorption sites available for adsorption [17]. Further, it can be accredited to the binding of metal ions onto the surface functional groups present on the biomass. Similar research findings have also been reported from other researchers [18 – 20].

Effect of contact time

From the economic system point of view, the role of the equilibrium time assessment is very important especially in many wastewater treatment applications. The effect of contact time on adsorption efficiency is depicted in Figure 3. The contact time needed to reach the maximum removal of Ni (II) ions by brown mustard biomass was dependent on the type of heavy metal. The equilibrium adsorption was attained through 150 min for Ni (II) at the pH of 4.5. The increased uptake of metal ions with contact time can be due to the decreased mass transfer coefficient of the diffusion controlled reaction between the adsorbent and the metal ions [3, 21]. The results suggest that, the adsorption process is progressively increases because of the initial abundant availability of active sites on the biomass. However, with the gradual occupancy of these sites, sorption becomes less efficient, leading to the slow stage [22]. On the other hand, the rapid sorption of Ni (II) may be due to the highly porous structure of the biomass. Rapid metal removal has significant practical importance, facilitating the use of small sorbent volumes, such as those used in these experiments, and ensuring efficiency and economy.

Effect of initial metal ion concentration

The relationship between the initial divalent nickel concentration of the solution and the percentage removal of Ni (II) is shown in Figure 4. Comparatively, the removal efficiency was significantly enhanced by the increase of initial metal ions concentration from 10 to 100 mg/L. The maximum percentage removal of divalent nickel ion was 98.40 (C_o = 100 mg/L). This is because the surface where the adsorption occurs reaches its maximum uptake. It is also suggest that increase in adsorbate concentration resulted in increase in number of available molecules per binding site of the adsorbent thus bringing about a higher probability of binding of molecules to the adsorbent [23]. This result also pointed out that less favorable sites present in the adsorbent become involved in the sorption process leading to the higher removal rate of metal ions in the synthetic wastewater.

Effect of temperature

The adsorption process may be an exothermic or endothermic in nature. Hence, it is important to study the influence of temperature on the adsorption process. The adsorption studies over brown mustard biomass was carried out between 30 - 80ºC for at the initial feed concentration of 100 mg/L and at adsorbent dose of 2.5 g/100 mL. It can be seen that the adsorption of divalent nickel ions increased when the temperature was increased (Fig. 5). It is observed that, initially the percentage removal increases very sharply with the increase in temperature, but beyond a certain value of 40ºC, the percentage removal reaches almost a constant value. The results also indicated that the sorption was endothermic in nature. The increased sorption with the rise of temperature may be diffusion controlled process. The increased sorption with the rise of temperature is also due to the increase in the number of the sorption sites generated because of breaking of some internal bonds near the edges of active surface sites of the sorbent [1].

Table 1. Physico-chemical properties of biomass of brown mustard (*Brassica juncea*)

Parameters	Values
Moisture content (%)	65.45
Bulk density (g/ml)	0.85
Total loss of ignition (%)	94.50
Total organic components (%)	82.65
Insoluble components (%)	10.78
Surface area (BET) (m2/g)	3.85
C content (%)	78.25
H content (%)	8.65

Fig. 1. Effect of pH on the removal of Ni (II) ions.

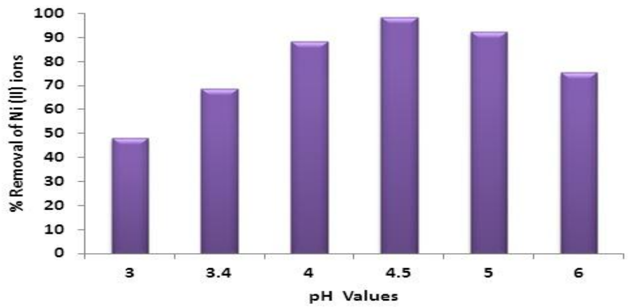


Fig. 2. Effect of biomass on the removal of Ni (II) ions.

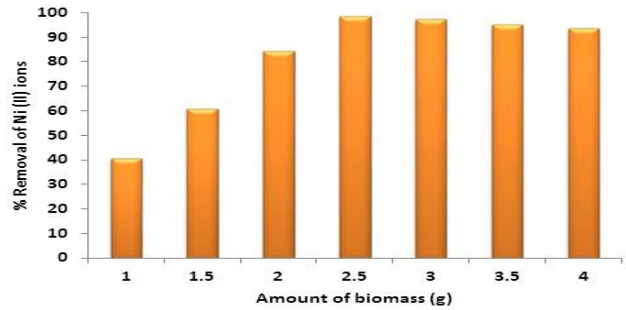


Fig. 3. Effect of contact time on the removal of Ni (II) ions.

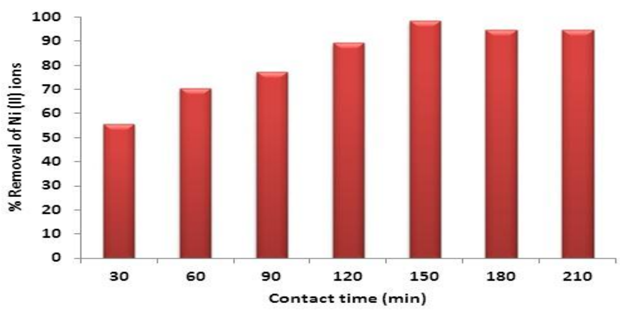


Fig. 4. Effect of initial concentration of Ni (II) on the removal process.

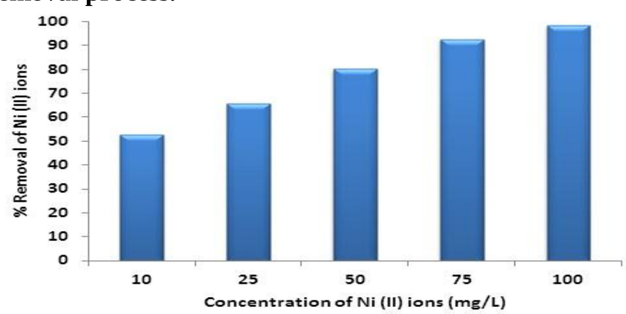
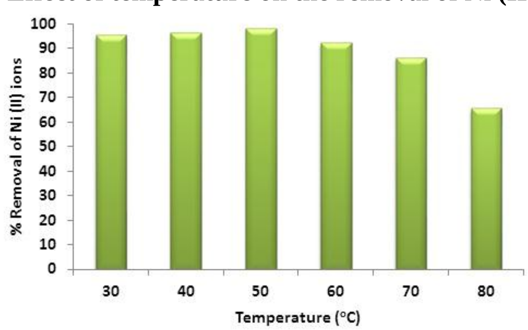


Fig. 5. Effect of temperature on the removal of Ni (II) ions.



CONCLUSION

The brown mustard biomass is an environmentally friendly and potential adsorbent for the removal of heavy metals. This research work examined the efficiency of this adsorbent in removal of Ni (II) ions from synthetic wastewater. The present investigation shows that the brown mustard biomass is an effective and inexpensive adsorbent for the removal of Ni (II) ions from waste water. Results showed that low cost adsorbents can be used for the removal of heavy metals with a concentration 100 mg/L. It was found that the percentage removal of heavy metals was dependent on the dose of low cost adsorbent and adsorbent concentration.

REFERENCES

1. Mousavi HZ, Hosseynifar A, Jahed V and Dehghani SAM. (2010). Removal of lead from aqueous solution using waste tire rubber ash as an adsorbent. *Brazilian J Chem Eng,* 27 (1), 79 – 87.
2. Samarghandi MR, Azizian S, Shirzad Siboni M, Jafari SJ, Rahimi S. (2011). Removal of divalent nickel from aqueous solutions by adsorption onto modified holly sawdust: Equilibrium and kinetics. *Iran J Environ Health Sci Eng,* 8 (2), 181 – 188.
3. El-Sayed GO, Dessouki HA, Ibrahim SSB. (2010). Biosorption of Ni (II) and Cd (II) ions from aqueous solutions onto rice straw. *Chem Sci J,* 9, 1 – 11.
4. Demirbas E, Kobya M, Oncel S, Sencan S. (2002). Removal of Ni (II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. *Biores Technol,* 84, 291 – 293.
5. Ahmaruzzaman M. (2011). Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Adv Coll Interface Sci,* 116, 36 – 59.
6. Al-Rashdi B, Somerfield C, Hilal N. (2011). Heavy metals removal using adsorption and nanofiltration techniques. *Sep Purif Rev,* 40, 209 – 259.
7. Bhatti MS, Reddy AS, Kalia RK, Thukral AK. (2011). Modelling and optimization of voltage and treatment time for electrocoagulation removal of hexavalent chromium. *Desalination,* 269, 157 – 162.
8. Kołodyńska D. (2010). Cu (II), Zn (II), Ni (II), and Cd (II) complexes with HEDP removal from industrial effluents on different ion exchangers. *Ind Eng Chem Res,* 49, 2388 – 2400.
9. Ojedokun AT, Bello OS. (2016). Sequestering heavy metals from wastewater using cow dung. *Water Resour Indus*, 13, 7 – 13.
10. Deng LP, Su YY, Su H, Wang X, Zhu X. (2007). Sorption and desorption of lead (II) from wastewater by green algae *Cladophora fascicularis*. *J Hazard Mater,* 143, 220 – 225.
11. Ali I. (2012). New generation adsorbents for water treatment. *Chem Rev*, 112, 5073 – 5091.
12. Barakat MA. (2011). New trends in removing heavy metals from industrial wastewater. *Arabian J Chem,* 4, 361 – 377.
13. Ali I, Asim M, Khan TA. (2012). Low cost adsorbents for the removal of organic pollutants from wastewater. *J Environ Manage*, 113, 170 – 183.
14. Rashed MN. (2011). Acid dye removal from industrial wastewater by adsorption on treated sewage sludge. *Int J Environ Waste Manag,* 7(1–2), 175 – 191.
15. Igwe JC, Abia AA. (2006). A Bioseparation process for removing heavy metals from wastewater using biosorbents - Review. *African J Biotechnol,* 5, 1167 – 1179.
16. Pagnanelli F, Esposito A, Toro L, Veglio F. (2003). Metal speciation and pH effect on Pb, Cu, Zn and Cd biosorption onto *Sphaerotilus natans*: Langmuir type empirical model. *Water Res,* 37, 627 – 633.
17. Meena AK, Kadirvelu K, Mishra GK, Rajagopal C, Nagar PN. (2008). Adsorptive removal of heavy metals from aqueous solution by treated sawdust (Acacia arabica). *J Hazard Mater,* 150, 604 – 611.
18. Bulut Y, Tez Z. (2007). Removal of heavy metals from aqueous solution by sawdust adsorption. *J Env Sci*, 19,160 – 166.
19. Rafatullah M, Sulaiman O, Hashim R, Ahmad A. (2009). Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust. *J Hazard Mater,* 170, 969 – 977.
20. Malkoc E, Nuhoglu Y. (2005). Investigations of nickel (II) removal from aqueous solutions using tea factory waste. *J Hazard Mater,* 127, 120 – 128.
21. Buasri A, Chaiyut N, Ponpatcharasakul N, Artsalee P, Potisook S. (2007). Factors affecting the removal of copper (II) and zinc (II) from aqueous solutions with clinoptilolite. *J Res Eng Technol*, 4, 1 – 17.
22. de Costa ACA, Leite SGF. (1991). Metals biosorption by sodium alginate immobilized *Chlorella homosphaera* cells. *Biotechnol Lett,* 13(8), 559 – 562.
23. Okeimen FE, Onyenkpa VU. (2000). Binding of cadmium, copper, lead and nickel ions with melon (*Citrullus vulgaris*) seed husk. *Biol Waste,* 29, 11–16.